Role of Anionic Chromium Species in Leather Tanning

by

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Abstract

Chrome tanned leathers are definitely unique in comparison with leather made from any other known tanning agents, especially in terms of thermal stability, cost and its reactive mechanism with collagen fibers. In our current studies, self basifying chrome tanning materials masked with different percentages of organic acid were prepared and applied after the de-liming stage of leather processing. This eliminated the need for pickling and basification steps. Tanned leathers resisted shrinkage up to 103 and 105±2°C while conventional chrome tanned leathers resisted up to 108±2°C. Also, interaction of anionic chrome species in tanning was studied. It was observed that the percentage of anionic species in the experimental chrome tanning material was higher than conventional chrome tanning material and the shrinkage temperature achieved by application of experimental tanning material proves that anionic species do involve in tanning. Tanned leathers were crusted and analysed for strength and organoleptic properties.

Introduction

Tanning is one of the important stages in leather processing for conversion of raw hides/ skins into leather. Tanning was practiced since ancient times and primary tanning material used were plant polyphenols of different origins,[1] these tanned leathers were used for broad array of applications ranging from clothing, footwear, strapping materials, etc.

Modern inventions lead to development of chrome tanning material in the 19th century, which revolutionised the tanning industry. Chrome tanning was initially done in two bath system[2] where acidified chromic (VI) oxide was treated with skins or hides and then reduced using a reducing agent in another bath. Various other methods for preparing tanning materials[3,4] were developed over the course of time. Single bath systems, self-basifying chrome liquors etc., were popular but the most widely accepted chrome tanning material is basic chromium sulphate (BCS). Numerous procedures have been reported for making chrome tanning material but the difference in properties vary with the type of acid and reducing agents employed; most common reducing agents being molasses, glucose and sugar.[5] BCS tanning material is popular because of its ease in tanning, high thermal stability and low cost. Currently, chrome tanned leathers account for majority share of about 70-90% of total leathers produced.[6] Conventional chrome tanning system utilizes up to 70% of the tanning material, thus lower exhaustion rates of tanning material contribute to higher chromium oxide content to discharge in effluent making chrome tanning effluent unfriendly to environment. Self basifying chrome tanning agents which automatically can adjust the final tanning bath pH are viable options and this type of system can increase the uptake capability of chrome tanning material by up to 95-98%.[7]

Basic chromium sulphate (33% basicity) is prepared by the reduction of hexavalent chromium with organic or inorganic reducing agents and contains up to 24-25% chromium as Cr_2O_3. Although the half-life of chromium species is in the range of several hours because of their kinetic inertness; many complex species persist for relatively longer periods of time in solution.[8] More than fifteen species of chromium are present in a typical chrome tanning salt, varying in the degree of polymerisation, charge present on the complex, nature and number of ligands attached to central chromium atom. These species are found to be in equilibrium when in aqueous solution. The unspent chrome liquor contains 50-60% of +3 and +4 charged species,[9] increase in the percentage of +3 charged species in spent chrome liquor (43%) from the freshly prepared chrome liquor (13-14%) shows that the species with charge other than +3 may have better affinity for protein and the conversion of other species to +3 charged species may be taking place during tanning.[10]

Chromium species differ in their kinetic lability and thermodynamic affinity towards the reactive sites of collagen.[11] Some species are kinetically so inert that they do not bind to collagen within the stipulated time for tanning and as a result one third of the total BCS used during tanning remains in effluent.[12] Chromium concentration in terms of total chromium in exhaust chrome liquor ranges from 1500-5000 mg/L.[13]

In this study anionic chromium complex with suitable ligands have been prepared and were used for tanning of skins. Anionic species were extracted and analysed using column chromatography. Leathers thus produced have been tested for shrinkage temperature, color measurement and physical strength properties. Experimental chrome tanned leathers found to be at par with the conventional chrome tanned leathers. Final tanning effluent liquor was also analysed for exhaustion of the chrome tanning material, Chemical Oxygen Demand (COD), and Total Solids (TS).

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Experimental Section

Reagents

Basic chromium sulphate from Vishnu Chemicals Pvt. Ltd. India. Oxalic acid, sodium dichromate and sulphuric acid procured from SD Fine Chemicals India Pvt. Ltd. Alkaline bate from Tex Bio sciences India Pvt. Ltd. Sodium chloride, formic acid and sulphuric acid acquired from Rankem India Pvt. Ltd. Ammonium chloride, sodium formate and sodium bicarbonate were purchased from Merk Chemicals India Pvt. Ltd. Dowex resin (1X4 chloride form) was purchased from Sigma Aldrich.

Preparation of tanning material

Basic chromium sulphate (33% basicity) was prepared from the stoichiometric amount of sodium dichromate using glucose as reducing agent.[14] The reaction may process as below

$$8Na_2Cr_2O_7 + 24H_2SO_4 + C_{12}H_{22}O_{11} \rightarrow$$
$$16CrOHSO_4 + 8Na_2SO_4 + 27H_2O + 12CO_2$$

Bi- dentate ligands such as oxalic acid were used for complexation in the molar ratio 1:0.45 (B45) and 1:0.6 (B60) to the chrome liquor at 70°C with constant stirring. Final product was cooled to room temperature. The final pH adjusted to 3.0 using sodium carbonate. Prepared tanning material was analysed for Cr_2O_3 content.[15]

Anion Exchange chromatography

Ion exchange chromatography was performed for the 10% aqueous solution of chromium complexes prepared and were passed through a column of 30 cm length and 1 cm diameter using Dowex Resin (1X4 chloride form). Anionic chromium species held by the stationery phase were eluted first with 1N NaCl and then with 2N NaCl solution. Anionic species present in the chromium solutions were estimated.

A control was run with commercial BCS powder with the same process and ion exchange chromatography was done for 10% solution with the same.

Particle size

Hydrodynamic diameters of chrome tanning agent in solution were determined using Dynamic light scattering (DLS) with high performance particle analyser (Zetasizer Nano series, Malvern) at 25°C. This instrument operates at 4 mW He-Ne laser power, scattering angle of 173° and wavelength of 633 nm.

Application as tanning material

Application of prepared tanning material was checked at tanning stage of leather processing. Detail description was mentioned in Table I. The chromium complexes were applied on de-limed goat skins. Chromium solution of 8% on pelt weight basis was offered in

Table I

Process employed for control and experimental chrome application

Process: Wet Blue Leather **Raw Material:** De-limed Goat Skins **Percentage of chemicals added on limed skin weight basis**
Markings: Process: Control (C)- BCS (Conventional), Experiment (E)- B45, B60

Process Description	Chemicals	Percentage (%)		Time in Minutes	Remarks
		C	E*		*Similar procedure followed for application of B45 and B60 tanning materials
Washing					
	Water	200	200	10	Wash/Drain
Pickling					
	Water	80	-		
	Sodium chloride	8	-	10	
	Formic acid	0.5	-	15	
	Sulphuric acid	0.3	-	In 3 feeds at 15 interval + 30 run	In 1: 10 dilution with water
					Adjust pH to 3
Tanning					
	Water		50		
	Pickle Bath	40	-		From previous stage of processing
	Chrome Tanning agent	4	4	30	
	Chrome Tanning agent	4	4	60	
	Water	60	50	30	
Basification	Sodium Formate	0.5	-	15	
	Sodium Bi Carbonate	1.5	-	In 3 feeds at 15 interval + 30 run	In 1: 10 dilution with water
					Adjust pH to 4-4.2

two feeds; initial offer 4% with 50% water and drum was rotated for 30 min at 4-6 rpm. Second feed was offered and drum was rotated for another 1 hr for uniform distribution of chromium and further 50% of water was added. Finally, the drum was rotated for another 30 min to attain uniform pH of 4-4.2. Leathers were rinsed and piled. Control leathers were made from pickled skins, tanning was done with 50% pickle float with 4% BCS tanning material on pelt weight basis was added to drum and rotated of 45 min and another 4% was added and rotated for another 45 min, additional 50% water added and finally leathers were basified using 0.5% sodium formate and 1.5% sodium bicarbonate in 1:10 dilution with water in three instalments of 10 min each. Final pH was set to 4 and drum was rotated for another 30 min and leathers were rinsed and piled on horse (wooden stand for piling leathers). Spent chrome liquor from experiment (B45 and B60) and control (BCS) were analysed for chromium exhaustion. Description of the leather processing is mentioned in Table I.

Exhaustion Studies and wastewater analysis

Exhaustion studies were done by estimation of total Cr_2O_3 content present in the final tanning solution after completion of tanning process.[15] Chemical Oxygen Demand (COD)[16] and Total Solids (TS)[17] in the effluent were also analysed. Water auditing from pickling to basification stages were also undertaken.

Scanning electron microscopy (SEM) analysis

SEM micrographs of crust leathers were studied using VEGA 3 SBU (TESCAN Orsay Holding) scanning electron microscope operating at 200V to 30kV at room temperature of 25°C and relative humidity of 50%. Leather samples were sputter coated with a thin layer of gold prior to examination. Samples were cut into 5x2cm^2 sections and mounted on adhesive stub for examination; samples were viewed for studying surface as well as cross section of the leather.

Physical strength properties and organoleptic properties

The samples for physical testing were cut from control and experimental glove leathers. The samples were conditioned to the required relative humidity of 65±2% at 20±2°C for 48 h.[18] The tensile strength was measured as per the standard procedures[19] and compared with UNIDO norms.[20] Values reported were average of four samples.

Organoleptic properties such as softness, fullness, grain smoothness and general appearance were evaluated by experienced leather technologists using a rating scale of 0-10 points for each functional property, where higher points indicate better properties exhibited.

Table II

Ion exchange chromatography of chrome species

	Cationic and non-ionic species (%)	Anionic -1 specie (%)	Anionic -2 specie (%)
Control	90	-	-
B45	35.65	58.86	5.48
B60	46.61	49.58	3.8

Results and Discussion

Speciation of chrome liquor prepared

Dicarboxylic acids are well known masking agents, reaction of dicarboxylates with single metal ion produce cyclic, chelate complexes with reduced activity. When the dicarboxylates form cross linkages between two metal ions the molecular size increases and so does its reactivity.[8] Oxalates are bidentate ligands which can either act as a bridge between two metal centers or can form a chelate. By increasing the molar ratio of oxalic acid, it forms more bridges between metal centers than getting attached with single metal ion and therefore the positive charge on a metal complex is neutralized to a lesser extent resulting in the formation of less anionic species and masking of labile sites occurs. From Table II, ion exchange chromatography shows that there was a reduction in the percentage of both -1 and -2 chromium species as the molar ratio of oxalic acid was increased from 0.45 to 0.6. High exhaustion of 93 and 94% for B45 and B60 tanning material was observed with anionic species to an extent of 64.34% and 53.38%, respectively in the tanning solution. This indicates that anionic species are also participating in chrome tanning process of hides and skins. Commercial BCS containing higher percentage of positive charged species do not penetrate in the skin matrix at the higher pH as it gets fixed with the ionized carboxylic groups of collagen side chains making the penetration difficult. In case of anionic species, the interaction between the charged carboxylic groups and the chromium complex was restricted at the initial stages and later upon hydrolysis, fixation takes place.

Analysis of tanning material

Tanning materials B45 and B60 contained chrome content of 16.8% with basicity[21] of 27%, while commercial BCS had 25% of Cr_2O_3 with basicity around 32-35%. Particle size of the B45 and B60 tanning material were in the range of 585 and 550±50nm while control BCS was measured to be around 300±10nm. Bigger particle size of experimental tanning material was due to anionic ligands acting as linkage between chromium complexes to form poly nuclear complexes.[22]

Table III Comparison of wet blue leathers			
	Shrinkage Temperature (°C)	Exhaustion (%)	Final pH
Control	108±2	68±2	4
B45	103±2	93±3	4.2
B60	105±2	95±3	4.5

Leather application

Prepared chrome tanning materials B45, B60 and control as BCS were applied at the tanning stage of leather processing. Experimental chrome tanning materials were applied after de-liming. Uptakes of tanning materials were found to be higher in case of experimental leathers and exhaustion levels were 93 and 95% in case of B45 and B60 tanning materials. Final leathers were aged for 48 hours after tanning and were analysed for shrinkage temperature. From Table III, shrinkage temperature of experimental chrome tanned leathers have resisted temperature in par with conventional BCS tanned leathers.

Scanning electron microscopy analysis

Scanning electron microscopy images showing the grain surface of commercial and experimental chrome tanned leathers at magnification of 150× and cross section of at magnification of 500× can be seen from Figure 1. Grain surface of the leathers was uniform. In case of B45, surface pores were slightly shrunk that might be due to the tanning at high alkaline pH, B60 tanned leather showed no shrinkage. Overall physical appearances of leathers were satisfactory. Fiber bundles were compact in case of B45 and B60 which indicates that the leathers produced were full and compact in nature. No looseness could be observed, increased fullness and tightness of the experimental leathers due to compactness of the fiber bundles, conventional BCS tanned leathers showed more spacing between fibers making leather empty.

Exhaustion and wastewater analysis

Effluent from the chrome tanning stage was analysed for COD, total solids and chromium was estimated as Cr_2O_3 and results were presented in Table IV. It can be observed that chrome content in effluent was reduced by 88 and 89% and there was a reduction in COD up to 35 and 50% when B45 and B60 high exhaust chromes

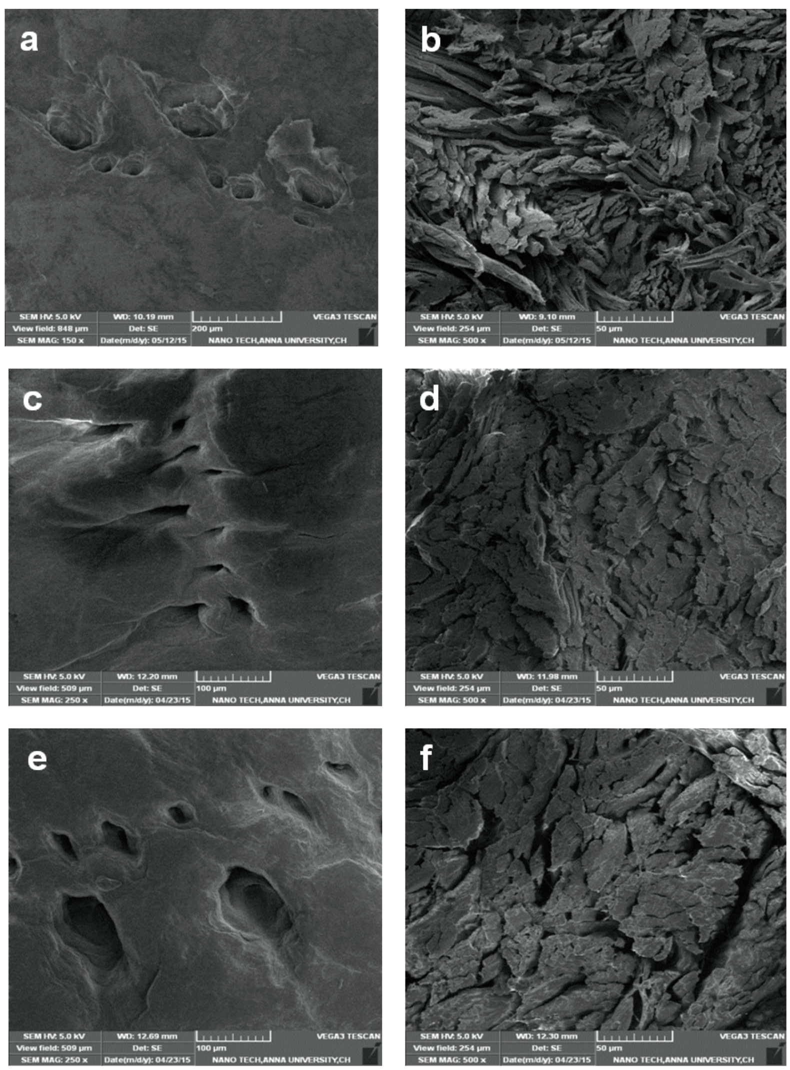

Figure 1. Scanning Electron Micrographs of chrome tanned leathers showing grain surface of **a)** control BCS, **c)** B45, **e)** B60 with magnification of 150× and cross section of **b)** control BCS **d)** B45 **f)** B60 with magnification of 500×

were used, also total solid content was reduced by 37 and 31% than conventional BCS processed effluent. Experimental leathers were processed at higher pH, where anionic chrome complexes were offered to the pelts. At such high pH most of the side chain carboxylic groups in collagen are found to be in ionized form which results in higher uptake of chromium and reduced chrome in the effluent.[11] The unit operations like Pickling and Basification have been completely eliminated during the experimental process. Thus, there was no offer of strong mineral acids or neutral salts which helps in significant reduction in TS and COD.

Water consumption in experimental tanning process was less, as pickling stage was completely avoided and there was a reduction of 44% in water consumption than control tanning process. Water audit was performed for pickling and tanning stage of leather processing, it was found that the conventional leather processing utilises up to 1.8L of water for processing one kilogram of hides/skins, while experimental chrome tanning with B45 and B60 tanning materials needed only 1L for processing one kilogram of hides/skins. There was a reduction of 44% with adoption of this pickle less and basification free system.

Table IV

Pollution load data from chrome tanning

	COD (mg/L)	Total Solids (mg/L)	Cr_2O_3 in tanning effluent (mg/L)	COD reduction (%)	Reduction in Total Solids (%)	Reduction in Cr_2O_3 (%)
Control	1600±20	26600±200	3300	-	-	-
B45	1040±20	16700±200	410	35	37	88
B60	800±20	18200±200	364	50	31	89

Table V

Comparison of mechanical properties of chrome tanned Upper Leather

	Tensile Strength (N/mm^2)	Elongation at break (%)	Grain Crack	
			Load(N)	Distance(mm)
Control	16±1	42±2	35±1	8±0.5
B45	15±0.5	51±2	30±1	11±0.5
B60	15±0.5	55±2	30±1	11±0.5
UNIDO standards	15	Not less than 40	-	-

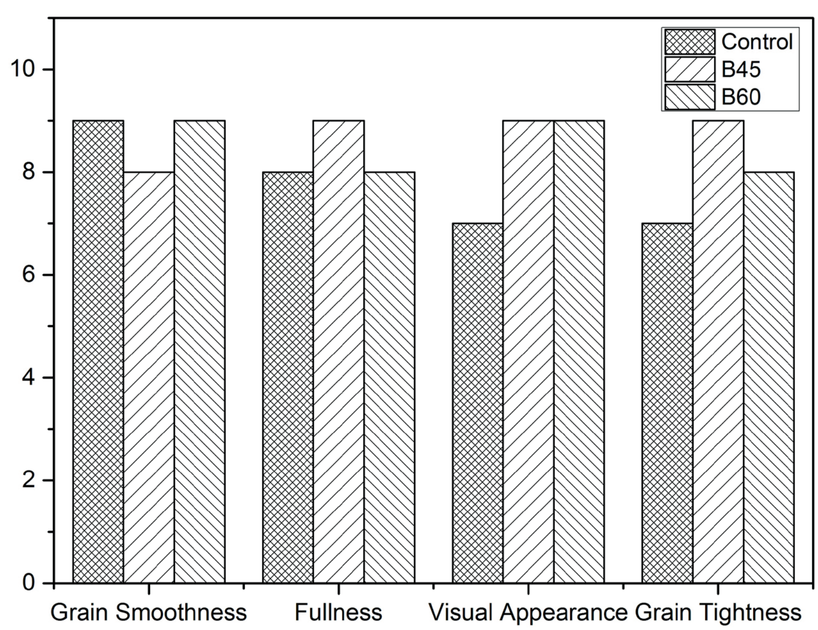

Figure 2. Comparison of organoleptic properties of upper leathers

Strength and organoleptic properties

Strength properties of the leathers tanned with experimental chrome tanning materials B45 and B60 were found to be in par with control BCS tanning material. All the leathers complied with UNIDO norms. From Table V, elongation at break values of B45 and B60 leathers elongated 21 and 30% higher, respectively than the conventionally tanned leathers, meaning increase in stretch ability of experimental leathers, which was also indicated in grain crack analysis data where distance of failure was higher than conventional leathers.

From Figure 2 organoleptic properties such as grain smoothness, grain tightness, fullness and visual appearance of B45 and B60 tanned leathers were comparable to that of conventional BCS treated leathers. B60 treated leathers had smoother grain and better visual appearance, on the other hand B45 treated leathers showed better fullness, grain tightness and better visual appearance than BCS treated leathers.

Conclusion

Chrome tanning material containing anionic chromium complex with suitable ligands have been prepared and employed in pickle-less chrome tanning of goat skins at elevated pH conditions eliminating the use of common salt and strong mineral acids. These chromium complexes owing to higher stability exhibited resistance to precipitation when offered to the de-limed pelt. Also, this new tanning material did not find any problem in penetrating into the collagen matrix and was evenly distributed over the surface. Moreover, due to the masking of coordinating sites, more amount of chromium was fixed to the collagen.

Experimental leathers thus produced have been found to have shrinkage temperature up to 105°C and exhibited 95% exhaustion. Pollution load assessment data shows that the B45 and B60 tanning materials have minimal impact on the environment than the conventional BCS tanning by eliminating use of acids and neutral salts in leather processing. This pickle less and self-basifying system opens new avenues for practising cleaner and safer chrome tanning process by minimising chromium metal in the effluent discharge.

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