Studies on the Development of Leathers from Formaldehyde-free Melamine Syntan

by

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Abstract

Syntans are indispensable for the manufacture of any kind of leather. Most of the retanning, replacement and filling syntans available today in the market are products made by condensation polymerization reaction using formaldehyde as a condensing agent. Formaldehyde is involved in condensation reaction with substrates such as phenol, naphthalene, melamine, dicyandiamide etc. The resulting products, most of the time, contain and contribute to more than acceptable limits of free formaldehyde in leather. Therefore, there is a growing need for syntans without formaldehyde to meet the stringent regulations on the use and presence of formaldehyde in leather and leather chemicals. Several international regulations call for products that are free of formaldehyde. Even though reducing formaldehyde in leather and leather chemicals is practiced, complete replacement of formaldehyde in condensation process is not well known. In the present study, syntans developed without the use of formaldehyde as a condensing agent for the manufacture of melamine syntan is presented. The physico-chemical analysis, morphological studies and emission loads of the formaldehyde-free melamine syntan have been compared with conventional melamine formaldehyde syntan.

Resumen

Los sintanes son indispensables para la fabricación de cualquier tipo de cuero. La mayoría de los sintanes de recurtición, sustitución y relleno disponibles hoy en día en el mercado son productos fabricados por reacción de polimerización por condensación usando formaldehído como agente de condensación. El formaldehído se emplea en la reacción de condensación con sustratos tales como fenol, naftaleno, melamina, diciandiamida, etc. Los productos resultantes, la mayoría de las veces, contienen y contribuyen a límites de formaldehido libre en el cuero mayores que los aceptables. Por lo tanto, existe una creciente necesidad de sintanes sin formaldehído para cumplir las estrictas regulaciones sobre el uso y la presencia de formaldehído en cuero y en productos químicos para cuero. Varias normas internacionales exigen productos que estén libres de formaldehído. Aunque la reducción de formaldehído en los productos químicos para cuero y en cuero se practica, la sustitución completa del formaldehído en el proceso de condensación no es bien conocida. En el presente estudio, sintanes desarrollados sin el uso de formaldehído como agente de condensación para la fabricación de un sintán melamínico, se presenta. El análisis físico-químico, estudios morfológicos y cargas de emisión del sintán melamínico, libre de formaldehído, han sido comparados con un sintán convencional de melamina-formaldehído.

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INTRODUCTION

The demand for eco-labeled leather and leather products are gaining importance in global leather industry.[1] This has forced the chemical manufactures to look for suitable alternative chemistry for preparation of syntans. Syntans are primarily manufactured with phenol, naphthalene, melamine and dicyandiamide condensed with formaldehyde to obtain retanning properties in different types of leathers.[2] Further, the post tanning operations use a combination of all these syntans to achieve the desired properties like grain tightness, fullness and roundness.[2,3] The technical challenge to the present tanner is to produce high quality leathers meeting eco standards from hides and skins of lower grade and quality.[1] Hence, selection of retanning, dyeing and fatliquoring operations, which is influenced by pH, requires chemicals that are selective.[4] However, improper choice of chemicals with specific reference to syntans and pH conditions across the cross section of the hide results in enduring stress due to differential "filling" at the adjoining layers.[4] Protein hydrolysates and a combination of polymeric tanning agents have been found to be used as fillers in retanning operations that have opened new perspectives.[5,6] Hence, there is an increasing need for those kinds of synthetic tanning materials, which not only brings about "filling" in belly areas but also the cross-section that produce fuller, firm and grain tight leathers. Hence, retanning agents, which are selective that afford full and yet tight leathers, at the same time that are formaldehyde-free are of great importance in the present scenario. Hence, a need has been felt to develop products for retanning, which are devoid of formaldehyde.

Formaldehyde is used to join together molecules to form larger molecular structures in leather chemical manufacture. The use of such condensation products is inevitable in the manufacture of various types of syntans and auxiliaries for the manufacture of different leathers. The presence of free formaldehyde in leather originates from the small excess used in the manufacture of syntans and pose constraints on the use of such products among global consumers.[7,8] Awareness of the eco-labeling concepts among the customers has forced the tanners to look into the manufacturing of formaldehyde-free leathers. Optimizing the use of various polymeric, protein hydrolysates based syntans along with vegetable tannins to provide desired properties to formaldehyde-free leather has been carried out in some investigations.[9,10] However, the leather industry is relooking at the possibility of increased use of natural products, which are organic and biodegradable.[11-13] The environmental impact of retanning agents that are produced from these natural products will have to be assessed, prior to their use in the industry. In this work, an attempt has been made towards the development of and use of a synthetic tanning agent, without the use of formaldehyde as a condensing agent, a product developed from waste natural materials as an alternative to conventional melamine-formaldehyde based products in retanning for different kinds of leathers.[11] The product has been developed from melamine and modified natural product, which confer to properties like fullness, softness, grain tightness, fine and wrinkle free grain, light fastness and intense depth of shade during dyeing.[12,13] The strength and bulk properties of the processed leathers have been analyzed. Scanning electron microscopy analysis of cross section of leathers has been carried out. Leathers have been analyzed for free formaldehyde and the spent post-tanning liquors from both the processes have been analyzed for COD and TS.

MATERIALS AND METHODS

Materials

Chemicals used for the preparation of the Formaldehyde-Free Melamine Syntan were of laboratory grade and procured from a local chemical house in India. Wet blue cow sides shaved to uniform thickness of 1.0-1.1 mm were used in this study. The chemicals used for leather processing were of commercial grade, while the chemicals used for analysis of spent liquors were of analytical grade. The quantity (%) of chemicals used was based on shaved weight.

Preparation of Formaldehyde-free Melamine Syntan

Sodium meta bisulfite (70 g) was taken along with the 500 g of natural condensing product (prepared from periodate oxidation of sodium alginate) and stirred for 4 h at 60°C. Melamine (240 g) was added with some additional sodium meta bisulphate (30 g). Further quantity of 150 g of natural condensing agent was added and the mixture was stirred for further 16 h. 110 g of prepared naphthalene sulfonic acid (50 g naphthalene, sulphonated with 60 g sulphuric acid (96-98%) at 160-165°C for 5 h and cooled) was added along with additional sodium meta bisulfite (20 g) and natural condensing agent (50 g). The final spray dried formaldehyde-free melamine syntan product was used for all the experimental leathers.

Characterization of the Prepared Formaldehyde-free Melamine Syntan Determination of Solid Content

A known quantity of product was weighed in an empty dish and dried at 103°C -105°C for 1 h as per the standard procedure.[14] Total solid content of the products was calculated based on dried weight.

Determination of Particle Size of the Prepared Syntan

The particle size was measured in a Zetasizer 3000HSA using the technique of photon correlation spectroscopy. With this technique the fluctuations in the intensity of light scattered by the particles were analyzed using a digital correlator to determine the diffusion coefficients. The diffusion coefficient is inversely proportional to the size of the particle and size was obtained from the Stokes-Einstein equation. The obtained diffusion constant values were converted to intensity average particle size and number average particle size using CONTIN software and employing Mie theory.

Evaluation of the Prepared Syntan

Post tanning recipe for control and experimental processes are given in Table I. For assessing the properties of the formaldehyde-free melamine syntan trials of the product was compared against leathers developed using commercial melamine-formaldehyde syntan.

Physico-Chemical Evaluation of the Leather

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method.[15] Specimens were conditioned at 80±4°F and 65±2% R.H. over a period of 48 h. Physical properties such as tensile strength, % elongation at break and tear strength were examined as per the standard procedures.[16]

Assessment of Softness through Digital Leather Softness Tester

The softness of the leathers was measured using a MSA ST 300 digital leather softness tester supplied by MSA Engineering Systems Limited.[17] The method permits measurement of softness of leather without defacing the hide. The measurements were performed using a 35 mm ring at 20 ±2°C with a relative humidity of 65±2% with thickness of leather being 1.1-1.2 mm. Higher value indicates higher softness. Measurements were carried out on 5 locations within the sampling area and reported as average.

TABLE I
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	1.5	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	2.0	30	
Formaldehyde-free melamine syntan	4.0	45	
Synthetic Fatliquor	4.0		
Semi-synthetic Fatliquor	2.0	60	Mixed in hot water
Formaldehyde-free melamine syntan	6.0	60	
Semi-synthetic Fatliquor	2.0		
Acid Dye	4.0	30	
Formic acid	1.5	4x10+20	The Exhaustion of the bath was checked. Drained.
Washing	100	15	Drained. The leathers were set twice, hooked to dry, conditioned, staked.

Color Measurements

Color measurement parameters *viz*., L, a, b, h and C were recorded using a Lambda 35 UV-Vis spectrophotometer employing an advanced spectroscopy software instrument for control and experimental crust leathers.[18] 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 ΔL, lightness difference; Δa and Δb, difference in 'a' and 'b' values, where 'a' represents red and green axis and 'b' represents yellow and blue axis; Δh, hue difference; Δc, chromaticity difference. ΔL, Δa, Δb and Δc were calculated by subtracting the corresponding values for experimental leathers from that of control leathers.

Fastness to Artificial Light

The resistance of the color of the experimental and control leathers to an artificial light source, Xenon lamp, was measured using standard test procedure. [19] One side of the leather was exposed to light from a xenon arc under prescribed conditions for 20 h, along with four dyed blue wool standards having increasing levels of fastness. Black panel temperature was maintained at 50±1°C and the relative humidity was 40±5%. Fastness was assessed by comparing the fading of crust leathers with that of the standards, from standard 1 (very low light fastness) to standard 4 (very high light fastness), where each standard being approximately twice as fast as that of preceding one. Rating was given on a scale of 1-4 points, where higher points indicate better fastness.

Fastness to Dry and Wet Rub

Samples of appropriate size (5 x 14 cm) were cut from the official sampling position and after conditioning they were tested according to standard test method using SATRA Crockmeter.[20]

Organoleptic Properties

Experimental and control crust leathers were assessed for softness, fullness, grain flatness, 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.[21] Samples were then cut into specimens coated with gold using an Edwards E306 sputter coater. A Leica Cambridge Stereoscan 440 scanning electron microscope was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different magnification levels.

Analysis of Post-Tanning Wastewaters

Chemical oxygen demand (COD) and TS of the wastewater were determined as per standard procedures. Emission loads were calculated by multiplying the concentration (mg/L) with volume of effluent (L) per tonne of hides processed.

RESULTS AND DISCUSSIONS

Formaldehyde-free melamine syntan was prepared by condensation of melamine with the oxidized sodium alginate as a natural condensing agent. The product obtained was water-soluble, light brown in color similar to that of commercial syntan. The product was of high viscosity and the solid content was adjusted to 40-50% to obtain good yield of spray-dried powder. The pH of 10% solution was in the range of 6.5. The product is expected to provide light fastness and not darken the leather on ageing, as there are no components, which can undergo photo degradation. A particular advantage of this condensing agent used, in contrast to conventional melamine syntans, is that they contain no formaldehyde, which constitute health hazard. Owing to the content of natural condensing substances, the melamine polymers are more readily biodegradable.

Particle Size Analysis of the Products

Particle size of 10% aqueous solution of the formaldehyde-free melamine and formaldehyde containing commercial syntan was obtained through a Zetasizer 3000 HSA instrument. The 10% solution of the commercial product had a pH of 7.1. At this pH, an equal distribution of particles at 598 nm (42%) and 1562 nm (38%) were observed. This indicates that large sized particles would fill up the intermediate layer, thereby providing the necessary compaction, while the remaining particles are expected to penetrate further and provide fullness and body to the leather. The prepared formaldehyde-free melamine syntan contained multiphase distribution of the particles. This product had the lowest particle size of 658 (42%) nm and the highest at 2796 nm (26%) and range of particles at 832 nm to 2561 nm. From the number average diameter of the particles, it is therefore expected that this formaldehyde-free melamine syntan would also penetrate well into the matrix as well as distribute uniformly in the matrix as it contains varied sized particles. With its large particle size greater than the commercial product, the product is expected to provide better-desired filling and compaction of looser ends in the final leathers.

Organoleptic Properties

A comparison of the organoleptic properties of commercial and formaldehyde-free melamine syntan is given Figure. 1. The leathers were evaluated for various organoleptic properties such as fullness, softness, grain tightness, roundness, dye affinity and general appearance by hand and visual evaluations. The average rating from two experienced tanners corresponding to each experiment was calculated for each functional property is given in Figure 1. Higher numbers indicate better property. The results observed indicate that a higher level of compaction is obtained when formaldehyde-free melamine type product is employed, while softer leathers are obtained when commercial product is employed. The control and formaldehyde-free melamine retanning provides for over all 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. Fullness is higher for leathers from formaldehyde-free melamine retanned leathers. Grain tightness, Grain smoothness, roundness, dye affinity and strength of leathers are similar to control leathers. In general, the appearance of experimental leathers is better than that of control leathers.

Physical Characteristics of 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 II. The grain crack strength for the crust leathers were also carried out. The mean values corresponding to each experiment were averaged and the values are given in Table II. It is evidenced that the results of physical testing in leathers with formaldehyde-free melamine syntan are comparable in terms of tensile, tear and grain crack strength with that of control leathers. Quantitative assessment of softness for both control and experimental leathers indicate that the control leathers are slightly softer than the formaldehyde-free melamine retanned leathers. This may due to particle size of formaldehyde-free melamine syntan being slightly higher than that of control leathers.

Color Difference Studies

Color measurement values for control and experimental leathers are given in Table III. It is observed that the experimental leathers show negative ‘‘ΔL’’ value, which means that the experimental leathers are darker in shade. The overall color difference (ΔE) for experimental leathers is 2.2, compared to control leather, indicating that there is increase in the shade between control and experimental leathers resulting in darker shades for formaldehyde-free melamine syntan retanned leathers.

Spent Post-Tanning Liquor Analysis

The spent post-tan liquors have been collected from control and experimental processes. COD and TS are the two parameters that have been chosen for analyzing the

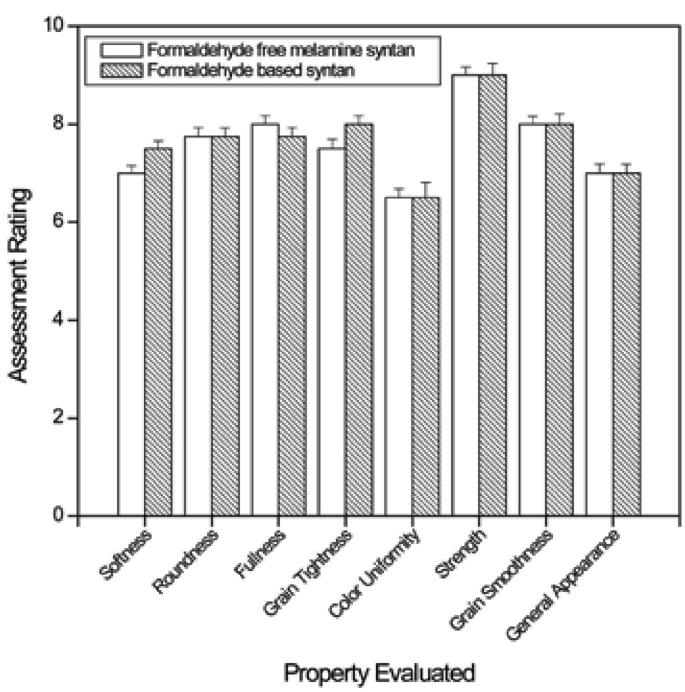

Figure 1. Comparison of organoleptic properties of leathers retanned with commercial product and formaldehyde-free melamine syntan

TABLE II
Physicochemical and Wastewater Characteristics for Leathers Retanned with Commercial and Zero Formaldehyde Syntans

Physicochemical properties	Leathers made using the products	
	Commercial	Formaldehyde–Free
Tensile strength (kg/cm^2)	258±18	242±23
Elongation at break (%)	74±7	72±8
Tear strength (kg/cm)	89±6	85±7
Softness	3.8±0.4	3.2±0.6
Light fastness	3±0.5	3±0.5
Wet rub fastness (felt)	40±0.5	4±0.5
Dry rub fastness (felt)	4±0.5	4±0.5

TABLE III
Comparison of Colour Difference Measurements Retanned with Commercial Product and Zero Formaldehyde Syntans (ZFS)

Leather	L	a*	b*	C	
Commercial	24.56	0.38	-0.06	0.43	
ZFS	23.24	0.41	0.23	0.56	
	ΔL	Δa	Δb	Δh	ΔE
	-1.76	0.11	0.24	0.18	2.2

TABLE IV
Wastewater Characteristics for Leathers Retanned with Commercial and Zero Formaldehyde Syntans

	Commercial	**Formaldehyde–free**
COD (ppm)	16821±214	7536±168
Total solids (ppm)	21543±349	14946±192
Volume of effluent (L/t of shaved weight)	1480±32	1420±31
Emission Load – COD (Kg/t of shaved weight)	25±2	11±1
Emission Load – Total Solids (Kg/t of shaved weight)	32±1	21±1

environmental impact. A direct correlation of the observed COD and TS values with the environment may not give proper consequences. Hence, the COD and TS values have been converted into emission loads. The COD and TS values and the calculated emission loads are given in Table IV. It is seen that a reduction in COD and TS load is achieved in formaldehyde-free melamine syntan based retanned leathers.

Scanning Electron Microscopic Analysis

Fullness of leathers can be assessed by viewing the cross section of leather samples using scanning electron microscopy. The scanning electron micrographs of control and experimental crust leather samples showing cross section are given in Figure 2A and 2B. The control and experimental samples show comparable compactness in the fibre structure throughout the cros-section indicating uniform filling of syntans. In specific, sample from formaldehyde-free melamine syntan based retanned leathers show more compact fibre structure.

Free Formaldehyde in Leather

Control and experimental leathers were analyzed for free formaldehyde using standard procedure. The free formaldehyde in experimental leathers is not detectable, while control leather contains about 828 mg/kg of free formaldehyde. This is primarily due to formaldehyde-free melamine syntan used for the manufacture of experimental leathers.

CONCLUSIONS

Environmental norms on formaldehyde are often not met by formaldehyde based syntan even when used in lower concentration. Present environmental regulations require the elimination of such products from leather processing. In the present work, it has been possible to find a complete replacement for formaldehyde as a condensation product for

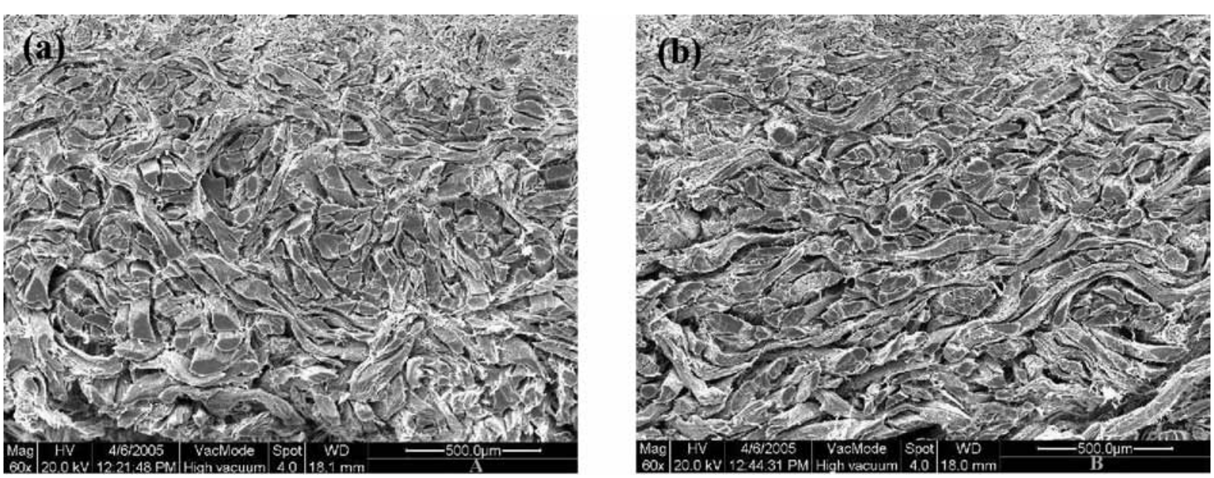

Figure 2. Scanning electron micrographs of cross section of the leathers retanned with (a) Commercial syntans (b) Zero formaldehyde syntans

the manufacture of melamine formaldehyde syntan. The condensation product is made from natural resource and hence offers COD reduction by 50% in post tanning. The product offers a complete replacement to melamine-formaldehyde type syntans as observed from the physico-chemical properties of leathers. The strength properties are comparable to that of control leathers. Color difference measurements show that the experiment leathers are darker in colour as compared to control leather, which is in agreement with visual assessment. Free formaldehyde in the experimental leathers is not detectable in contrast to control leathers. In specific, the leathers obtained from experimental formaldehyde-free melamine syntan possess better properties than that of other experimental and control leathers.

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