

Expanding the Practical Approach for Salt-Free Tanning: A Chrome-free System

by

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Abstract

Our research group previously established a practical approach for salt-free chromium tanning by changing the order of addition of masking salts (COAMS) for electrolyte-cum-masking effect. The present work deals with the modified COAMS process for developing a salt-chromium-free tanning system using aluminium. The tanning conditions such as Al to masking salt (citrate) ratio, Al₂O₃ offer, the effect of phenolic syntan, and its order of addition on tanning performance have been studied in detail. It was found that the addition of 3% sodium carbonate (based on the weight of aluminium sulfate) along with aluminium sulfate reduces the acidity without affecting the tanning performance and leather quality. The ideal conditions for the pickle-free aluminium tanning were found to be 1.5% Al₂O₃ offer, 5% phenolic syntan offer, and an Al to citrate ratio of 1:0.2. It was also found that the order of addition of phenolic syntan did not affect the tanning performance. Furthermore, in comparison to leather produced without syntan, the combined effect of aluminium and phenolic syntan raises the shrinkage temperature by 6°C (Without syntan: 74°, with syntan-80°) and decreases the rate of shrinkage by 74%. However, the addition of phenolic syntan did not improve Al exhaustion and leaching resistance to water. The physical characteristics and fiber compactness have been improved by the addition of phenolic syntan. SEX-EDAX study reveals that the aluminum is uniformly distributed throughout the cross-section.

Introduction

The discharge of total dissolved solids from the tanning process and its impact on the end-of-pipe treatment is one of the long-standing problems associated with the leather industry. For a considerable amount of time, there have been multiple attempts to reduce the Total Dissolved Solids (TDS) load in tannery wastewater. Several technological interventions such as low-salt pickling, salt-free pickling¹⁻² and pickle-free tanning³⁻⁶ processes have been implemented at commercial scale to reduce the TDS load. However, it is not widely applied due to some practical difficulties. Recently, our research team developed practical approaches for pickle-free chromium tanning⁷ and the process details are given below:

(i) Salt-free Chrome Tanning in Delimiting Liquor (CTDL)

In this system, the delimiting is carried out at 50% float followed by H₂O₂ treatment to convert the sulfide into sulfate. After, delimiting the salt concentration in delimiting liquor was around 3.5% and it was sufficient to adjust the pelt pH to 5.0 without acid swelling. The pH-adjusted pelts were subjected to chromium tanning without any further treatment.

(ii) Changing the Order of Addition of Masking Salts (COAMS)

Generally, masking salts are added before the basification (i.e) after the acidification and chromium treatment to improve the precipitation point of chromium. Whereas in the COAMS process, the masking salts were added before the acidification and chromium treatment, therefore it can also act as an electrolyte that prevents the acid shock while adjusting the delimited pelt pH to 5.0.

Both approaches are simple and easy to adopt at a commercial scale. Further, the process does not involve any specialty chemicals and also reduces the consumption of acid/alkali. Therefore, the above methods are environmental/tanners-friendly and economically beneficial.

On the other hand, globally the search for chromium-free tanning systems is increasing due to the toxicity associated with chromium compounds, especially Cr(VI).

Considerable attempts have been made to develop chromium-free mineral tanning systems. Patent no PCT/NL2020/050773 deals with the modification of zeolite with acid and used as tanning agent in leather manufacturing.⁸ In this method, the pickled pelt (pH: 3.0) is treated with the modified zeolite. Xinhua Liu et al., developed a salt-free pickling and chrome-free tanning technology using epoxy-terminated hyperbranched polyamine-ester (EHBP) and aluminium (III) salt as pickling and tanning agent, respectively.⁹ Madhan et al., developed the complexes of aluminium (III) & Zinc(II) using different ligand combinations such as sodium citrate, triethylenetetramine, phthalic acid, and sodium tartrate.¹⁰ An attempt had been made to develop Zirconium-Aluminium-Titanium complex as a tanning agent and the shrinkage temperature of the leather was increased up to 95° (Patent No CN102787181A).¹¹ Chandrababu et al., extensively studied the use of Iron (III) as a self-tanning agent by chelating with

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Manuscript received February 15, 2024, accepted for publication March 12, 2024.

the suitable ligands viz. fatty acid, aliphatic/aromatic carboxylic acid to increase the stability of iron complex and also to increase the hydrothermal stability of the final leather.¹² Further, Fathima et al., developed an iron-tetrakis hydroxymethyl phosphonium sulfate (THPS)-based combination tanning and optimized the iron to THPS ratio on thermal stability of the tanned leather.¹³ Further, they have also studied the influence of various ligands on the thermal stability of the final leather. US patent no 4731089 deals with the development of a mixed metal tanning system using aluminum and titanium complex masked with the salt of polyhydroxy mono carboxylic acid. Recently, Zhicheng Jiang et al., employed trojan horse strategy for the development of Al-Zr-Oligosaccharides complex and used them as a tanning agent.¹⁴

Further to reduce the salinity in wastewater, few attempts have been made to develop pickle-free and chromium-free tanning technologies. The US patent no US 7169191 provided the process for the preparation of synthetic aluminium tanning agent by incorporating the aluminum into the formaldehyde-free polymeric matrix as a solo tanning agent for pickle-free

processes.¹⁵ Further, Patent No CN115011742 provided the process for pickle & chrome-free tanning-based epoxy-modified collagen polypeptide.¹⁶

It is evident from literature that limited attempts have been made to develop pickle-chromium-free tanning systems. While searching for an alternative chromium-free mineral tanning agent, aluminium is found to be a suitable material because of its low cost and availability. In this work, we have attempted to develop pickle-chromium-free tanning using aluminium with the modification of our previously established COAMS process.

Materials and Methods

Conventionally processed goat delimed pelts have been taken as raw material for tanning trials. $\text{Al}_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$ and trisodium sodium citrate dihydrate were procured from M/s Merck. Commercial-grade chemicals were used for leather processing. Analytical-grade chemicals were used for analysis.

Table I
Process recipe for salt-chromium-free tanning
Raw material: Goat delimed pelts, Thickness (Neck): ~ 1.5 mm

Process/Chemicals	% Offer	Time	Remarks
Masking Salt Treatment			
Water	50		
Sodium citrate	"X"		
Sodium formate	1	30 min	
Acidification			
Formic acid	0.5		
Water	5	3*15 min+30 min	
Sulfuric acid	0.2		
Water	10	2*30 min+60 min	pH adjusted to around 5.0
Tanning			
Phenolic syntan	"Y"	30 min	
Al as Al_2O_3	"Z"		
Sodium carbonate	3*	2*60+60 min	After the complete addition aluminium pH dropped to around 3.0. Aluminium penetration was checked using pyrocatechol violet indicator
Basification			
Sodium carbonate	1.0-1.5		
Water	10	3*30 min+120 min	pH adjusted to 4.0. Drained and Piled

*% offer based on the weight of aluminium sulfate

Y – Phenolic syntan offer varied from 0 to 10 % (0, 1, 2.5, 5, 7.5 and 10%)

Z – Al_2O_3 offer varied from 1 to 3% (1, 1.5, 2, 2.5 and 3%)

Optimization of Aluminium to Masking Salt Ratio

Thirty goat delimed pelts were grouped into 6 (each group contains 5 delimed pelts), marked, and subjected to tanning process as per the recipe given in Table I. The amount of Al offer was kept constant (Al_2O_3 : 1.5% w/w - Based on pelt weight) and for every mole equivalent of Al, the sodium citrate mole equivalent was varied from 0 to 0.3% w/w (0, 0.1, 0.15, 0.2, 0.25, 0.3).

Effect of Phenolic Syntan on Tanning Performance

Six groups of delimed pelts were marked (each group having 5 delimed pelts) and subjected to the tanning process as per the recipe given in Table I where the optimized Al: Sodium citrate ratio and 1.5% Al_2O_3 were offered. The amount of phenolic syntan offered (based on pelt weight) was varied from 0 to 10% w/w. The effect of phenolic syntan on aluminium exhaustion was analyzed using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

Changing the Order of Addition of Phenolic Syntan on Tanning Performance

Six groups of delimed pelts were marked (each group having 5 delimed pelts) and subjected to the tanning process (Al: Sodium citrate ratio and 1.5% Al_2O_3) where the order of addition of phenolic syntan was varied.

- (i) Phenolic syntan followed by aluminium before basification
- (ii) Phenolic syntan and aluminium together
- (iii) Aluminium followed by syntan before basification
- (iv) Aluminium followed by syntan after basification

Optimization of Al_2O_3 Offer

Five groups of delimed pelts were marked (each group having 5 delimed pelts) and subjected to the tanning process as per the recipe given in Table I. The optimized Al:Sodium citrate (1:0.2) ratio was kept constant and the amount of Al_2O_3 offer (based on pelt weight) was varied from 1.0 to 3.0% w/w (1, 1.5, 2, 2.5, 3.0). The aluminium exhaustion for different percentages of Al_2O_3 offer was estimated through Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES).

Optimized Tanning Process

Further, ten delimed pelts were cut along the backbone, marked, and grouped separately. The left and right halves were subjected to an optimized tanning process with and without phenolic syntan treatment, respectively. After 15 days of aging, the tanned leathers were converted into crust leather as per the process recipe given in Table II.

Analysis of Aluminium Leaching

The tanned leather obtained from the optimized tanning process was aged for 48 hrs and subsequently, a specimen was taken from the official sampling position. Further, the specimen was cut into small pieces. Fifteen grams (moisture-free basis) of cut pieces were added into a conical flask containing 150 ml of double distilled water and agitated at 250 rpm. Every 1 hr time interval, the leachate was drawn from the conical flask and subjected to aluminium estimation through ICP-OES.

Hydrothermal Shrinkage Temperature Measurements

Prolific shrinkage temperature was used for the measurement of hydrothermal shrinkage temperature. The test specimens of 50*3 mm size (I*b) were cut from the samples to be tested. The jig is placed inside the beaker containing water and it has a fixed pin at its lower end and a hook at its upper end for holding the test specimen in between. The thread from which the hook is suspended passes over a lightweight aluminium pulley, which also carries the circular scale. The other end of the thread has a dead weight attached to it to apply the specified tension on the test specimen. Further, the system was heated at the rate of 2°/min with constant stirring. The temperature at which the test specimen has shrunk to such an extent that moving the dial (circular scale) half a division from the initial position is noted as shrinkage temperature. Once the movement of the dial started, the division of the circular scale was noted at different time intervals to analyze the rate of shrinkage.

Physical Strength Characteristics and SEM Analysis

According to the IULTCS standard procedure, specimens for a variety of strength characteristics, including tensile strength, % elongation at break, tear strength, grain crack load, and distension at grain crack, were obtained. Before analysis, every specimen was conditioned for twenty-four hours at 25±1°C and 65% RH.¹⁷⁻²⁰ TESCAN-CLARA scanning electron microscope was employed to analyze the morphological characteristics and aluminium distribution (EDAX mapping).

Table II
Post-tanning process recipe (Thickness: 1.0 mm)

Process/Chemicals	% Offer	Time	Remarks
Wetting back			
Water	100		
Wetting agent	0.1	30 min	Drain
Neutralization			
Water	100		
Sodium Formate	1		
Sodium bicarbonate	0.7	pH: 5.0-5.2	Drain/Wash
Re-tanning			
Sulfone syntan	5.0		
Melamine syntan	4.0		
Acrylic syntan	2.0	90 min	
Fatliquoring			
Vegetable oil based fatliquor	5.0	30 min	
Synthetic fatliquor	6		
Sulfited fatliquor	4	150 min	
Fixing			
Formic acid + Water	1.5 + 5	2 × 10 min + 60 min	Drain/Wash, drying and staking

Results and Discussion

Salt-Free Aluminium Tanning – Process Strategy

The previously established COAMS process deals with the addition of masking salts before the acidification. In this process, the masking salts not only alter the charge/hydrolytic behaviour of chromium but also increase the ionic strength, and therefore the ionic imbalance of the system will be reduced. Hence, the delimed pelt pH can be reduced to the required tanning pH (5.0) without acid swelling/acid shock. A similar concept has been employed in the present work with minor modifications. In our previous study (chrome tanning) sodium acetate was used as masking salt but the present study employed tri-sodium citrate and sodium formate as masking salts. Further, it is a well-known fact that the acidity of aluminium sulfate is higher than basic chromium sulfate due to the high charge-to-size ratio. Hence there may be a possibility for the occurrence of acid swelling after adding aluminium sulfate even if the system has masking salt as an electrolyte. After conducting a series of experiments, it has been found that the addition of aluminium sulfate along with 3% sodium carbonate (% based on the weight of aluminium sulfate) reduces the aluminium acidity without affecting the tanning performance. After the complete

addition of aluminium sulfate, the system's pH would be around 3.0 and it will be increased up to 4.0 at the end of tanning.

Optimization Study

In order to optimize the Al:Citrate ratio, 6 different trials were carried out and the shrinkage temperature of tanned leather was taken as the basic criteria for shortlisting an ideal ratio. The shrinkage temperature of each tanning trial is given in Table III. It is evident from Table III that the shrinkage temperature of the 1:0, 0.1, 0.15 system is around 71° whereas it has been increased up to 74° for a 1:0.2 ratio. However, it falls when the citrate equivalent is increased beyond 0.2. It may be due to the over-masking and generation of stable Al-citrate complex. Hence, the 1:0.2 ratio has been optimized. It is well established that the combination of aluminium with plant polyphenols improves the tanning performance as well as quality of the final leather. However, the wattle-aluminium complex imparts ash color to the tanned leather. This work mainly focuses on understanding the effect of phenolic syntan offer and its order of addition on the tanning performance. The Al: Citrate ratio and Al₂O₃ offer is 1:0.2 & 1.5%, respectively. It is evident from Figure 2 that no change in shrinkage temperature for 0, 1% phenolic syntan offer (74°), and a minor change in 2.5% offer

(75°). However, a considerable increase in shrinkage temperature has been observed for 5% (80°) and it remains unaltered for 7.5% and 10%. Therefore, 5% phenolic syntan offer would be an ideal offer. On the other hand, it was found that the order addition of phenolic syntan does not affect shrinkage temperature and other tanning characteristics.

Subsequently, tanning trials have been carried out with the optimized ratio (Al:Citrate – 1:0.2, Phenolic syntan – 5%) where the Al_2O_3 offer has been varied from 1 to 3.0%. Further, two sets of trials have been carried out with and without phenolic syntan. The shrinkage temperature and aluminium exhaustion is given in Table III. In the case of without phenolic syntan treatment

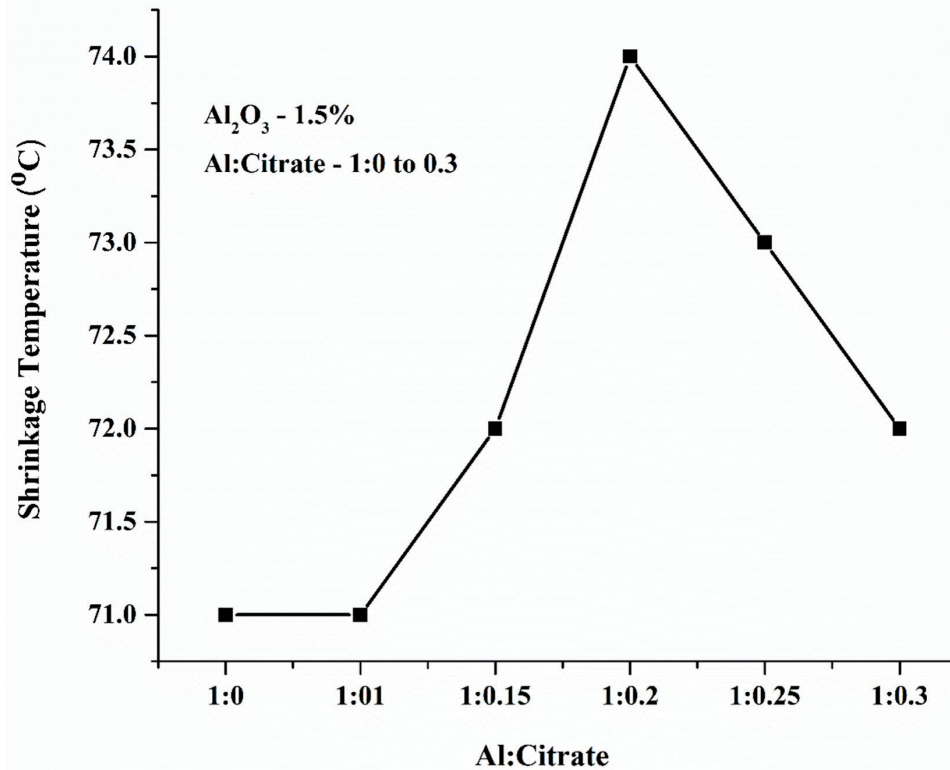


Figure 1. Optimization of Al:Citrate ratio

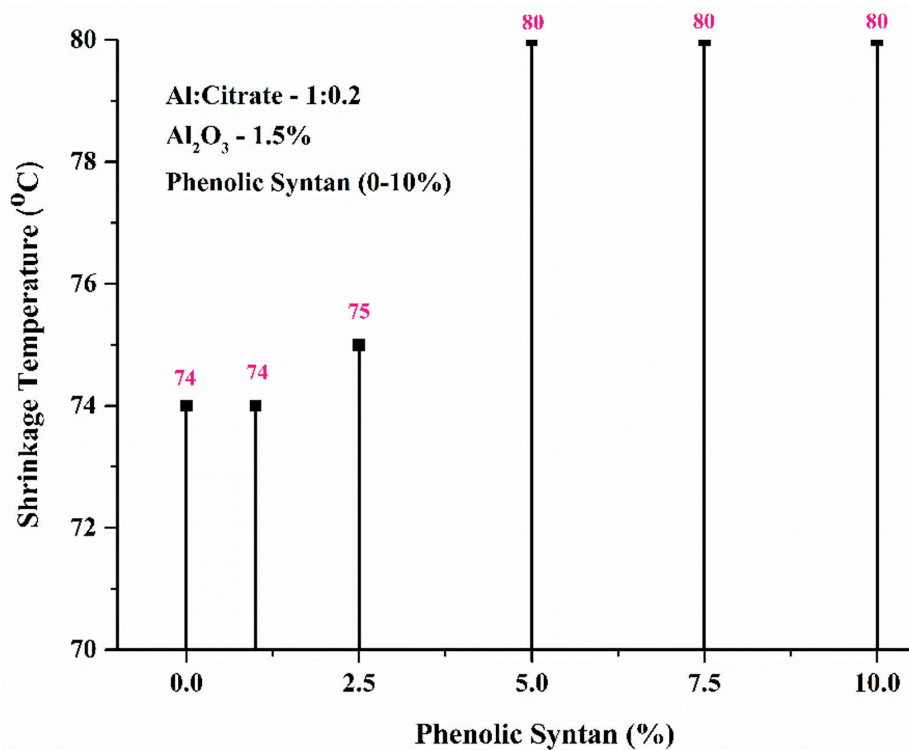


Figure 2. Optimization of phenolic syntan offer

Table III
Optimization of Al₂O₃ offer

Al: Citrate	Al ₂ O ₃ Offer (%)	0% Phenolic syntan		5% Phenolic syntan	
		Shrinkage Temperature (°C)	Al exhaustion (%)	Shrinkage Temperature (°C)	Al exhaustion (%)
1:0.2	1.0	71±1	76	76±1	77
	1.5	74±1	81	80±1	81
	2.0	74±1	83	80±1	84
	2.5	74±1	75	80±1	76
	3.0	76±1	70	82±1	72

the shrinkage temperature of 1% Al₂O₃ offered leather was 71° whereas it was 74° for 1.5 to 2.5% and further, it was increased to 76° for 3.0%.

On the other hand, the aluminium exhaustion for 1% system was 76% and subsequently increased to 81% and 83% for 1.5% & 2.0%, respectively. It is also clear from Table III that the Al uptake falls when the offer increases to 2.5 and 3%. Similarly, it was found that the addition of phenolic syntan increased the shrinkage temperature and also a marginal increase in exhaustion has been observed. For 1% and 1.5% offer, shrinkage temperature is 76° and 80°, respectively. Further, it remains unaltered for 2.0 & 2.5% and a marginal increment has been observed for 3.0%. The exhaustion pattern of tanning trials with and without phenolic syntan is

almost similar. Hence, it can be concluded from the study that the optimized tanning conditions are (i) Al:Citrate – 1:0.2 (ii) Phenolic syntan offer– 5% (iii) Al₂O₃ offer – 1.5% (iv) Order of addition – any place after acidification.

Leaching Study

It is a well-known fact that aluminium-tanned leather has poor resistivity against water leaching due to the formation of labile complexes with protein carboxyl groups. In order to understand the effect of phenolic syntan on the leachability of aluminium, the matched pair of tanned leather obtained from the optimized tanning process has been subjected to water leaching. The leachability of aluminium at different time intervals is shown in Figure 3. It is evident from the Figure that the leachability pattern

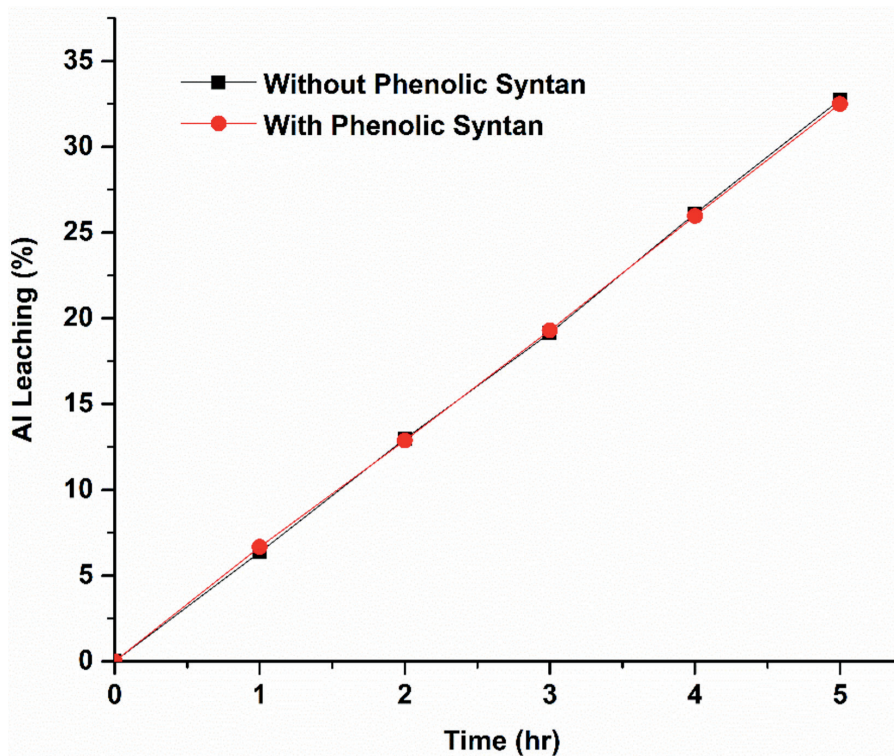


Figure 3. Effect of phenolic syntan on Al leaching

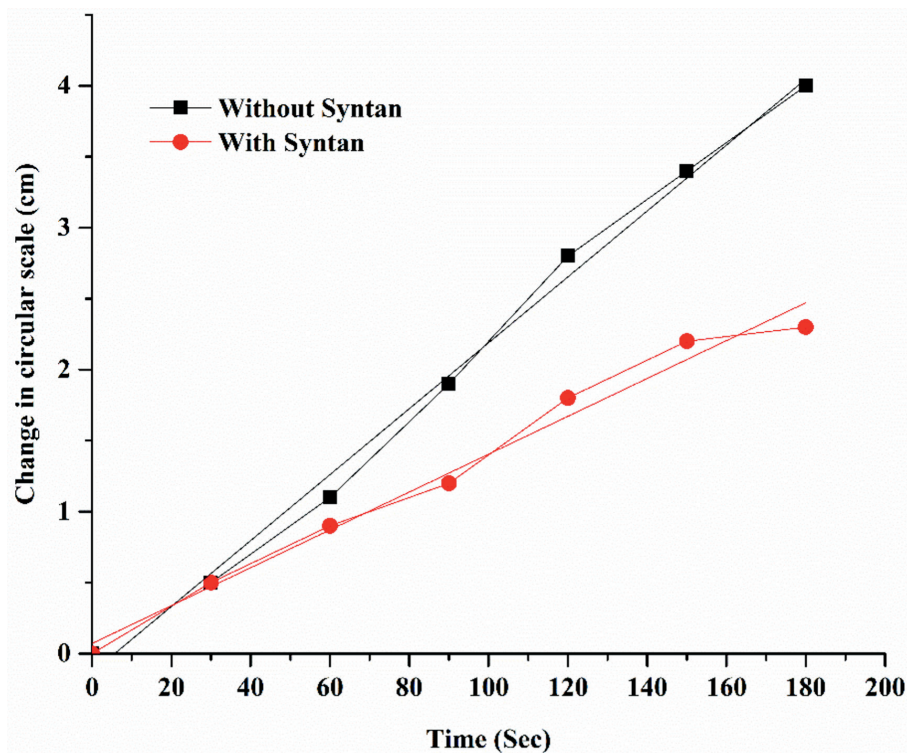


Figure 4. Rate of hydrothermal shrinkage

of leather treated with syntan and without syntan is similar and no considerable difference has been observed. It was also observed that around 6-7% of aluminium is leached out for every 1 hr time interval. After 5 hrs around 32% of the aluminium is leached out. From this experiment, it can be concluded that the addition of phenolic syntan is not reducing the aluminium leaching.

Rate of Hydrothermal Shrinkage

It is understood from the previous experiments that the addition of phenolic syntan increases the hydrothermal shrinkage temperature. Further, in order to understand the effect of phenolic syntan on the rate of leather shrinkage, the change in the circular scale division due to the contraction of the test specimen as a function of time has been monitored (refer to method for further details). It is evident from Figure 4 that the shrinkage pattern obeys the liner model. The correlation co-efficient (R^2) value of without and with syntan-treated leather is 0.99325 and 0.98043, respectively. Further, the corresponding slope value can be correlated with the rate of shrinkage (higher the slope, faster the shrinkage). The slope value of leather from without syntan treatment is 0.0232 whereas it is 0.0133 for syntan treated leather. Hence, the shrinkage rate of leather processed without syntan treatment is 74% faster than the syntan-treated leather.

Further, it is also evident from Figure 4 that the leather without syntan treatment reached the final division (4 cm) of the circular scale within 180 seconds whereas syntan-treated leather reached only about 2.3 cm within 180 seconds. These results demonstrate that the syntan-treated leather has better hydrothermal resistance

and also a slow shrinkage pattern. This may be due to the synergetic effect of aluminium and phenolic syntan and also the formation of a multipoint network.

Physical Strength Characteristics

The physical strength characteristics of the crust leathers (with and without syntan) have been analyzed and results are given in Table IV. Further, the variations in strength characteristics with respect to the without syntan system are shown in Figure 5. The tensile strength of syntan-treated leather is 23% higher than the without syntan system and also a 7% reduction in elongation at break. Similarly, 4%, 7%, and 3% increase in tear strength, load at grain crack and distension at grain crack, respectively. Further, 10% reduction has been observed for water vapor permeability. The reduction in elongation and water vapor permeability indicates the compactness of the syntan treated system.

SEM Analysis

The distribution of Al in the crust leather has been mapped using EADX analysis and the same is shown in Figure 6. It is evident from the Figure that the Al is distributed uniformly throughout the cross-section. Further, the aluminium to the sulfur ratio is also similar for both syntan-treated and non-syntan systems. Further, the cross-sectional view of the crust obtained from both systems is shown in Figure 7. It is evident that the fiber structure of the syntan-treated leather is more compact and cemented than the without syntan system, Further, it is also observed that the fiber splitting of the syntan-treated leather was good when compared to the non-syntan system.

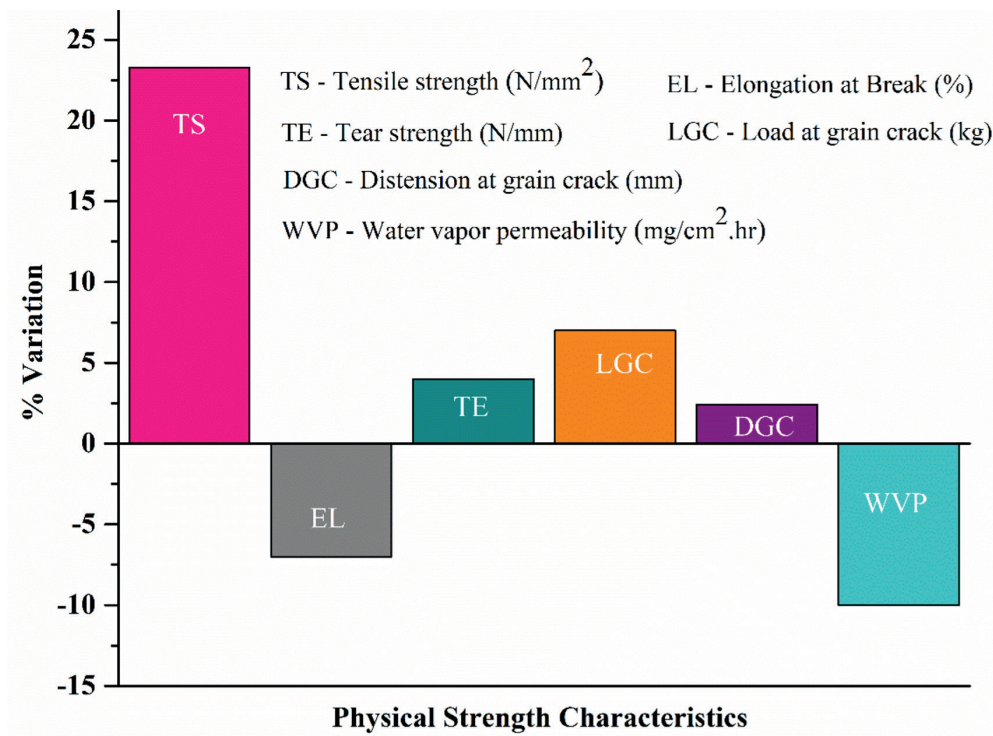


Figure 5. Rate of hydrothermal shrinkage

Table IV

Physical strength characteristics of salt-free aluminium tanned leather with and without syntan treatment

Physical Strength Characteristics	Without Syntan	With Syntan
Tensile Strength (N/mm^2)	23.04	28.4
Elongation at Break (%)	65.2	60.7
Tear Strength - N/mm	106	110
Load at Grain Crack (kg)	28.1	30
Distension at grain crack (mm)	8.3	8.5
Water vapor Permeability ($\text{mg/cm}^2 \cdot \text{hr}$)	3.7	3.33

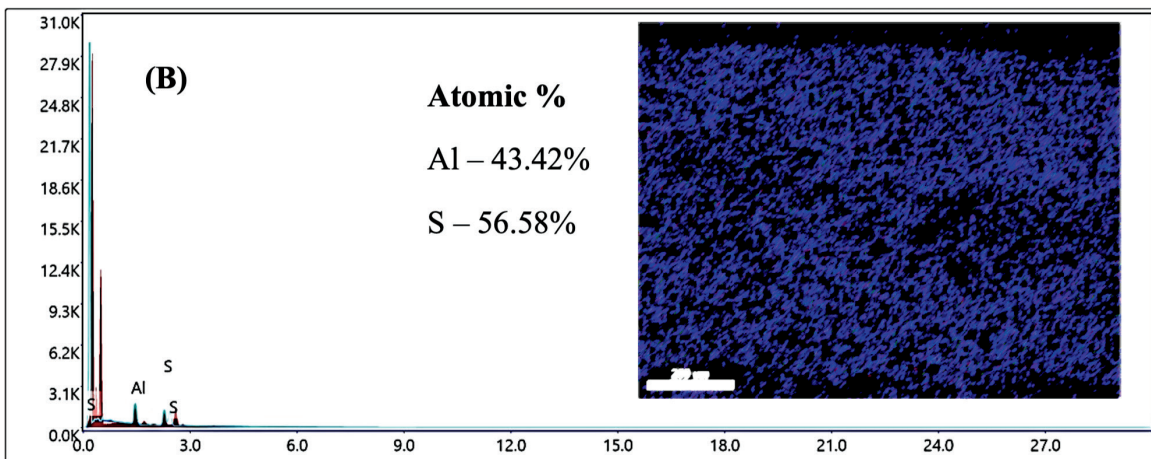
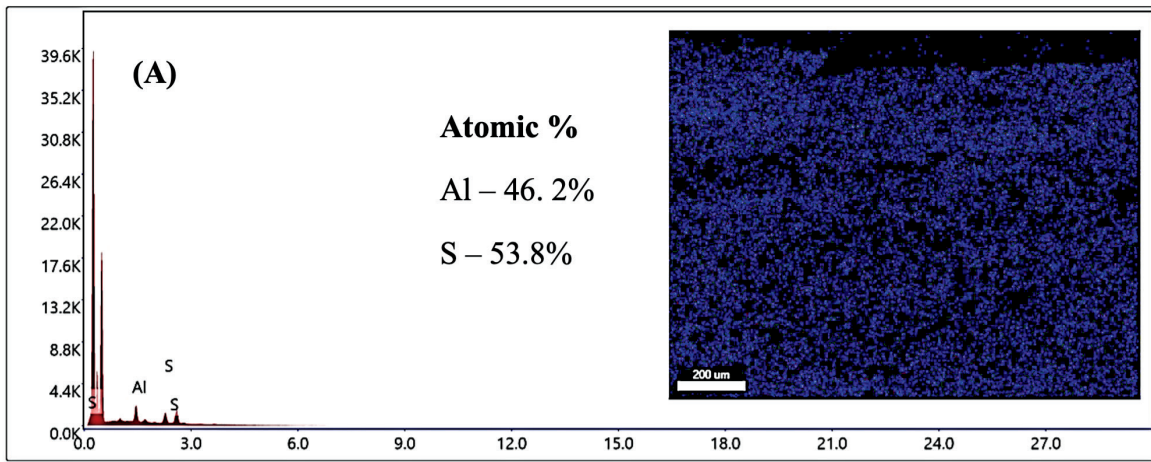


Figure 6. Elemental mapping of crust leather:
Cross-sectional view (a) without syntan and (b) with syntan

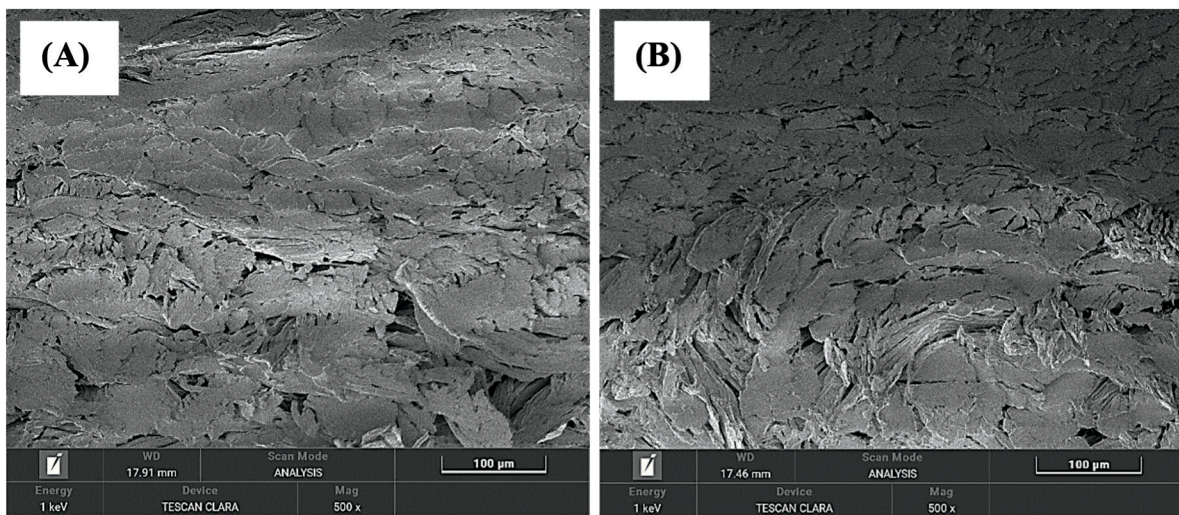


Figure 7. Cross-sectional view (a) without syntan and (b) with syntan

Conclusions

A practically viable salt-free aluminium tanning has been developed by changing the order of addition of masking salt (i.e) the addition of masking salt before the acidification process to increase the electrolyte concentration in the system. Further, it was optimized that the addition of 3% sodium carbonate (based on the weight of aluminum sulfate) along with aluminium sulfate neutralizes the acidity without affecting its tanning performance. The addition of 1.5% Al_2O_3 , 5% phenolic syntan, and Al to citrate ratio of 1:0.2 was found to be an optimal condition for high-performance tanning. Further, the synergetic effect of aluminium and phenolic syntan increased the shrinkage temperature by 6°C and lowered the rate of shrinkage by 74% when compared to leather produced without syntan. However, no considerable differences have been observed for aluminium exhaustion and aluminium leaching. The order of addition of phenolic syntan and its effect on tanning performance is negligible, however, it improves the mechanical properties and fiber compactness. SEM-EDAX study indicates that the aluminium was uniformly distributed throughout the cross-section. Hence, the developed chrome-free tanning system is easy to practice with environmental/economic benefits.

Acknowledgement

The authors thank the Council of Scientific and Industrial Research (CSIR), India for financial support (OLP-2319) and the CSIR-CLRI-CATERS division for SEX-EDAX analysis. CSIR-CLRI's Communication Number 1947.

Conflict of Interest

Authors declare that no conflict of interest exists.

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