Development of Aluminum-melamine Formulation for Retanning Application

by
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Abstract

The process of preparation of a large number of syntans is based on enhancement of the molecular weight of low molecular weight aromatic/aliphatic monomers etc., through addition polymerization and condensation reactions. The disadvantage associated with condensation process is the use of formaldehyde, which is a proven carcinogen. In addition, one of the major drawbacks with chrome tanning, the lack of fullness, is addressed during post tanning processes by employing synthetic tanning agents. With these issues in focus, formaldehyde free aluminum based melamine syntan has been prepared having particle size distribution in the range of 450-700 nm and stable up to pH 4.5. The prepared syntan has been used as retanning agent in leather processing. The experimental leather exhibits superior organoleptic properties such as fullness, grain tightness, and physical strength characteristics such as tensile, tear strength compared to control leather. Also, experimental leather exhibits higher dye intensity compared to control leather. It is evident from the air permeability and pore size distribution analysis that the prepared product has significantly arrested the pores thereby increasing the fullness of leather. Scanning electron microscopic image shows that the experimental leathers have a flat and compact fiber structure.

Introduction

The hides/skins used for leather manufacturing are anisotropic in nature. Removal of non-leather making materials such as elastin, reticulin, proteoglycan, fat and various other chemical/mechanical actions on hides/skins further increases the anisotropicity. The economic value of the final leather strongly lies in the homogeneity of the substrate. Usage of vegetable tannins in leather making provides tanning cum filling action thereby increasing the homogeneity of the substrate. But today, 90% of the leather is made by using chromium(III) salt due to the unavailability of vegetable tannins and lack of other properties such as shrinkage temperature and strength properties.[1] Even though chromium salt is superior to vegetable tannins in terms of hydrothermal stability and mechanical properties, the substrate homogeneity is not improved during chrome tanning process. In commercial language, tanners generally say "chrome tanned leathers are empty in nature." The drawbacks associated with chrome tanning, such as lack of fullness, are addressed during post-tanning processes by employing synthetic tanning agents. In general, the process of preparation of a significantly large number of syntans is based on enhancement of molecular weight of low molecular weight aromatic compounds, monomers etc., through addition, polymerization and condensation reactions.

One of the significant drawbacks associated with condensation process is the use of formaldehyde, which is a proven carcinogen. The presence of free formaldehyde in leather and leather products, even at 30-100 ppm, is becoming a huge cause of concern for leather manufactures. On the other hand, re-chroming is one of the processes in leather manufacturing that is generally carried out to ensure the uniform tannin content of leather procured from different sources. Non-uniformity in tannin content leads to patchy dyeing. However, the usage of chromium in re-chroming process leads to more unfixed and loosely bound chromium, which can be easily converted into chromium(VI) during the neutralization and fatliquoring processes where the alkali and unsaturated oils are used.[2-4] Chromium(VI) is one of the most restricted substances in leather and leather products because of its carcinogenicity. Consumer awareness and statutory stipulation norms are forcing the leather chemical industries to seek formaldehyde free re-tanning agent as alternatives. Since formaldehyde poses a known toxic hazard, an attempt has been made to produce a formaldehyde free re-tanning agent.[5,6] Alginate-chitosan based biopolymer has been prepared and used as a retanning agent in leather processing.[7] Protein hydrolysate from leather waste has been prepared and used as a retanning agent with and without modification. Swarna v. Kanth *et al*., reported that preparation of formaldehyde free melamine based re-tanning agent by using dialdehyde starch as a crosslinkers.[10] Denatured starch-gelatin complex has been

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prepared and used as retanning agent.[11] In this work, an attempt has been made to prepare formaldehyde and chromium free re-tanning agent for environment friendly leather manufacturing. The developed product is based on aluminum-melamine formulation and it has been characterized for particle size, potentiometric titration and surface charge measurement. The developed product has been used as a re-tanning agent in leather processing and the salient features of the work have been presented in this paper.

Materials and Methods

Chemicals used for preparation of retanning agent such as melamine, glyoxal and aluminum sulfate were of laboratory grade procured from Himedia and S.D Fine- Chem Limited in India. Wet-blue goat skins having an average area of 4-5 square feet and shaved to a thickness of 1.1-1.2 mm were used as starting material to assess the re-tanning ability of the developed product. The chemicals used for leather processing were of commercial grade. The amount of chemicals (%) offered for leather processing was based on shaved weight.

Preparation of Aluminum-Melamine Formulation

Preparation of Melamine-glyoxal Resin (MGR)

200 gram of melamine and 200 gram of sodium salt of halogenated carboxylic acid was added into the reaction vessel containing 2 liters of distilled water. The vessel was then placed on a thermostatic reactor and the temperature was maintained at 75°C with constant stirring (200 rpm) for 2 hrs. 220 ml of formic acid (85% v/v) was added drop by drop to the heated solution and stirred for 30 minutes. 540 ml of glyoxal (40% v/v solution) was added drop wise to the acidified solution and further stirred for 45 minutes to get melamine-glyoxal resin (MGR).

Incorporation of Aluminum into MGR

A known quantity of MGR was taken into the round bottom flask and heated at 75°C into which aluminum sulfate was added to get the final product with Al_2O_3 content about 10% w/w. The mixture was further stirred for 60 minutes to get a homogenous solution of aluminum-melamine formulation. The solution was then spray dried and used for subsequent experiments

Characterization of Aluminium-melamine Formulation

Potentiometric Titration

The pH titration curve of prepared aluminum-melamine formulation was obtained as follows: 50 ml of 10% (w/v) solution of the formulation was taken in a 100 ml beaker and titrated against 10% sodium carbonate solution. 4 ml of 10% sodium carbonate solution was added to the aluminum-melamine formulation step wise and the corresponding pH change in the solution was recorded. A plot of pH vs volume of sodium carbonate was drawn.

Analysis of Particle Size, Surface Charge

The prepared sample was centrifuged at 5000 rpm for 5 minutes in ordered to remove the impurities. The centrifuged sample was transferred into another vial and sonicated in a bath sonicator for 10 minutes to avoid the interference of particle aggregation. The average particle size and surface charge of the sonicated sample were analyzed using Malvern Zetasizer.

Evaluation of Aluminum-melamine Formulation in Re-tanning Process

In order to evaluate the developed aluminum-melamine syntan, five wet-blue goat leathers having the thickness of 1.1-1.2 mm were cut into two halves along the backbone and marked as left and right. These left and right halves were grouped separately and their weights were noted. Left halves were treated with commercial aluminum syntan (Control) and right halves were taken for the experimental process where developed aluminum-melamine formulation was used as re-tanning agent and the process recipe has been tabulated in Tables I and II.

Organoleptic Properties and Physical Strength Characteristics

Experienced persons from the leather industry analyzed the control and experimental leathers for various organoleptic properties such as fullness, softness, grain tightness, grain smoothness and roundness. They were rated on a scale of 1-10, where higher points indicate better properties. The physical properties such as tensile strength[12], percentage elongation at break and tear strength[13] were examined for both control and experimental leathers. The specimens for various testing as mentioned above were obtained as per IULTCS standard method. Specimens were conditioned for 24 hr at 25 ± 1°C and 65 ± 2% RH[14].

Analysis of Air Permeability and Throat Pore Size Distribution

PMI capillary flow porometer was used to study the air permeability and throat pore size distribution of control and experimental leathers. A sample size of 2.5 cm was rounded from butt area of control and experimental leathers and the thickness was noted. Calwick (Wetting liquid supplied by PMI porous material company) with a defined surface tension of 15.9 dynes cm^{-1} was used as wetting liquid for porometry measurements. In this technique, the sample was placed between two disks and dry air passed through the sample with increasing pressure. Then the same sample was saturated with Calwick wetting liquid and dry gas was again sent through the sample with increasing pressure. The flow rate was measured as a function of pressure for dry and wet sample. The flow rate of dry sample gives air permeability and flow rate profile of dry and wet sample provides throat pore size distribution. It is the only technique to provide information about throat diameter of through pores.

Color Measurements

Color measurement parameters viz., L, a, b, h and C were recorded using a Lambda 35 instrument for grain side of control and experimental crust leathers. "L" represents lightness, "a" value represents redness and greenness, "b" value represents yellowness and blueness, "c" value represent chromaticity and "h" value represents hue.

Morphological Analysis

The control and experimental leathers were cut into specimens with uniform thickness. All the specimens were coated with gold using a JEOL JFC-1100E ion-sputtering device. A JEOL JSM-5300 scanning electron microscope was used in order to study the morphological characteristics of control and experimental leathers.

RESULT AND DISCUSSION

Preparation of Aluminum-melamine Formulation

Solubility of melamine in water is very poor, but it can be solubilized through condensation with aldehyde under acidic condition. Here, glyoxal has been used as cross linker to form melamine-glyoxal resin. Dispersion of melamine in acidic hot water produces a curdy precipitate. The precipitate becomes a transparent pale yellow solution after the addition of glyoxal. Temperature of the reaction medium is directly proportional to the degree of crosslinking. Increase in temperature leads to formation of a high molecular weight resin, which reduces the water solubility. The optimum temperature for the reaction has been found to be around 75-80°C. The completion of the reaction has been ascertained by the change of color of the

TABLE I
Evaluation of aluminium-melamine formulation - Process recipe
Raw material- Goat wet-blue (1.1 mm thickness).

Control process			**Experimental process**		
Acid washing			**Acid washing**		
Water	100%		Water	100%	
Acetic acid	1%		Acetic acid	1%	
Water	5%	2x10+45 min pH 3.0-3.2	Water	5%	2x10+45 min pH 3.0-3.2
Re-tanning					
Water	100%		Water	100%	
Commercial Aluminium syntan	**6%**	**60 min**	**Aluminium-melamine formulation**	**6%**	
Sodium citrate	1%	30 min	Sodium citrate	1%	30 min
Sodium bicarbonate	1%		Sodium bicarbonate	1%	
Water	5%	2x10+60 min pH 3.8-4.0 Pile over night	Water	5%	2x10+60 min pH 3.8-4.0 Pile over night
Note: Percentage of chemicals are based on shaved weight					

solution from pale yellow to dark orange. At this condition, calculated quantity of aluminum sulfate has been incorporated into the homogenous solution of melamine-glyoxal resin. After adding aluminum sulfate, the color of the solution turned to wine red. Finally, the spray drying of the blended formulation has been carried out to get aluminum-melamine syntan in powder form.

TABLE II
Process recipe for the manufacture of softy upper leathers re-tanned leather.

Process/Chemicals	% Offer	Time	Remarks
Washing			
Water	100	10 min	Drained
Neutralization			
Water	150		
Sodium formate	1		
Water	10	15 min	
Sodium bicarbonate	1		
Water	10	3x15+30 min	pH adjusted to 5.2 – 5.5. Drained
Washing			
Water	200	15 min	Drained
Retanning, dyeing & fatliquoring			
Water	100		
Acrylic syntan	2		
Water	10	30 min	
Phenolic syntan	4		
Tara powder	4		
Acid dye (Blue)	2	90 min	Penetration was checked
Synthetic fatliquor	4		
Semi synthetic fatliquor	5		
Water	25	2x10+45 min	
Fixing			
Formic acid	2.5	3x15+30 min	Exhaustion was checked. Drained. Crust leathers were set twice, hooked to dry and staked.

Characterization of Aluminum-melamine Formulation

Leather manufacturing is mainly a pH dependent process. Efficiency of the process depends on pH of the substrate as well as that of the product. The pH of 10% prepared aluminum-melamine syntan has been found to be around 3.0. Potentiometric titration has been performed in order to find out the alkali stability of the product and the titration curve has been shown in Figure 1. It could be observed from the figure that the pH of the solution increased gradually up to 4.5.Upon reaching the pH of around 4.5, there is a formation of a precipitate, which does not go in to solution again. Hence, it could be seen that the prepared product is stable up to the pH of 4.5.

The spray dried product has been observed to be completely water soluble and the pH of 10% solution is around 3.0. The particle size and surface charge of the syntan are the two factors, which could influence the distribution of the product in to the leather matrix. The particle size distribution curve of aluminum-melamine syntan is shown in Figure 2.

It could be observed from the figure that the particles are distributed in the range between 450-700 nm (diameter) and the maximum intensity is at 520 nm. Murali and co-workers had studied the pore size distribution of wet-blue from different animal species, such as goat and sheep[15] and reported that the average throat pore diameter (the most constricted diameter of through pore) is around 1000 nm. Therefore, the prepared aluminum-melamine syntan can even fill up the constricted diameter of wet-blue leathers. The surface charge analysis result showed that the prepared product is cationic in nature (Zeta potential: +11.24 mV).

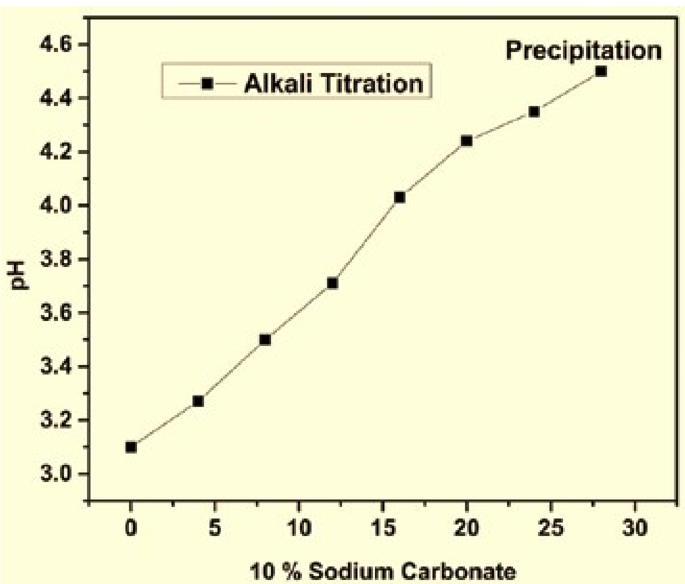

Figure 1. Potentiometric titration curve of aluminum-melamine syntan.

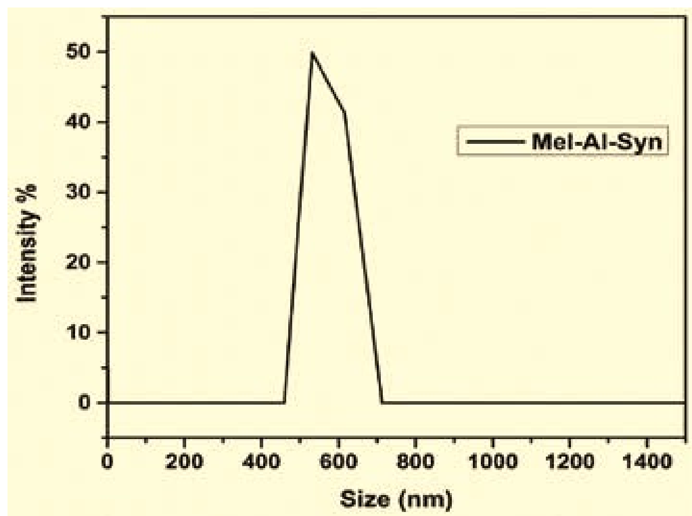

Figure 2. Particle size distribution of aluminum-melamine syntan.

TABLE III

Physical strength characteristics of control and experimental leathers.

Parameters	Control	Experiment
Tensile strength (N/mm^2)	19.4±0.2	23.4±0.1
Elongation at break (%)	75±3.4	68±4.2
Tear strength (N/mm)	67±2.8	76±2.8
Load at grain crack (kg)	13.6±0.8	12.45±0.5
Distension at grain crack (mm)	7.4±0.1	7.2±0.2

Note: The values are mean ± standard deviation of three determinations.

Organoleptic Properties and Physical Strength Characteristics

Organoleptic properties of control and experimental leathers are shown in Figure 3. It could be observed that experimental leathers exhibit better fullness, grain tightness and roundness than control leathers. Softness of control leathers has been found to be slightly better than that of experimental leather and no difference has been observed in grain smoothness.

Physical strength characteristics of control and experimental leathers have been tabulated in Table III. It is evident from the table that experimental leathers exhibit increased tensile strength (23.4 N/mm^2) and tear strength (76 N/mm) as compared to control leathers. It is also evident that the elongation of control leather (75%) is higher than experimental (68%) leather. No significant difference has been observed in load at grain crack and distension at grain crack.

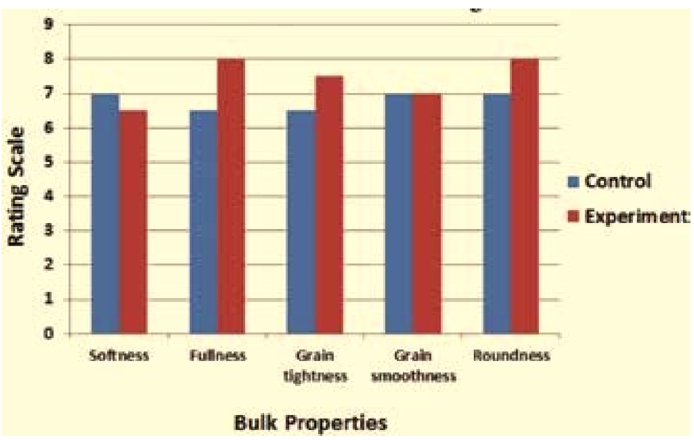

Figure 3. Organoleptic properties of control and experimental leather.

Analysis of Air Permeability and Throat Pore Size Distribution

Air permeability is one of the unique features of leather among various synthetic materials. The efficiency of retanning agents or fillers can be indirectly measured by conducting air permeability test. The amount of air passed through the sample is indirectly proportional to the efficiency of re-tanning agent or in other words, higher the filling action (fullness), lower the air permeability. In order to compare the permeability of control and experimental leathers, air permeability test has been carried out and the permeability graph is shown in Figure 4.

It could be observed that the control leathers permeate more amount of gas to flow as compared to experimental leathers. Flow rate of control leather at 60 PSI is about 750 cc/sec, whereas in case of experimental leather is only about 570 cc/sec.

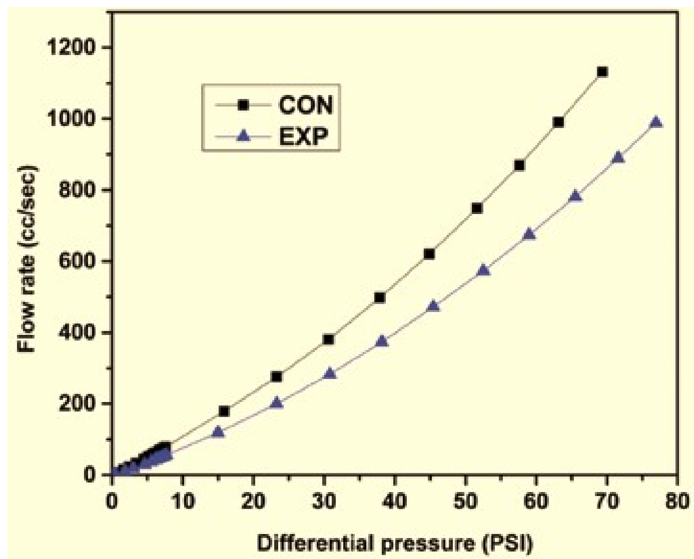

Figure 4. Air permeability of control and experimental leather.

TABLE IV
Color measurements of control and experimental leathers.

Sample ID	L	a*	b*	c*	H	Shade card
Control	60	-7.3	-16.3	16.4	246	
Experiment	50	-7.0	-16.4	18.5	248	

This result clearly states that the air permeability of control leather is higher than experimental leather. Therefore, the reduction in porosity owing to the use of aluminum-melamine syntan indicates increase in fullness of leathers. The same result has been observed by hand evaluation also. Pore size and its distribution is also an important factor, which can provide the information about fullness of leathers.

$$\text{Pore size and distibution} \propto \text{Air permeability} \quad (1)$$

$$\text{Pore size distribution and air permeability} \propto \frac{1}{\text{Degree of fullness}} \quad (2)$$

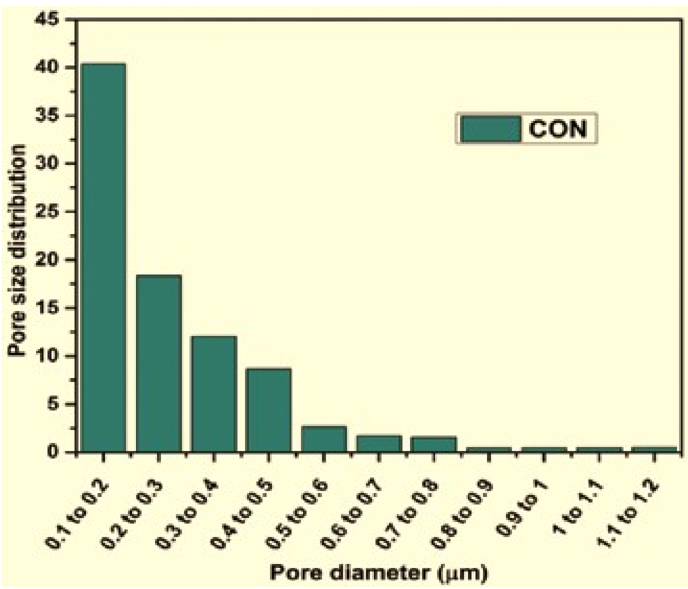

Figure 5a. Pore size distribution of control leather.

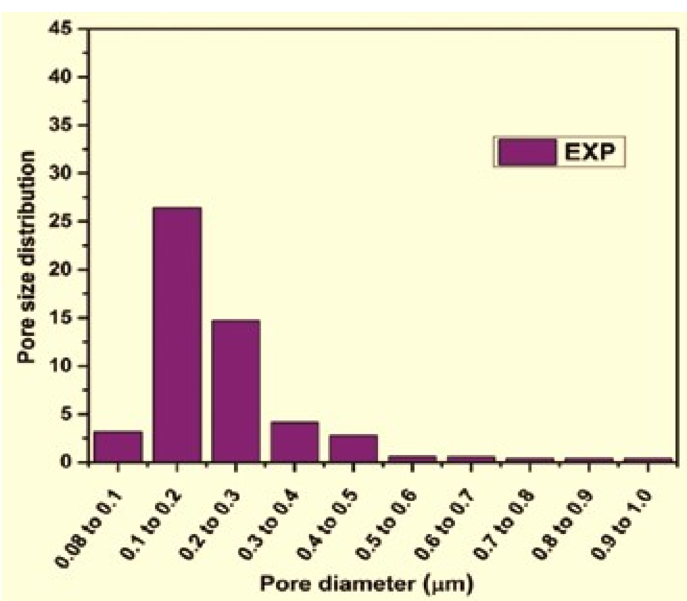

Figure 5b. Pore size distribution of experimental leather.

Capillary flow porometry is one of the techniques, which provide information about throat diameter (most constricted diameter) of through pores. The capillary flow porometry [16-17] is an emerging technique and is used for several industrial applications. For the first time, Murali and co-workers have studied the pore size distribution of wet-blue leathers. Capillary flow porometry technique has been performed in order to analyze the pore size distribution of control and experimental leathers. The pore size distribution has been computed from the flow rate of dry and wet samples. The pore size distribution graphs of control and experimental leathers have been shown in Figure 5a and b, respectively. It is evident from Figure 5a that pores distribution is high in the size of 0.1-0.6 μm, whereas in the case of experimental leather the pore population is greatly reduced. These results show that the prepared aluminum-melamine syntan has better filling action than the conventional aluminum syntan.

Color Measurements

Color measurements of the control and experimental leathers have been carried out using Lambda 35 instrument. The results are tabulated in Table IV.

Experimental crust leather has low value of L as compared to control leathers. This indicates that experimental crust leathers are darker in shade when compared to control crust leathers

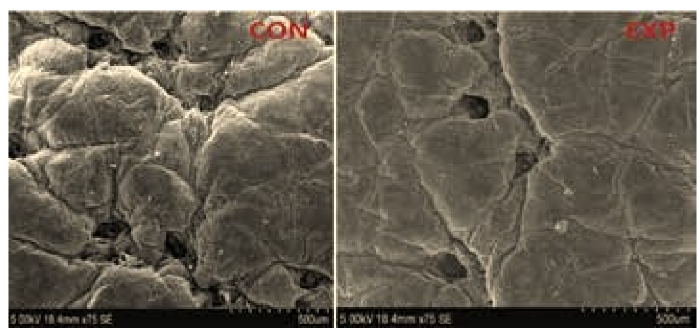

Figure 6a. Microscopic view of grain surface of control and experimental leather.

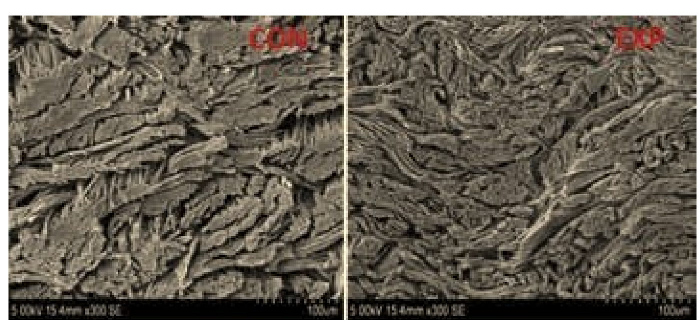

Figure 6b. Microscopic view of cross-section of control and experimental leather.

(Shade card is shown in Table IV). Values of b* indicate that experimental crust leathers are having more blue intensity than control crust leathers. It has also been observed that chromaticity and hue of experimental leather are higher than control leather.

Morphological Analysis

Figure 6a shows the scanning electron micrograph of control and experimental leathers. It is evident from the figure that the grain structure of experimental leather is flatter than that of control leather. This clearly indicates that the developed aluminum- melamine formulation has low astringency. It is evident from Figure 6b that the fiber bundles of experimental leather are more cemented than control leather. This clearly indicates that the aluminum-melamine syntan provided better filling action than commercial syntan.

Conclusions

In the present study, an aluminum-melamine formulation was prepared and used as a re-tanning agent in leather manufacturing. The advantages of using aluminum-melamine formulation in leather manufacturing are summarized below.

- The prepared product is completely free from formaldehyde
- It is possible to avoid the use of chromium in re-chroming process
- This product imparts uniform filling and improves the grain tightness and roundness
- Increases the color intensity
- Increases the tensile and tear strength of the leather
- The leather produced by using aluminum-melamine syntan exhibits flatter grain.

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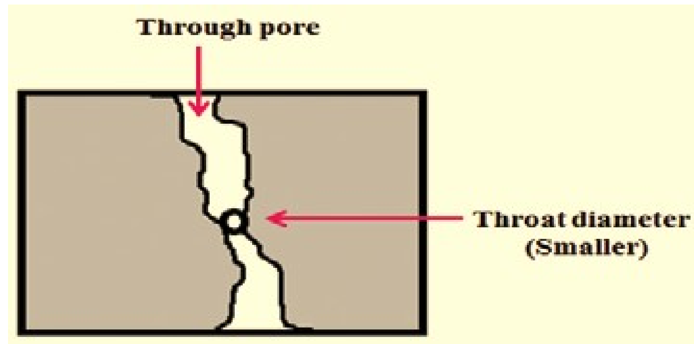
Glossary

Pore size

Also known as pore width (Diameter); The distance of two opposite walls of the pore.

Throat diameter

The most constricted part of through pore.



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