Zero Formaldehyde Syntan

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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. However, 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. REACH, a European Regulation calls 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 established. In the present study, we have developed syntans without the use of formaldehyde as a condensing agent for the manufacture of melamine syntan. The chemical characteristics of the zero formaldehyde melamine syntan (ZFMS) and the physical properties imparted to the leather are presented.

Keywords: syntan; melamine; formaldehyde; condensation; zero formaldehyde melamine syntan

1 Introduction

The demand for eco-labeled leather and leather products and the awareness of the eco labeling concepts among the customers has forced the tanners to look into the manufacturing of formaldehyde-free leathers[1,2] in global leather industry. This has forced 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. Further, the post tanning operations use a combination of all these syntans to achieve the desired grain tightness, fullness and roundness. Many of these chemicals are not eco-friendly and hence affect the environment significantly. 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 leathers. The presence of free formaldehyde in leather originated from the small excess used in the manufacture of syntans that do not react with aromatic substances, pose constraints on the use of such products among global consumers. Optimizing the use of various formaldehyde-free and formaldehyde-based syntans for application as single syntans by analyzing their ability to provide desired properties to leather has been carried out in some investigations[3]. Study on producing leather without free formaldehyde by employing combination of optimized formaldehyde-free syntans is also reported[4]. This work reports the development and use of a syntan without the use of formaldehyde as a condensing agent, condensing agent developed from waste natural materials as an alternative to formaldehyde in the

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development of ZFMS in retanning process for different kinds of leathers. 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. Spent post-tanning liquors from both the processes have been analyzed for COD and TS.

2 Experimental

2.1 Materials

Chemicals used for the preparation of the ZFMS 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.

2.2 Preparation of syntan

The detailed manufacturing details and the modified natural condensation product used in this study are patented. Sodium meta bisulphite was taken along with natural condensing agent and stirred for 4 hours. Then melamine was added with some additional sodium meta bisulphite and the natural condensing agent. This mixture was stirred for 16 hours and prepared naphthalene sulphonic acid was added along with additional sodium meta bisulphite and natural condensing agent. The final spray dried ZFMS product was used for all the experiments.

2.3 Characterization of syntan

2.3.1 Determination of solid content

A known quantity of product was weighed in an empty dish and dried at 103^{o}C -105^{o}C for 1 h as per the standard procedure[5]. Total solids contents of the products were calculated based on dried weight.

2.3.2 Determination of Particle Size

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 employing Mie theory.

2.4 Evaluation of the product

Post tanning recipe for control and experimental processes are given in Tab 1. For assessing the properties of the ZFMS syntan trials of the product was compared against leathers developed using commercial melamine-formaldehyde syntan.

2.5 Physico-chemical evaluation of the leather

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method[6]. Specimens were conditioned at 80±4^{o}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[7,8].

2.6 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[9]. The method permits measurement of softness of leather without defacing the hide. The measurements were performed using a 35 mm ring at 20 ±2^{o}C and with a relative humidity of 65±2% with thickness of leather being 1.0-1.1mm. Higher value indicates higher softness. Measurements were carried out on 5 locations within the sampling area and reported as average.

2.7 Color measurements

Color measurement parameters *viz.*, L, a, b, h and C were recorded using a Lambda 35 UV-Vis spectrophotometer for control and experimental crust leathers. 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.

Tab 1. Post-tanning Recipe for the Manufacture of Upper Leather from Cow 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	
Zero Formaldehyde Melamine Syntan*	4.0	45	
Synthetic Fatliquor	4.0		
Semi-synthetic Fatliquor	2.0	60	Mixed in hot water
Zero Formaldehyde Melamine Syntan*	6.0	60	
Semi-synthetic Fatliquor	2.0		
Acid Dye	2.0	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.

* Commercial melamine formaldehyde syntan was used for retanning control leathers

2.8 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[10]. A 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^{o}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.

2.9 Fastness to dry and wet rub

Samples of appropriate size (5 x 14 cm) were cut from the official sampling position[6] and after conditioning they were tested according to standard test method using SATRA Crockmeter[11].

2.10 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.

2.11 Scanning electron microscopic 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[12]. 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 grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different magnification levels.

2.12 Analysis of wastewaters

Chemical oxygen demand (COD) and TS of the wastewater were determined as per standard procedures[13]. Emission loads were calculated by multiplying the concentration (mg/L) with volume of effluent (L) per tonne of hides processed.

3 Results and discussions

ZFMS was prepared by condensation of melamine with a modified natural condensing agent. The product obtained was similar in color to commercial syntan. The product was of high viscosity and the solid content was adjusted to 40-50% to obtain good amount of spray dried powder. The product pH was in the range of 6.5-7.0. 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.

3.1 Particle size analysis of the products

Particle size of 10% aqueous solution of the products was obtained through a Zetasizer 3000 HSA instrument. The 10% solution of commercial product had a pH of 7.2. The number average diameter of the particles indicated a multiphase distribution in the commercial product. 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 10% solution of the prepared product ZFMS had a pH of 6.5. The number average diameter of the particles also indicated a multiphase distribution in ZFMS product. The ZFMS product had the lowest particle size of 859 nm and the highest at 3488 nm. It is therefore expected that this product ZFMS would also penetrate well into the matrix. With a large particle size, product ZFMS is expected to provide the desired filling and compaction of looser ends better than the commercial product

3.2 Organoleptic properties

A comparison of the organoleptic properties of commercial and ZFMS products are provided in Fig. 1 based on hand evaluation. 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 Fig. 1. Higher numbers indicate better property. The results observed indicate that a higher level of compaction is obtained when ZFMS type product is employed, while softer leathers are obtained when commercial product is employed. The control and ZFMS 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, grain tightness and dye affinity of leathers are higher for leathers from ZFMS retanned leathers. In general, the appearance of experimental leathers is comparable to or even better than that of control leathers.

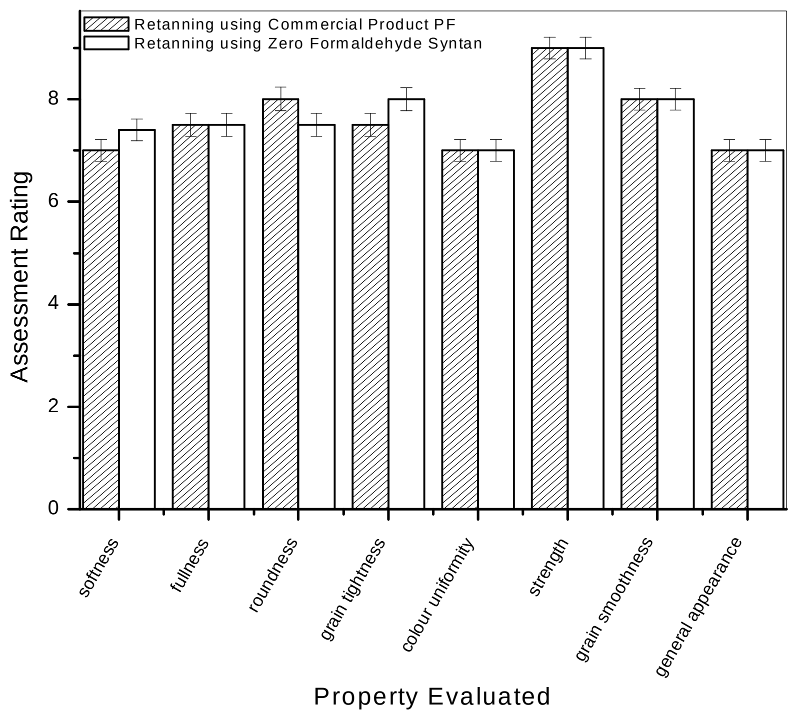


Fig.1 Comparison of organoleptic properties of leathers retanned with commercial product and zero formaldehyde melamine syntan

3.3 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 for each strength character and given in Tab 2. 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 Tab 2. It is evidenced that the results of physical testing in leathers with ZFMS are comparable in terms of tensile, tear and grain crack strength with that of control leathers. However, ZFMS retanning provide leathers with very slight lower tensile and grain crack strength values. This may be due to higher compaction imparted by ZFMS syntans to leathers. Quantitative assessment of softness for both control and experimental leathers indicate that the control leathers are slightly less softer than the ZFMS retanned leathers. This may due to mild effect of natural condensing agent in ZFMS syntan.

Tab.2 Physicochemical and Wastewater Characteristics for Leathers Retanned with Commercial and Zero Formaldehyde Melamine Syntan

Physicochemical properties	Leathers made using the products	
	Commercial	ZFMS
Tensile strength (Kg/cm^2)	341±10	332±12
Elongation at break (%)	75±6	72±8
Tear strength (kg/cm)	99±6	95±4
Softness	3.6±0.4	3.8±0.2
Light fastness	3±1	3±1
Wet rub fastness (felt)	4±1	4±1
Dry rub fastness (felt)	4±1	4±1
COD (ppm)	16821±225	18536±146
Total solids (ppm)	23543±328	32946±296
Volume of effluent (L/t of shaved weight)	1480	1420
Emission Load – COD (Kg/t of shaved weight)	22±2.6	31±2.1
Emission Load – Total Solids (Kg /t of shaved weight)	26±1	42±2

3.4 Color difference studies

Color measurement values for control and experimental leathers are given in Tab 3. It is observed that the experimental leathers show negative ‘‘DL’’ value, which means that the experimental leathers are darker in shade. The overall color difference (DE) 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 ZFMS retanned leathers.

Tab 3. Comparison of Color Difference Measurements Retanned with Commercial Product and Zero Formaldehyde Melamine Syntan

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

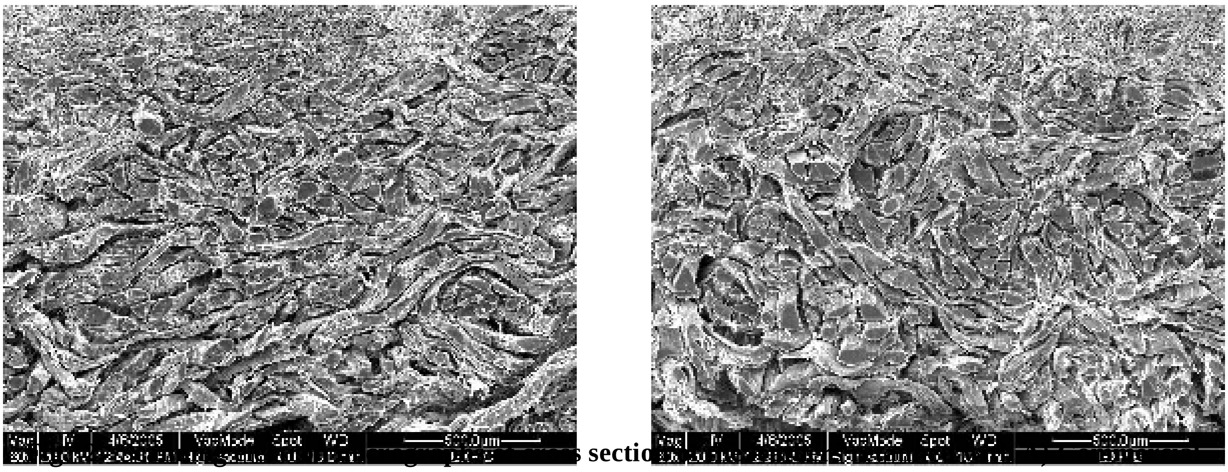
3.5 Spent post-tanning liquor analysis

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 analysing the environmental impact. A direct correlation of the observed COD and TS values with the environment may not give proper consequences. Hence, COD and TS values have been converted into emission loads. The COD and TS values and the calculated emission loads are given in Tab 2. It is seen that a reduction in COD and TS load is achieved in ZFMS retanned effluent liquors.

3.6 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 Fig. 2A and 2B. The control and experimental samples show comparable compactness in the fibre structure throughout the cross section indicating uniform filling of syntans. In specific, sample from ZFMS retanned leathers show more compact fibre structure compared to experimental sample.

A) B)



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syntans B) Zero formaldehyde melamine syntans

3.7 Free formaldehyde in leather

Control and experimental leathers were analyzed for free formaldehyde using standard procedure. The free formaldehyde content in both control and experimental leathers is given in Tab 4. Free formaldehyde in experimental leathers is not detectable, while control leather contains about 828 mg/kg free formaldehyde. This is primarily due to ZFMS used for the manufacture of experimental leathers.

Tab 4. Comparison of Free formaldehyde in Leathers Retanned with Commercial Product and Zero Formaldehyde Melamine Syntan

Leather	Free formaldehyde
Commercial	828 ± 13
ZFMS	Not detectable

4 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 the manufacture of melamine formaldehyde syntan. The product is made of natural product and hence offers reduction in pollution load 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 or even better than that of control leathers upon using ZFMS syntans. Color difference measurements show that the experiment leathers are darker in color 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 ZFMS possess better properties than that of other experimental and control leathers.

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