An Organic Approach for Wet White Garment Leathers

by

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Abstract

To meet the growing demand for white garments and pastel shade leathers, a new combination tanning system based on acetaldehyde, glutaraldehyde and tetrakis (hydroxymethyl) phosphonium sulphate (THPS) has been developed. The advantages of this tanning system include not only producing white leathers but also completely doing away with chrome. Three separate combinations viz. acetaldehyde-THPS, glutaraldehyde-THPS and acetaldehyde-glutaraldehyde-THPS have been studied. The shrinkage temperature of the leathers obtained using acetaldehyde-glutaraldehyde-THPS combination is 86ºC. The organoleptic and the strength properties of the leathers made using this combination system have been found to be on par with that of conventional chrome tanned leather. Aldehyde tanning is known to yellow on ageing and exhibit poor light fastness. However, this new tanning system exhibits good light fastness owing to the presence of THPS.

Resumen

Para cumplir con la creciente demanda de cueros blancos y tonos pasteles en vestimenta, un novedoso sistema de curtición combinada basado en acetaldehído, glutaraldehído, y sulfato de tetraquis (hidroximetil) fosfonio (THPS) han sido desarrollados. La ventaja de este sistema de curtido no es solo para poder producir cueros blancos, pero para también completamente eliminar el cromo. Tres combinaciones separadas v. y g. acetaldehído-THPS, glutaraldehído-THPS, y acetaldehído-glutaraldehído-THPS han sido estudiados. La temperatura de contracción de los cueros obtenidos en la combinación de acetaldehído-glutaraldehído-THPS es de 86°C. Las propiedades de tacto y resistencias físicas de los cueros así producidos se han encontrado ser equivalentes a las del cuero convencionalmente curtido al cromo. Curtido al aldehído se conoce amarillear por envejecimiento y exhibir poca solidez a la luz. Sin embargo, este nuevo sistema de curtición demuestra buena solidez a la luz debido a la presencia de THPS.

Introduction

Technological advances are based on industrial demands. In leather research, from environmental point of view, replacement for chromium is being sought after actively in the recent times. Many chrome free, less chrome tanning technologies have been explored in the recent past.[1-4] From fashion point of view, there is demand for wet white leathers. Few tanning systems have been reported in the past, which produce wet white leathers.[5-7] However, limitations in the form of leather quality and environmental compliances exist for these tanning systems. Hence, to meet these challenging demands, a combination tanning system based on THPS has been explored in this present study. THPS has been found to give Ts of about 90ºC with excellent strength characteristics.[8] THPS benefits also include low toxicity, low recommended treatment level, rapid breakdown in the environment, no bioaccumulation, and it provides reduced risk to both human health and environment. THPS in combination with iron has been shown to reduce the negative effects of iron as well.[9] Recently, THPS in combination with tannic acid has been shown to produce leathers of good quality.[10] Glutaraldehyde and next higher aldehyde, acetaldehyde have been chosen in his work along with THPS as their combination will result in wet white leathers.

In this study, various combination tanning systems based on THPS, glutaraldehyde, acetaldehyde have been attempted. The tanning conditions, environmental impact and leather quality are presented in this paper.

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EXPERIMENTAL

Materials

Wet salted sheepskins (5-6 sq.ft area) were chosen as raw materials for garment leather production. Tetrakis (hydroxymethyl) phosphonium sulfate (THPS) liquid formulation (AlbriteR AD75E, 75% w/w concentrated THPS) was procured from Rhodia Consumer Specialties Ltd., UK. All chemicals used for leather processing were of commercial grade and the chemicals used for the analysis of leather were of analytical grade.

Selection of Combination Systems

Three different combination systems were chosen viz. THPS-glutaraldehyde, THPS-acetaldehyde and THPS-glutaraldehyde-acetaldehyde. Selection of percentages of THPS, glutaraldehyde and acetaldehyde (on pelt weight basis) for better shrinkage and leather characteristics was carried out. The various combinations taken along with the percentages are given in Table 1. All the experiments were carried out on conventionally processed pickled sheepskins.

TABLE I
Various Combinations of THPS, Acetaldehyde and Glutaraldehyde

Experimental Trails			
	Exp. I	Exp. II	Exp. III
THPS	1.5	1.5	1.5
Acetaldehyde	2	-	1
Glutaraldehyde	-	2	1

THPS -Glutaraldehyde-Acetaldehyde Combination Tanning

Wet salted sheepskins were processed to pickled stage by conventional method.[9] The pickled skins at a pH of 2.8 were taken for both control and experimental tanning system. Six pickled skins were taken. Two skins were used for each trial. Pickled skins were treated with 50% pickle liquor, optimized amount (1.5%) of THPS and drummed for 45 min. In the Exp I, acetaldehyde 2% was then offered and the drum was run for another 60 min. The drum was flooded with 50% water and run for 10 min. Basification was then carried out by the addition of 0.5% sodium formate, drummed for 15 min and 1.0-1.2% sodium bicarbonate (1:10 dilution and given in 3 feeds with 10 min interval). Finally, the drum was run for 2 hrs and the pH was checked to be 4.5-5.0. Then the leathers were piled over night. Next day, hydrothermal stability of wet tanned leathers was measured using a shrinkage tester. For Exp II, glutaraldehyde 2% was added instead of acetaldehyde and for Exp III both glutaraldehyde and acetaldehyde each 1% was added.

Control chrome tanned (2 sheepskins) leathers were obtained by conventional tanning procedure.[10] Then the leathers were piled overnight. Next day, the hydrothermal stability of the wet tanned leather was measured using a shrinkage tester.

Post Tanning Process

Tanned leathers were shaved to a uniform thickness of 0.7-0.8 mm and post tanned to obtain garment crust leathers using the recipe described in Table II for both control and experimental leathers. After post tanning operations, the leathers were piled overnight. Next day, the leathers were sammed, set, hooked to dry, staked and buffed.

Determination of Shrinkage Temperature

The shrinkage temperature, which is a measure of hydrothermal stability of leather, was determined using a Theis shrinkage meter.[11] Each value reported is an average of three measurements.

Physical Testing and Hand Evaluation of Leathers

Physical properties such as tensile strength, % elongation at break and tear strength were examined as per the standard procedures for garment leathers (both experimental and control).[12-15] Each value reported is an average of four (2 along the backbone, 2 across the backbone) measurements with standard deviation. Experimental and control crust leathers were assessed for softness, grain smoothness, fluffiness and general appearance 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.

Color Measurement

Reflectance measurements were made for experimental leathers using Gretagmacbeth Spectrolino hand held spectrophotometer.[16] The L, a, b and c values were calculated. 'L' indicates the lightness, 'a' represents red and green axis, 'b' represents yellow and blue axis and 'c' represents chromacity. The values reported are average of three values.

Environmental Impact Assessment

Spent tan liquors from control and experimental leather processing were collected and analyzed for chemical oxygen demand (COD) and biological oxygen demand (BOD) as per the standard procedure.[17] The values reported are average of 3 experiments along with their standard deviations.

Fastness to Artificial Light

The samples from official sampling position were tested for xenon light fastness after conditioning as before, according to IS 6191-1971 (LF:4).[18] The samples were exposed to Xenon arc light under prescribed conditions for 20 hrs, along with the 8 dyed blue wool standards. The black panel temperature was maintained at 63±1^{o}C and the relative humidity was 30±5%.

TABLE II

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 6.0-6.2
Washing	Water	100	10	
Fatliquoring	Water	50		
	Lipoderm Liq.SAF[a]	4		Fatliquors are emulsified with hot water at 60°C (1:20 dilution)
	Lipoderm Liq FB 16[a]	4		
	Vernaminol Liq.ASN[a]	4	60	
	Lipodern Liq.PU[a]	3		
Retanning	Vernatan R40[b]	4		
	Basyntan DLX[a]	2		
	Basyntan SL[a]	2	60	
Fixing	Formic acid	2		
	Water	20	3 ×10 + 30	Check exhaustion and drain
Washing	Water	100		Rinse and pile

(% based on shaved weight) [a] Procured from BASF, India; [b] Procured from Colour Chem Ltd.; except sodium formate, sodium bicarbonate and formic acid.

Note
Basyntan DLX: Light fast syntan with strong tanning action from BASF, Germany.
Basyntan SL: High fastness syntan for tight grain from BASF, Germany.
Vernaminol liquor ASN: Synthetic oil based fatliquor from Clariant Ltd., India.
Lipoderm liquor SAF: Synthetic oil based fatliquor from BASF, Germany.
Lipoderm liquor FB16: Semi-synthetic oil based fatliquor from BASF, Germany.
Lipoderm liquor PU: Synthetic oil based fatliquor from BASF, Germany
Vernatan R40 : Acrylic based syntan for white leathers from Clariant Ltd., India

Scanning Electron Microscopic Analysis

Samples from experimental crust leathers were cut from the official sampling position (IUP 2). A Quanta 200 series scanning electron microscope[19] was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at low vacuum with an accelerating voltage of 30 KV in different lower and higher magnification levels.

RESULTS AND DISCUSSION

Aldehyde based tanning is being employed in manufacture of wet white leathers especially for garment purposes. However, limitations of this tanning include poor light fastness and leather properties. In this study, two aldehydes, namely acetaldehyde and glutaraldehyde are taken along with THPS for obtaining better shrinkage temperature and leather properties. The offer of THPS of 1.5 % was considered based on the shrinkage temperature and better organoleptic properties attained, which has been reported previously.[20] The amount of THPS was kept constant throughout the combination and trials were conducted using varying the combinations with acetaldehyde, glutaraldehyde.

Shrinkage Temperature

The shrinkage temperature was comparable to all the three combinations carried out. The offer of 1.5 % THPS ensured the attainment of shrinkage temperature above 80°C for all the combinations. The shrinkage temperature obtained for THPS-acetaldehyde and THPS-glutaraldehyde was 82 and 84°C, respectively. The shrinkage temperature of THPS-acetaldehyde-glutaraldehyde combination was found to be 86°C.

Physical Strength Characteristics of Wet White Leathers

The tanned leathers were converted to garment crust leathers after post tanning and various leather properties were studied. Tensile, tear and % elongation tests were carried out along and across the backbone line for both control and THPS-aldehyde combination garment crust leathers. The mean values corresponding to each experiment were averaged and values are given in Table III. It is seen from the table that both control and experimental garment leathers exhibit comparable tensile, tear and % elongation values to that of UNIDO norms.[21] The attained value of 211 kg/cm^2 for acetaldehyde-glutaraldehyde-THPS combination is best suited for garment leather than the other two combinations.

The organoleptic properties of leathers were assessed and are given in Figure 1. It can be seen that the various properties including grain smoothness and softness of the acetaldehyde-glutaraldehyde-THPS combination leather are on par with or better than the control chrome leather.

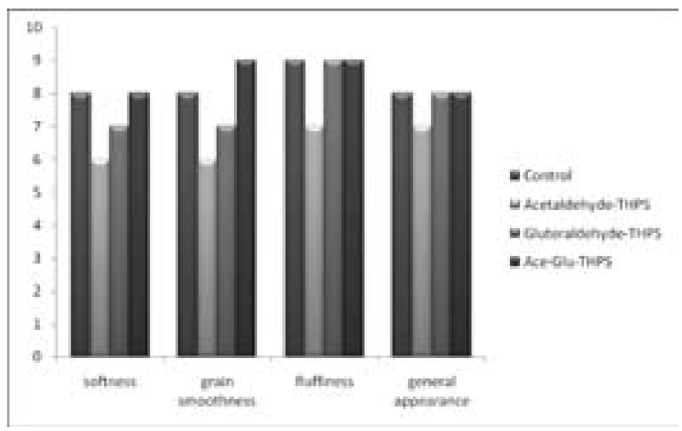

Figure 1: Organoleptic properties of wet white combination tannages

TABLE III

Strength Characteristics of Garment Leathers made from Different Experiments and Controls

Experiments	Tensile strength (Kg/cm^2)	% Elongation	Tear strength (Kg/cm)
Control	168 ± 5	51 ±2	27 ± 2
E I	205 ± 3	49 ±2	29 ±2
E II	202 ±3	76 ±2	29 ±2
E III	211 ±5	66 ±2	30 ±2
UNIDO	120	-	20

TABLE IV

Color Measurement Data for Control and Experimental Leathers

	L	a	b	c	Blue Wool Standard
E I	93.408	-0.458	6.115	6.132	3/4
E II	90.735	-0.323	6.829	6.837	3/4
E III	89.526	-0.065	6.802	6.802	3/4

Reflectance Measurement and Light Fastness to Artificial Light

Reflectance measurements were carried out for all combination leathers. The 'L', 'a', 'b' and 'c' values, the parameters used to assess color are given in Table IV. 'L' represents whiteness, which on a scale of 0-100, 100 means pure white. 'a' represents red and green axis, where 'a'>0 means red and 'a'<0 means green. 'b' represents yellow and blue axis, where 'b'>0 means yellow and 'b'<0 means blue. 'c' represents the chromacity of the color, which means the intensity of the color. The acetaldehyde-THPS combination has 'L' value of 93.4, which is better compared to that of glutaraldehyde- THPS and acetaldehyde-glutaraldehyde-THPS which has 90.7 and 89.52, respectively. As seen from the table, the 'a' value for experimental leather is less than 0. The 'b' values for experimental leathers are greater than 0 indicating that the color obtained has yellow shade. The values of 'c' shown in the table indicate the color obtained has less intensity or depth shade making it to be suitable for white leathers and pastel shade.

The comparative study made for light fastness using blue scale gave a similar value of grade 3 out of 4 for all three experimental. Hence, it can be concluded that the type of combination has not much influence on the light fastness characteristics of the leather as all the three combination have THPS. This also shows that the presence of THPS improves the fastness properties of aldehyde tanned leathers, which are known to exhibit poor light fastness properties.[22]

Spent tan Liquor Analysis of Combination Tanning System

Spent tan liquors were collected and analyzed from the tanning trials conducted for both control and experimental leathers to understand the impact of pollution load that is left to the environment. Higher BOD and COD values tend to have deleterious effect on the environment and lead to lower biodegradability. The value of BOD and COD for control and all three combinations are listed in Table V. Experiment III has higher COD when compared to other two combinations. This is because of the presence of both aldehydes, which are known to increase the COD. It can also be seen from the table that the COD values of the experimental tanning systems are slightly on the higher side when compared to control tanning system. However, the more biodegradable nature of aldehydes and THPS makes it an eco-friendly alternative to chrome tanning.

TABLE V

Spent Tan Liquor Analysis of Control and Experimental Leathers

Experiment	COD (ppm)	BOD (ppm)
Control	3100 ± 75	280 ± 25
E I	5392 ± 60	283 ± 25
E II	4313 ± 40	309 ± 30
E III	6009 ± 50	395 ± 20

Scanning Electron Microscopic Studies on Combination Leathers

Scanning electron microscopic analyses of experimental crust leather were carried out to understand the surface and cross section fiber compaction. The micrographs of the experimental crust leathers are given in Figure 2. The surface layers for all combination crust leathers were taken for 100x magnification to visualize the surface. It can be seen that there are no surface depositions, which could be the reason for the smoothness property evidenced by hand evaluation. There is good fiber compaction as seen from the figure, which could be due to the filling nature of aldehydes.

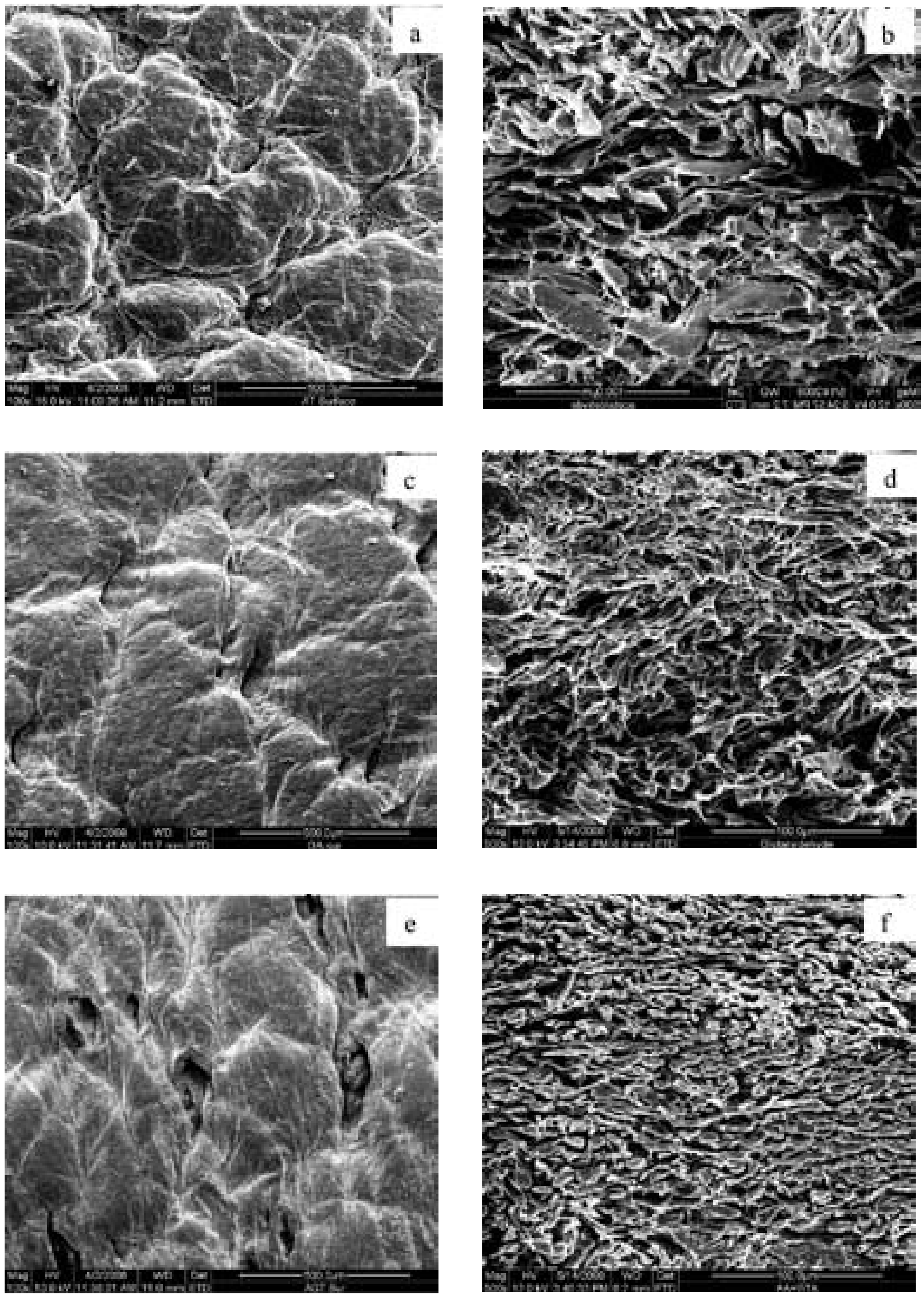

Figure 2: SEM micrographs of experimental leathers (i) grain surface (100x magnification) a, c and e and (ii) cross section (500x magnification) b, d and f for experimental leather I,II and III respectively.

CONCLUSIONS

A new combination tanning system, which could produce white leathers without chromium, is required for today's need for garment leathers. A combination tanning using acetaldehyde, glutaraldehyde and THPS has been explored for making chrome free wet white leathers. The amount of THPS, acetaldehyde and glutaraldehyde has been selected as 1.5, 1 and 1%, respectively, to get better leather characteristics. The shrinkage temperature of the leathers obtained from the THPS-acetaldehyde-glutaraldehyde combination is 86ºC. The leathers exhibited good light fastness. Scanning electron microscopy studies show good fiber compaction owing to the crosslinking potency and filling nature of the tanning system. The strength properties of the experimental leathers are well above the stipulated norms.

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