

METAL ORGANIC BASED SYNTAN FOR MULTI-STAGE LEATHER PROCESSING

by

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ABSTRACT

The leather industry in India and elsewhere have adopted a two stage processing methodology wherein hides/skins are processed up to wet blue in stage one, and subsequently converted to value added products in stage two. The process of rechroming carried out when wet blue leathers are sourced from various vendors thus attains significance. Many tanners prefer to employ chromium based synthetic tanning agents for rechroming, as against basic chromium sulfate, so as to provide for a tanning at higher pH values of above 3.5 – 4.0. Chromium based synthetic tanning agents in addition to employing masked chromium salts also provide for increased fullness to the leather. A significantly large number of these synthetic tanning agents are based on formaldehyde condensed aromatic intermediates, the use of which could result in the presence of free formaldehyde in the crust leathers. Instances of poorer raw material quality also call for the use of melamine-based syntans for preferential filling of the belly regions. In this work, the application of a chromium based melamine syntan devoid of the use of formaldehyde for condensation is reported. The product has been evaluated in tanning, rechroming and post tanning (as a retanning agent). In tanning, the product provides for a shrinkage temperature of 106°C, 3.25-3.75% Cr₂O₃ content (dry weight) alongside good belly filling. On use in rechroming or post tanning, the product provides for fuller leathers complete with physical properties meeting standard norms. The results indicate that the newly developed product has a significant scope in increasing the cutting value of the leathers by way of providing uniform substance alongside good tanning properties.

INTRODUCTION

Green technology is one of the fascinating concepts used in recent days in most of the manufacturing sectors.¹ Leather manufacturers are facing stringent regulations from environmental pollution agencies to meet the standard norms. This has made the leather fraternity and researchers focus on sustainable technologies to combat environmental disasters.² There are several chemical and physical operations performed during leather manufacture. The most polluting operations are

pretanning followed by tanning and post tanning operations. Several end of pipe treatment systems have been developed to meet the standards.

Recently, leather researchers have focused their attention in developing green technologies, which results in either zero discharge or sustainable products for leather making.³ Generally, phenol, naphthalene, melamine, natural tannins, protein hydrolysate, dicyandiamide and acrylics are condensed with formaldehyde to manufacture syntans.

The presence and release of free formaldehyde is still a challenge, although several methods are available.^{4,5} Combination of syntans are usually used during post tanning process to incorporate special properties.⁶ Depending on the end applications, the choice and percentage offer of syntans vary. Widely manufactured leathers are chrome-tanned leathers that usually require higher level of filling, specifically in belly and shank regions. Melamine syntans are predominantly used for selective filling and it is manufactured as a formaldehyde condensation product. Alternatively, protein hydrolysate in combination with phenolic-based syntans is also used for filling. However, size of the syntan is one of the critical factors in determining the filling character. Mineral based syntans are used in the leather industry to reduce the duration of processing. When skin/hide are treated with mineral syntans, it usually supplements with chemical auxiliaries to fill the loose portion. R&D on leather auxiliaries have grown in isolated spaces with products based on formaldehyde condensed aromatics, condensed aromatics free of formaldehyde, melamine condensed products and mineral syntans based on phenol/naphthalene condensates based on HCHO being available in the market. This has led to a need to use multiple products such as chromium based syntan for normalizing chromium content on wet blue sourced from different markets (through a process known as rechroming), followed by use of phenol condensates for filling and melamine condensates for preferential belly filling. In the present study, chrome-melamine syntan without use of formaldehyde for condensation reaction has been prepared and complexed with basic chromium sulfate to incorporate multi functionality. Chrome-melamine syntan thus developed has broader usage such as in tanning, rechroming

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and post tanning agent. The prepared product has been evaluated as a chrome-tanning agent and also for its ability to function as a syntan that provides preferential filling of belly regions. With pickle free chrome tanning being suggested as a need to reduce salinity in wastewaters, the product was also tried out for tanning without pickling, through a normal reduction in pH using formic acid alone.

MATERIALS AND METHODS

Materials

Chemicals used for the preparation of the formaldehyde-free chrome-melamine syntan were of laboratory grade and procured from SD Fine Chemicals, India. Goat wet blue leathers were shaved to uniform thickness of 1.0-1.1 mm. The chemicals used for leather processing were of commercial grade, while the chemicals used for analysis were of analytical grade. The quantity (%) of chemicals used was based on shaved weight.

Preparation of Chrome Melamine Syntan

Chrome-melamine syntan is prepared through eco-friendly sustainable process that is free of formaldehyde and incorporating special properties like filling loose portions. Melamine-chrome complex represented by a 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. The said complex being characterized by the presence of imine groups as well as complete absence of amine groups, the complex being further characterized by Cr_2O_3 content in the range of 12-18%. 10% solution of the complex exhibited pH in the range of 3.1- 3.5.

TABLE I
Process recipe for chrome tanning process.

Chemicals	% Offer	Time	Remarks
Pickle Liquor	50		Check pH 2.8-3.0
Chrome-Melamine syntan	10	60 min	Check penetration
Water	50	30 min	
Sodium formate	1	15 min	
Sodium bicarbonate	1-1.5		
Water	15	4x10 min + 1 h	Check pH 3.8-4.0 Drain: aged for 24 h

The final spray dried chrome melamine syntan product was used for all the experimental leathers.⁷

Evaluation of the Prepared Syntan

Chrome tanning, pickle less chrome tanning (chrome tanning at a pH of 5.0 without conventional pickling), rechroming and post tanning recipe processes are given in Table I, II, III and IV respectively. Similarly, conventional chrome tanned

TABLE II
Process recipe for pickle less chrome tanning process (from delimed pelt.)

Chemicals	% Offer	Time	Remarks
Float	50		
Formic acid Water	0.5-0.75 10	30 min	2 feeds Adjust pH to 5.0
Chrome-Melamine syntan	5	30 min	Check penetration
Chrome-Melamine syntan	5	60 min	Check penetration
Water	50	30 min	
			Check pH 3.8-4.0 Drain: aged for 24 h

TABLE III
Process recipe for rechroming process.

Chemicals	% Offer	Time	Remarks
Acetic acid	0.2		
Chrome melamine syntan	4	30 min	Check penetration
Water	50	30 min	
Sodium formate	0.5	15 min	
Sodium bicarbonate	1		
Water	50	4x10 min + 1 h	Check pH 3.8-4.0 Drain: aged for 24 h

leathers are rechromed with prepared syntan and evaluated for the organoleptic properties. For assessing the properties of the chrome-melamine syntan, leather was compared against leathers developed using commercial melamine-formaldehyde syntan. C - Conventional chrome tanned leathers; E1 - Chrome melamine syntan - chrome tanned leathers; E2 - Chrome

melamine syntan - rechromed wet blue leathers. P - Conventional post tanned leathers; F1 - Conventional retanned leathers from chrome melamine syntan - chrome tanned leathers; F2 - Conventional retanned leathers from chrome melamine syntan, rechromed wet blue leathers); F3 - Chrome melamine syntan used for retanning.

TABLE IV
Post-tanning recipe for the manufacture of upper leather from wet blue.

Process/chemicals	%	Duration (min)	Remarks
Washing			
Water	100	10	Drained
Neutralization			
Water	150		
Sodium formate	1.0	10	
Sodium bicarbonate	1.0	3x15+45	pH – 5.0 - 5.2, Drained.
Washing			
Water	200	15	Drained
Retanning, Dyeing and Fat liquoring			
Water	100		
Grain tightening acrylic syntan	3.0	30	
Semi-synthetic fatliquor	3.0	45	
Acid dye	2.0	30	
Synthetic fatliquor	3.0		
Phenol –naphthalene based syntan	3.0		Mixed in hot water
Chrome-Melamine syntan*	6.0	60	
Semi-synthetic fatliquor	4.0	30	
Wattle	4.0	30	
Formic acid	1.5	4x10+20	The dye exhaustion was checked. Drained.
Washing	100	15	Drained. Crust leathers were set twice, hooked to dry, conditioned, and staked.

*Chrome melamine syntan used for retanning experiments (F3), conventional melamine syntan used for F1 and F2 post tanning trials.

Physico-chemical Evaluation of the Leather

Leather samples were collected by IUC 2 procedures and prepared as per IUC 3 procedures for measurement of chromium content using IUC 8-2 procedures. Free formaldehyde content in the leathers treated with the syntan was determined as per ISO 17226-1: 2008/Analysis using HPLC-DAD. For measurement of shrinkage temperature (IUP 24), tensile strength and percentage elongation (IUP 6) and tear load (IUP 8), the samples were prepared and conditioned as per IUP 1 and 3.

Organoleptic Properties

Experimental and control crust leathers were assessed for softness, fullness, grain smoothness, grain tightness (break) and general appearance by hand and visual examination. The leathers were rated on a scale of 0–10 points for each functional property by three experienced tanners, where higher points indicate better property.

Scanning Electron Microscopy Analysis of Processed Leathers

Samples from control and experimental tanned leathers were cut from the official sampling position from the crust leather. Samples were first washed in water. Subsequently, samples were then dehydrated gradually using acetone and methanol as per standard procedures. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 15 KV with different magnification levels.¹

RESULTS AND DISCUSSIONS

Formaldehyde free chrome-melamine syntan was prepared using non-toxic crosslinking and condensing agent.¹² During the preparation of melamine syntan, mineral-tanning agent was also co-linked with the melamine syntan for multi-functionality. The prepared product was water soluble and green in color due the presence of chromium(III) tanning agent. The solid content was adjusted to 50–60% to obtain good yield of spray-dried powder. The pH of 10% solution was in the range of 2.5–3.5. The product was expected to provide light fastness and not darken the leather on ageing, as there are no components that can undergo photo degradation. A particular advantage of condensing agent used, in contrast to conventional melamine syntans, is that they contain no formaldehyde. Owing to the content of natural condensing substances, the melamine polymers are more readily biodegradable.

Chrome Tanned Leathers

Conventionally delimed pelt was used for pickle-less and pickled chrome tanning process. Chrome-melamine syntan (10%) was used as a tanning agent and the chrome content in the chrome tanned leather found to be 3.25%; pickle-less chrome tanned leather was found to have 3.75% of Cr₂O₃. The shrinkage temperature of the wet blue leather was 112 and

114°C for pickled and pickle-less tanned leathers respectively. The pickled and pickle-less tanned leathers were visual assessed for chrome patches, color uniformity, grain smoothness and general appearance (Table V and Fig. 1). Pickled processes resulted in better grain smoothness, fullness and color uniformity when compared with pickle-less. From the shrinkage temperature result and visual assessment, it was found that the mineral based syntan performed as a better tanning agent by incorporating bulk properties to the leather. This is mainly due to the effect of melamine, which acts as filling agent during chrome tanning and fills the loose portion.

Rechromed Leathers

Before neutralization of wet blue leathers, rechroming is practiced to obtain uniform distribution of chromium and color to the leathers. In most of the cases, wet blue leathers were received from different lots and different merchandiser.¹³ However, during this process, there are no special properties incorporated in leathers. Chrome-melamine syntan was used as a rechroming agent with 4% as an offer and basified with conventional chemicals. The experts evaluated the rechromed leathers to ascertain its bulk properties and the results are given in Figure.1. From the result it is observed that most of the bulk properties are achieved using chrome-melamine syntan and finds impeccable application in leather manufacture.

Wet End Finished Leathers

A comparison of the organoleptic properties of commercial and chrome-melamine syntan is shown in Figure. 2. The leathers were evaluated for various organoleptic properties such as general appearance, grain smoothness, grain tightness, fullness, color uniformity, strength and roundness by hand and visual

TABLE V
Visual assessment data
for the wet blue leather.

Parameter	Pickled wet blue	Pickle-less wet blue
Color of the wet blue	9	8
Belly filling	5	8
Chrome patches	Nil	Nil
Grain smoothness	8	9
General appearances	9	9

*rating on a scale of 1–10 with 10 being the best

evaluations.¹⁴⁻¹⁶ The average rating from three experienced tanners corresponding to each experiment calculated for each functional property is given in Figure 2. Higher number indicates better property. From the result it can be observed that most of the bulk properties are found to be higher for mineral based melamine syntan when compared to commercial melamine syntan. The post-tanned leathers were found to be more full due to the deposition of melamine and crosslinking effect of chromium. Formaldehyde-free melamine retanning provides overall compaction and filling of the cross-section and can be used along with other type of syntans like those based on resins, acrylics etc. for upper leathers. Grain tightness, grain smoothness, roundness, color uniformity and strength of leathers are similar to control leathers.

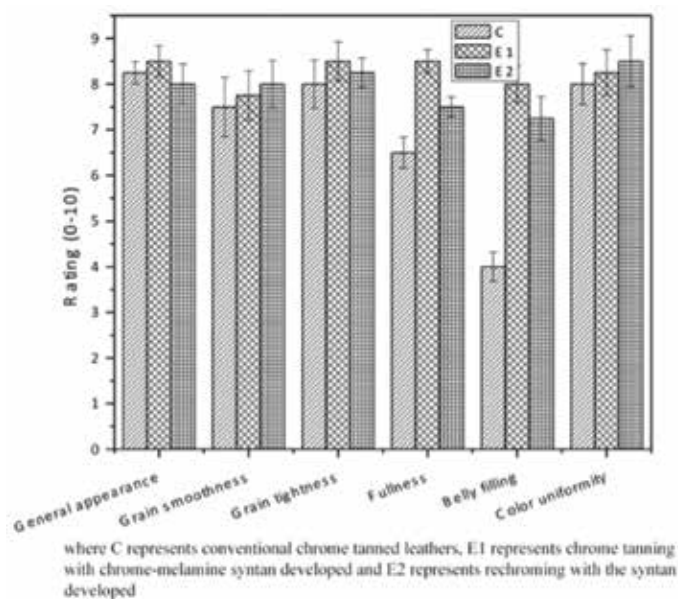


Figure 1. Organoleptic properties of wet blue leather (C - Conventional chrome tanned leathers; E1 - Chrome melamine syntan - chrome tanned leathers; E2 - Chrome melamine syntan - rechromed wet blue leathers.)

Tensile and tear strength tests were carried out for the crust leathers both along and across backbone line. The mean of the values corresponding to along and across backbone was calculated for each side and strength character and given in Table VI. The grain crack strength for the crust leathers was also carried out. The mean values corresponding to each experiment were averaged and the values are given in Table VI. From the results, it is observed that the experimental leathers met the ISO norms for upper leathers. No free formaldehyde was detectable in the experimental leathers. This is primarily due to formaldehyde-free melamine syntan used for the manufacture of experimental leathers.

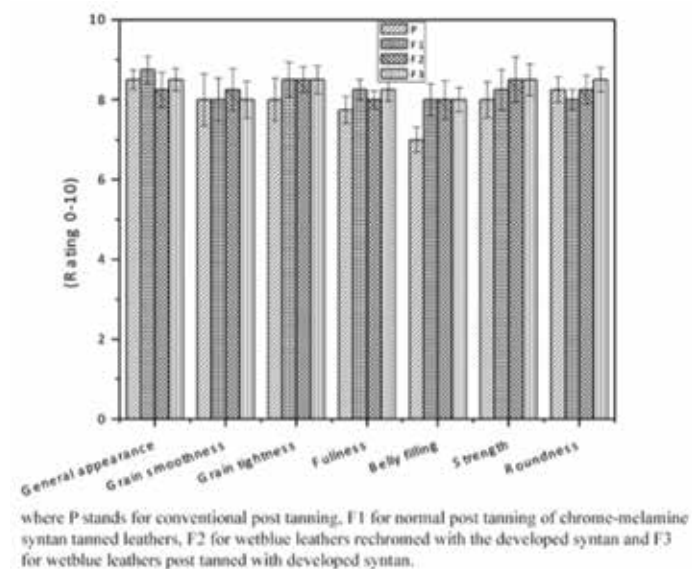


Figure 2. Organoleptic properties of crust leathers (P - Conventional post tanned leathers; F1 - Conventional retanned leathers (from Chrome melamine syntan - chrome tanned leathers); F2 - Conventional retanned leathers (Chrome melamine syntan - rechromed wet blue leathers); F3 - Chrome melamine syntan used for retanning.)

TABLE VI
Strength parameters for leathers processed using chrome-melamine syntan offered at various stages.

Tanning system	Tensile strength (kg/cm ²)	Tear strength (kg/cm)	Grain crack resistance	
			Load (kg)	Distension (mm)
Pickled Pelt	195± 2	36± 1	26.0±4	8.0±0.3
Pickle less	230± 1	39± 2	28.5±1	8.35±0.1
Rechromed	220± 3	40± 2	27.0±1	8.25±0.1
Retanned	200± 2	38± 2	26.5±1	7.85±0.1

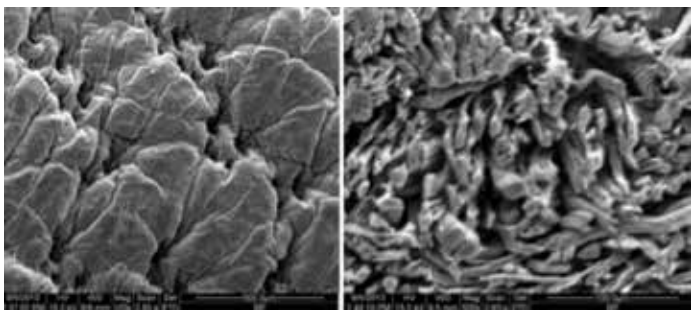


Figure 3. Morphological evaluation of chrome-melamine syntan tanned leathers-Pickled method.

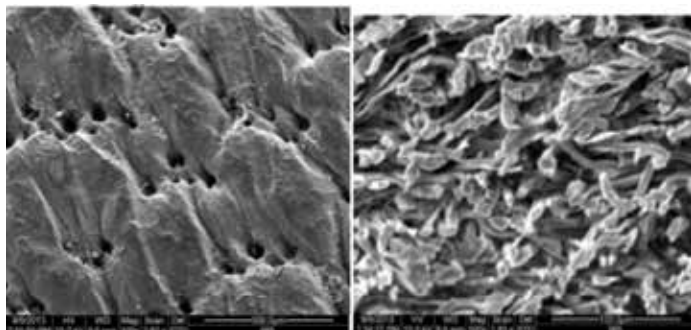


Figure 4. Morphological evaluation of chrome-melamine syntan tanned leathers-Pickle less method.

Scanning Electron Microscopic Analysis

By viewing the cross section one can assess fibre characteristics and grain properties of surface of leather samples using scanning electron microscopy. The electron micrographs of tanned leathers processed through both conventional pickling as well as pickle free methods is presented in Figure 3 and 4. The leathers show compactness in the fibre structure throughout the cross-section indicating uniform filling of syntans.

CONCLUSIONS

The present investigation reports a multi functional chrome-melamine syntan for tanning, rechroming and post tanning. This is a versatile product that serves the leather manufacturers to meet the environmental norms through eco-labeling. Chrome tanning carried out through pickle and pickle-less methods have shown shrinkage temperature of 112°C and 114°C, respectively. The morphological evaluation ascertains that the fibers are well ordered and is characterized by absence of coalescence. Conventional wet blue leathers rechromed using chrome-melamine syntan and evaluated for various organoleptic properties had an increase in fullness and uniform color distribution due to the presence of melamine and chrome in the experimental leathers. Wet end finished leathers also showed better bulk properties and physical strength characteristics. From the results, it can be attributed that the prepared product can be used as a replacement of conventionally used melamine syntans. Moreover, this product can be called a sustainable product, as it is prepared free of formaldehyde.

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