Chrome-melamine Syntan: A Step Towards Developing Fuller Leather

by

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Abstract

The leather industry operates in stages. Many of the finished leather manufacturers source their wet blue leathers from various regions or tanners. In order to have uniformity of metal oxide content, almost all the leathers are rechromed. For this, the industry employs masked chromium(III) salts provided by the leather auxiliary industry in the form of complexes co-linked to phenol/ naphthalene condensates. Also, tanners who use hides/skins from ill fed animals treat their tanned substrate with melamine condensates, so as to get a preferential filling of the belly region. Metal ion complexes co-linked to melamine condensates are rather scarce. For the first time, this paper reports the application studies using a chromium-melamine condensate devoid of formaldehyde as cross linker. The said product has been employed in rechroming and evaluated for multiple properties such as providing an equalization of chrome content and filling of belly region. Our studies clearly indicate a marked advantage of employing such a product in the place of commercial chrome syntans alongside melamine condensates, more so for ill fed cowhides.

Introduction

Transformation of byproduct of the meat industry – hides/ skins into leather calls for a number of steps that could accommodate the variations in substrate features. Looseness of the belly region, for instance, is a common origin of substrate dependent feature that requires to be solved through tanning/post-tanning operations.[1] Through specific choice of retanning agent, assuming chrome tanning as the most prominent tanning today, parameters such as fullness, roundness, softness, feel, color intensity and belly filling can be achieved. In addition to this, leather industry in countries like India,[2] also adopt a metal ion based retanning – such as rechroming to normalize the Cr_2O_3 content in all the hides/ skins in a batch. Rechroming thus needs to be performed at pH values of around 3.5 – 3.8, where conventional basic chromium(III) sulfate would have to be replaced by masked systems that can withstand precipitation to higher pH level

The leather auxiliary industry provides such masked chromium(III) in the form of mineral syntans, wherein chromium-ligand complexes are coupled to condensed aromatic sulfonates. In such syntans, the preferred aromatic compound is the phenol or naphthalene and the condensation is carried out in the presence of formaldehyde as cross linker. Use of such mineral syntans results in the reduction/ avoidance of aromatic syntans in subsequent post-tanning.

In the case of ill fed animals, preferential belly filling is achieved in the retanning stage through use of melamine-formaldehyde condensates.[3-5] Survey of the auxiliary market indicates that melamine-formaldehyde products are devoid of metal ions. A lacuna of this kind forces the tanner to employ a variety of aromatic condensates to achieve the desired fullness, roundness etc. Keeping in view of the above overview of the leather industry and the auxiliary market, this work pertains to the application studies associated with a newly developed product – chromium based melamine condensate devoid of the use of formaldehyde as crosslinker. Through this study, the ability of such a product to perform multiple functions, viz., equalization of chromium content in a given batch, alongside fullness of the belly is evaluated.

Materials and Methods

Materials

Chemicals used for the preparation of the chrome-melamine syntan were of commercial grade. Wet blue cow sides of Indian origin were chosen for the study and were procured from local vendor. The chemicals used for leather processing were of commercial grade and the chemicals used for analysis were of analytical grade. The quantity chemicals used was based on shaved weighed.

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Preparation of Chrome Melamine Syntan

Melamine was mixed with 600 to 1000% v/w, of water and the resulting solution was heated to a temperature in the range of 75 to 90°C for a period in the range of 15 to 60 minutes under stirring condition to obtain melamine solution. 35 to 110%v/v, of organic acid was added to this solution under stirring condition. This was followed by the addition of 45 to 150% v/v, of formaldehyde free crosslinking agent. Stirring was continued for a period in the range of 30 to 120 minutes to obtain transparent pale yellow color solution. Pale yellow solution was then allowed to settle for a period of 15 to 60 minutes, when the color of the solution turned dark

TABLE I
Process Recipe for Manufacture of Upper Leather from Wet Blue cow hides.

Process	Process/chemicals	% (based on shaved weight)	Duration (minutes)	Remarks
Wet back	Water	300		
	Wetting Agent	0.5	30	
	Degreasing Agent	0.3	30	Drained
Acid Wash	Water	80		
	Formic Acid	0.3	15	pH 2.8 to 3.0
Rechroming	**Commercial chrome syntan/ SYN1**	**5.0**	**30**	
Basification	Sod. Formate	1.0		
	Sod. Bicarbonate	1.0	3x10+30	pH 3.8 to 4.0
				Drained
Neutralization	Water	150		
	Neutralizing syntan	2	3x15+45	Check for pH 5.0 -5.2, Drained.
Retanning , Dyeing and Fat liquoring	Water	100		
	Acrylic resin	3		
	Synthetic fatliquor	1	30	
	Phenolic replacement syntan	8		
	Melamin condensate	4	30	
	Sulphited synthetic fatliquor	6		
	Vegetable Semi synthetic fatliquor	1		
	Sulphited fish oil	1	2x10+60	
	Formic acid	2	3x10+30	Drained
	The leathers were set twice, Hook dried, conditioned and staked.			

orange. Chromium(III) salt was dissolved in 500 to 1000% v/w and the solution treated with 5 to 50% w/w, of organic ligand at a temperature in the range of 70 to 90°C to obtain masked chromium salt solution. This solution was reacted with 0.1 to 1% v/v of the transparent dark orange liquid at a temperature in the range of 80 to 90°C for a period in the range of 5 to 30 minutes to obtain melamine-chrome complex liquid. This liquid was spray dried. The developed product could be represented by the general molecular formula $(C_xH_yN_6O_z)_{n}$-Cr(III),'x' being an integer ranging from 5 to 9, 'y' an integer between 8 to 12, 'z' an integer between 2 to 6 and 'n' an integer between 10-50.[6] The product is described in the subsequent text as SYN1.

Characterization of SYN1

The prepared chrome-melamine syntan was characterized for various properties such as pH, moisture content, total soluble matter and chrome content as per the standard procedures.[7] Particle size analysis of the sample was also carried out using Malvern Zetasizer and was compared with that of the commercially available chrome syntan.

Experiments Employing SYN1

Two wet blue cowhides were cut in to 4 sides. The left halves were used for control trial and the right halves were used for experimental trial. The sides were sammed and shaved to a uniform thickness of 1.1±0.2 mm. The leathers were trimmed and the corresponding shaved weight was noted and subsequently taken for processing. The chemicals were offered on the shaved weight basis. SYN1 was used during the rechroming stage. A commercial chrome syntan was used for control trial. The leathers were subsequently processed in to upper leathers. The post tanning process employed for both control and experimental processes are provided in Table I. The experiments were carried out in laboratory stainless steel drum revolving at 12-13 RPM.

Physical Testing and Hand Evaluation of Leathers

Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures for upper and garment leathers (both experimental and control).[8-10] Samples from control and experimental tanned leathers were cut from the official sampling position[11] from the crust leather. Each value reported is an average of three (2 along the backbone, 2 across the backbone) measurements with standard deviation. Experimental and control crust leathers were assessed for belly filling, softness, fullness, grain smoothness, grain tightness, firmness, roundness 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.

Morphological Analysis

Samples from control and experimental crust leathers were cut from the belly portion and coated with gold using an Edwards E306 sputter coater. A Quanta 200 series scanning electron microscope was used for the analysis. The grain as well as cross-section was examined under the microscope at varying magnifications. The micrographs were obtained by operating the SEM at a voltage of 30 KV with different zoom level.

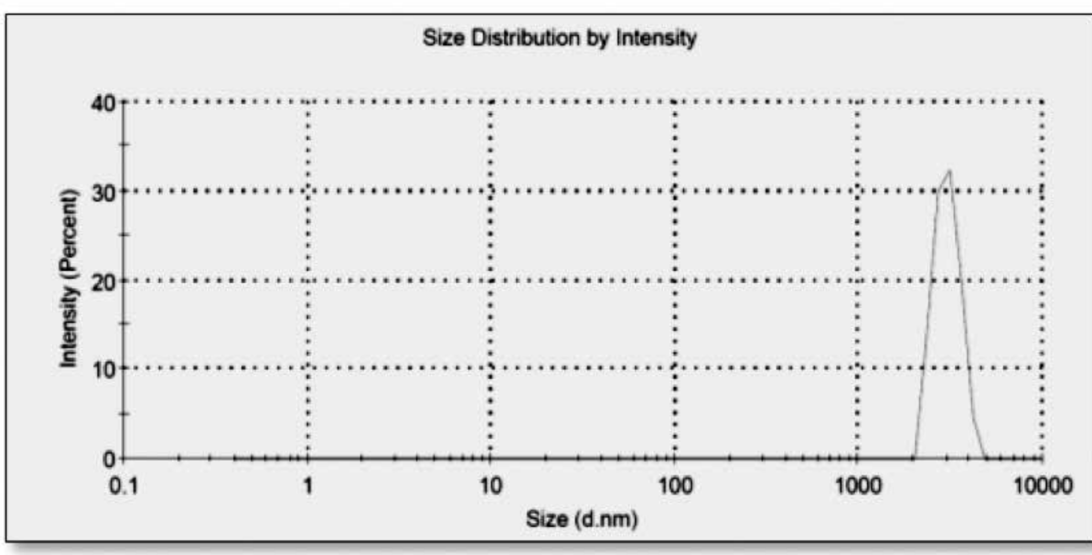

Figure 1. Particle size distribution analysis for SYN1.

Analysis of Rechrome Liquor

The spent liquor after rechroming and basification was collected from control and experimental trials and the volume was noted. The liquor was filtered and then analyzed for chromium content (%Cr_2O_3), total dissolved solids (TDS) and chemical oxygen demand (COD). As per standard procedure.[7]

RESULTS AND DISCUSSION

Preparation of SYN1

SYN1 has been prepared by condensing melamine using an alternative to formaldehyde as crosslinking agent.[5] The prepared melamine condensate has been co linked with masked chromium(III) sulfate. The prepared chrome melamine syntan has been used in the rechroming of wet blue cow leathers. This product has the dual benefit of having chromium and melamine linked together as a single product so that retanning with chromium and filling of looser portion by melamine can be achieved at the same time. During spray drying required amount of sodium bicarbonate has been added to the liquor in order to bring the final pH of the 10% solution of SYN1 to be around 3.5±0.5.

Characterization of SYN1

SYN1 had a moisture content of 10.3±0.4%, pH (10% solution) around 3.5±0.5 and Cr_2O_3 content 12±0.5%. Particle size analysis results are depicted in Figure 1. Intensity average diameter of SYN1 was observed to be around 2616 nm. The particle size of BCS and commercial chrome syntan has also been analyzed and observed to be around 1813 and 1644 nm, respectively. Thus, it could be inferred that owing to complexation with melamine, SYN1 had higher particle size compared to conventional BCS or commercial chromium syntan. This could probably lead to improved belly filling and firmness of the final leather.

Physical Testing and Hand Evaluation of Leathers

Crust leathers rechromed using SYN1 have been characterized for physical and organoleptic properties. Tensile, % elongation, tear strength, load at grain crack and distension at break for the control and the leathers processed SYN1 are given in Table II. It could be observed that the physical properties of leathers rechromed with SYN1 are on par with that of the control leathers and the values are higher than those of standard norms. The organoleptic properties of the crust leathers, which are rechromed with commercial chrome syntan and SYN1, have been detailed in given in Table III. It could be clearly observed that the crust leathers rechromed using SYN1showed better belly filling and improved firmness compared to the leathers rechromed with commercial chrome syntan. The images of the both control and crust leathers are depicted in Figure 2. It could be clearly seen that both the leathers have good color uniformity. In the case of experimental leathers, there are no color patches or yellowness being found.

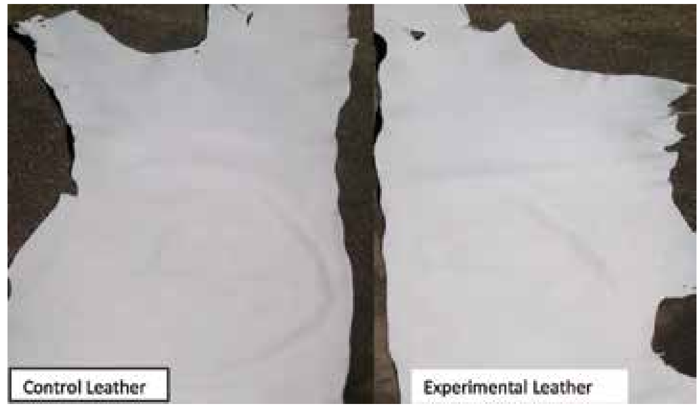

Figure 2. Photographic images of control and experimental crust leathers.

TABLE II
Physical properties of control (Commercial chrome syntan) and experimental (SYN1) leathers.

Physicochemical Properties	Control	Experiment
Tensile Strength (N/mm^2)	23±1	21±1
Elongation at break (%)	60±1	62±1
Tear Strength	20.3±0.5	21.7±0.6
Load at grain crack (kg)	32±1	29±1
Distention at grain crack (mm)	9.10±0.2	8.70±0.2

TABLE III
Hand Evaluation of crust Leathers rechromed using commercial chrome syntan (Control) and SYN1 (Experimental).

Samples	Control	Experimental
Belly filling	8±0.5	9±0.5
Fullness	7±0.5	9±0.5
Roundness	7±0.5	8±0.5
Firmness	6±0.4	8±0.5
Softness	7±1	7±1
Color uniformity	9±0.5	9±0.5
Overall appearance	7±1	9±0.5

Morphological Analysis

Grain and cross section from the belly portion of the crust leathers obtained from control and experimental process employing SYN1 have been analyzed using SEM (Figure 3 and 4, respectively). Grain surface of the experimental crust leathers was found to be clean without any deposits on the surface. SEM images of the cross section of the experimental crust leather obtained from belly portions shows a compact fiber structure. This could be attributed to the filling nature of SYN1. Though the control and experimental samples show comparable compactness in the fiber structure throughout the cross-section indicating uniform filling of syntan, crust leather rechromed using SYN1 showed more compact fiber structure.

Analysis of Wastewater

TDS, COD and % Cr_2O_3 are the three parameters that have been chosen for analyzing the environmental impact of spent rechroming liquor. Results are provided in Table IV. COD, TDS and %Cr_2O_3 values were on par for the wastewater from both control and experimental processes. Thus, it could be inferred that the use of SYN1 does not give rise to any additional pollution load.

TABLE IV

Effluent Analysis	Chrome Syntan	SYN1
TDS (ppm)	20,000±24	20,000±28
COD (ppm)	6500±12	6800±10
% Cr_2O_3	673±5	606±13

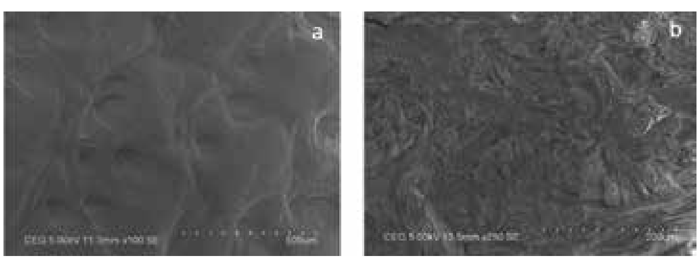

Figure 3. Scanning electron micrographs of (a) grain and (b) cross section of crust leathers rechromed with commercial chrome syntan.

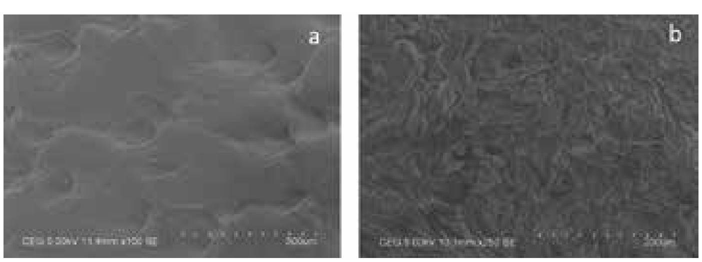

Figure 4. Scanning electron micrographs of (a) grain and (b) cross section of crust leathers rechromed with SYN1.

CONCLUSION

In this work, SYN1 has been prepared and used in the rechroming of wet blue cow upper leather. SYN1 had a characteristic Cr_2O_3 content of 12±0.5%. Use of this chrome melamine syntan (SYN1) resulted in improved belly filling and firmness of the final leathers. The physical properties were on par with that of the conventionally rechromed leathers. SYN1 does not give rise to any coloration on the final crust leathers. Analysis of the rechroming liquor from both control and experimental process showed that all the parameters are comparable.

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