Effect of Acid Swelling and Its Impact on the Properties of Cow Industrial Glove Leathers

by

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Abstract

The development of commercially successful salt-free chrome tanning technology is the need of global leather sector to reduce the total dissolved solids in wastewater. Though some attempts have been made to develop salt-free chrome tanning technology, drawbacks such as slow diffusion of chromium, unevenness in softness and other organoleptic properties are the major concern. The generation of localized acid swelling might be a reason for the above drawbacks and no scientific literature available for the same. Hence, it is important to analyze the effect of acid swelling and its impact on the diffusion of chromium, ageing characteristics of wet-blue leather and physical properties of crust leather. The results show that the acid swelling delays the diffusion of chromium in tanning process and also enhances the growth marks on wet-blue leather. The ageing study reveals that the wet-blue obtained from acid swollen system dehydrates faster than the conventional salt based chromium tanning system. In addition, the wet-blue leather from acid swollen system is prone to fungal attack. The industrial glove leather obtained from acid swollen system has reduced strength characteristics viz., 15% reduction in tensile strength, 17% reduction in tear strength and 20% reduction in grain crack/bursting strength. Further, the degree of heterogeneity in softness is high for crust leather obtained from acid swollen system and also more looseness with internal emptiness. Color value measurements reveal that the crust leather obtained from the conventional tanning system is lighter in shade than the acid-swollen system. The results will be useful to design commercially viable salt-free or low-salt tanning systems as well as to tackle the inadvertent industrial scenario where the tanners are looking for solutions for accidental acid swelling and subsequent salvage of the leathers for possible recovery and applications.

Introduction

Sodium chloride is commonly used in the pickling process to avoid the osmotic swelling of collagen fiber during the acid treatment. More specifically, sodium chloride acts as an electrolyte that eliminates the Donnan potential and subsequently prevents the swelling of the collagen matrix.[1] Though it found a prominent place in leather making, the drawbacks such as discharge of high total dissolved solids (TDS) load in wastewater[2] and the requirement of a sophisticated end-of-pipe treatment system motivate leather manufacturers to develop salt-free tanning systems. Considerable attempts have been made to develop salt-free tanning systems such as (a) pickling with non-swelling acid and (b) pre-treatment using weak organic acid.

i. ***Pickling with Non-Swelling Acid*** – In this method, aromatic sulfonic acids such as naphthol 3-6-disulphonic acid, p-hydroxy diphenyl sulphonic acid, blend of naphthalene and naphthol sulphonic acids, and polyacrylic acid have been used in pickling process up to the level of 2% offer without salt to adjust the pH to 2.8-3.0. Subsequently, tanning is done using basic chromium sulfate (BCS) followed by regular basification. Further, the variation in swelling as the function of chemical compounds and its influence on pickling/tanning baths and also the mechanical properties of leather have been studied in detail.[3-4]

ii. ***Pre-treatment with Weak Organic Acid*** – In this method, the delimed pelt is pre-treated with weak organic acids like acetic acid, formic acid, and its mixture to adjust the pH up to 5.0-5.5 without salt. Subsequently, the pelts are treated with BCS without basification.[5-8]

Though the salt-free tanning systems are environmentally sustainable the following limitations have been observed based on our research experience and also feedback obtained from the tanners.

1. Achievement of complete penetration of chromium is difficult for thicker hides (complete penetration is normally achieved during ageing).
2. Requirement of longer neutralization than for conventional wet-blue.
3. Need for modification in the post-tanning process recipe.
4. Unevenness in softness.

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Hence, it is important to understand the causative factors for the above-mentioned limitations in order to develop a commercially successful salt-free tanning system.

Further, the authors hypothesized that the nucleation of localized acid swelling during the addition of BCS could be a possible reason. In addition, there are situations in leather industries where occasionally the tanners are faced with the problem of acid swelling inadvertently and there is no scientific literature available currently to salvage the swollen pelts. Hence, a study on acid swelling and its effect on the physical properties of final leather may help to understand the above problems. Herein, we carried out conventional pickling-basification based chrome tanning process with and without the addition of salt to understand the effect of swelling on the physico-chemical properties of the tanned leathers. After tanning, the leathers were post-tanned to prepare industrial glove leathers and their morphology, physical and organoleptic properties were analyzed.

Materials and methods

Wet-salted cow hides were conventionally processed and taken as raw material for chromium tanning. All the chemicals used for leather processing were of commercial grade and analytical grade chemicals used for analysis.

Chromium Tanning and Post-Tanning Process

The delimed pelts were cut along the backbone and the left (With Acid Swelling -WAS) halves were subjected to acid swelling (pH: 3.0) without the addition of sodium chloride whereas right halves (Without Acid Swelling-WOAS) were subjected to a conventional pickling process (Sodium chloride + Sulfuric Acid) followed by chromium tanning. The detailed process recipe is given in Table I. Further, the obtained wet-blue leathers were subjected to mechanical operations and converted into industrial glove leather as per the post-tanning process recipe given in Table II.

Analysis of Thermal Stability

Hydrothermal stability of the pelts and wet-blue leather was measured using SATRA shrinkage tester (SATRA STD 114).

Ageing Characteristics of Wet-Blue Leather

The wet-blue leathers obtained from both experimental/control processes were piled at room temperature (35°± 1°C) and stored in an airtight cover. The leathers were continuously monitored for changes in color, fungal growth and, drying nature.

Microscopic Analysis

Celestron handheld microscope and the Phenom tabletop scanning electron microscope were used to analyze the surface/cross-sectional morphology of the leathers.

Table I

Process recipe for tanning the delimed cow pelts

WAS (Left halves)		WOAS (Right halves)	
Acid Swelling		***Pickling***	
Water	100%	Water	100%
Salt	0%	Salt	10%
Sulfuric acid Water	1.2% 10% 4 × 10min + 120 min pH: 3.0	Sulfuric acid Water	1.2% 10% 4 × 10min + 120 min pH: 3.0
Tanning			
BCS	6% 2 × 30 min + 180 min	BCS	6% 2 × 30 min + 180 min
Basification			
Sodium formate	1% - 30 min	Sodium formate	1% - 30 min
Sodium bicarbonate Water	1% 10% 3 × 20 min + 180 min pH: 4.0 Drain/Pile	Sodium bicarbonate Water	1% 10% 3 × 20 min + 180 min pH: 4.0 Drain/Pile

Table II

Process recipe for the manufacture of cow industrial glove leather from chrome tanned cow wet blue (Thickness: 1.0-1.1 mm)

Process/Chemicals	% Offer	Time	Remarks
Wetting back			
Water	100		
Wetting agent	0.1	30 min	Drain
Acid bating			
Water	100		
Sodium formate	1	30 min	pH: 4.5-4.8
Acid bate	0.5	4 hrs	
Bleaching			
Sulfuric acid + Water	0.5 + 10	2 × 10 min + 30 min	
Potassium permanganate	0.5	60 min	
Oxalic acid	0.5		
Sodium bisulfite	0.5	60 min	Drain/Wash
Rechroming			
Water	100		
BCS	1.5	60 min	
Sodium formate + Sodium bicarbonate	0.25 + 0.5	pH: 4.0	O/N, Drain/Wash
Neutralization			
Water	100		
Sodium bicarbonate	1		
Ammonium bicarbonate	1	pH: 6.0-6.5	Drain/Wash
Fatliquoring			
TiO_2	1.5	30 min	
Synthetic fatliquor	15		
Sulfited fatliquor	5	150 min	
TiO_2	1	30	
Fixing			
Formic acid + Water	1.5 + 5	2 × 10 min + 60 min	Drain/Wash, drying and staking followed by dry milling (3 hrs). Final staking

Note: Process recipe collected from commercial industrial glove leather manufacturing unit in Kolkata, West Bengal, India.

Physical Strength Characteristics and Organoleptic Properties

Physical strength characteristics (tensile strength,[9] tear strength[10] and bursting strength[11]) of the crust leathers processed from experimental/control wet-blue were analyzed as per the standard methods. All the specimens were conditioned at 25°± 1°C and 65% RH for 24 hr[12] before the test performance. Further, a group of leather experts evaluated the final crust leathers and provided their remarks on different organoleptic properties such as softness, stretchiness, grain smoothness, uniformity, internal softness, looseness and touch.

Color Value Measurements

Color measurement parameters viz., L, a, b, were recorded using a Lambda 35 instrument for grain side of experimental and control crust leathers. “L” represents lightness, “a” value represents redness and greenness, “b” value represents yellowness and blueness. The wet-blue leathers were subjected to a controlled dehydration process before the measurement.[13]

Table III
Changes in weight of cow pelts and leathers

Process	WAS (kg)	WOAS (kg)
Deliming	3.4	3.6
Acid swelling/Pickling	4	3.0
After chrome tanning	3.2	3.2
After sammying	2.4	2.3

WAS – With Acid Swelling ; WOAS – Without Acid Swelling

Results and Discussion

Effect of Acid Swelling on Weight and Dimensional Properties
Collagen fiber, the leather-making protein, is considered as a charged material and the change of pH leads to an alteration of its charge. The alkaline pH leads to negative charge potential due to ionization of carboxylic group of amino acid sidechain whereas it becomes positive under acidic condition due to the protonation of amino group. Besides, the non-diffusible ionic nature of collagen matrix tends to produce an osmotic pressure gradient in an aqueous medium leading to osmotic swelling under acid/alkali conditions. Generally, the osmotic swelling ruptures the matrix structure and changes the dimensional properties. Further, the excess amount of water will be absorbed by the collagen matrix to equilibrate the osmotic potential.[1,14] The change in weight of cow hides subjected to acid swelling/conventional picking and subsequent tanning process is given in Table III.

It is evident from Table III that the acid swelling increases the delimed pelt weight up to 17% whereas 17% weight reduction was observed for conventional pickling and this may be due to the dehydration effect of sodium chloride used in pickling process. It is also worth noticing that the addition of tanning salt into the acid swollen pelt reduces the weight (-20%). The ionicity induced by neutral salt present in BCS and the formation of different charged chromium complexes may reduce the osmotic potential thereby reversing the swelling state in WAS system. In the case of conventional process, the weight has increased after the tanning (+6%) and it may be due to the absorption of chromium/neutral salts. It is also evident from Table III that after sammying, the weight reduction of acid swollen wet-blue is 3% lesser than the conventional wet-blue and it may be due to the high water holding capacity of the acid swollen wet-blue. The effect of acid swelling on pelt thickness at various processing stages is shown in Table IV. Because of the heterogeneity, the thickness was measured at various places and averaged.

It is evident from Table IV that the acid swelling increases the thickness and reduces the area. Whereas in conventional pickling, the thickness was reduced[14] and marginal increase in area was observed. The photographic images of the acid swollen and conventional pickled pelt are shown in Figure 1.

Effect of Acid Swelling on Chromium Diffusion
The diffusion of chromium at different time intervals of chrome tanning has been monitored for both WAS and WOAS systems. The micrographic images taken at different time intervals are shown in Figure 2. It is evident from the figure that the diffusion of chromium in WAS system is much slower than in the conventional salt-based tanning system. In the case of WOAS system, complete diffusion was achieved within 4 hrs whereas it is incomplete in the case of WAS system even after 24 hrs. The reason for delayed chromium diffusion in WAS system is unknown and a separate study needs to be conducted in order to understand the phenomena. However, the following factors may have contributed to the delayed chromium diffusion in WAS system.

Table IV
Changes in thickness and area of cow pelts and leathers

Process	WAS		WOAS	
	Thickness (mm)	Area (cm^2)	Thickness (mm)	Area (cm^2)
Deliming	1.63 ± 0.4	10531.3	1.55 ± 0.4	11121.2
Acid swelling/Pickling	2.52 ± 0.3	9684.1	1.36 ± 0.3	11513.5
After chrome tanning	2.20 ± 0.5	9080.3	2.05 ± 0.4	9880.8

WAS – With Acid Swelling ; WOAS – Without Acid Swelling

Figure 1. Photographic image of **(a)** acid swollen pelt and **(b)** conventional pickled pelt

a) Acid swelling may cause differential strain at different layers of collagen matrix and could have resulted in the loss of interconnectivity between pores.

b) Increase in fiber diameter may predominantly reduce the porosity contributed by macro pores. The study carried out with plant-based fibers revealed that the porosity/permeability of the swollen fiber is reduced than the normal fibers.[15]

c) The removal of hyaluronic acid from the matrix is essential because its viscous nature inhibits the penetration of process chemicals. The hyaluronic acid carried forward after the beam house process is generally removed by neutral salt present in the pickling process by collapsing its gel structure. Due to the absence of neutral salt in WAS system, the carry forwarded hyaluronic acid may be transformed into a gel-like structure and act as a barrier for chromium diffusion. It is also reported that the presence of residual hyaluronic acid after the beam house processes inhibits the diffusion of chromium.[16]

Analysis of Hydrothermal Shrinkage Temperature

The hydrothermal shrinkage temperature of the cow matrix taken from different processing stages is given in Table V. Further, it is reported that the shrinkage temperature of the acid swollen pelt is below 45°C in the absence of salt.[17] As expected, the hydrothermal stability of acid-swollen pelt is lower (-27%) than the pickled pelt.

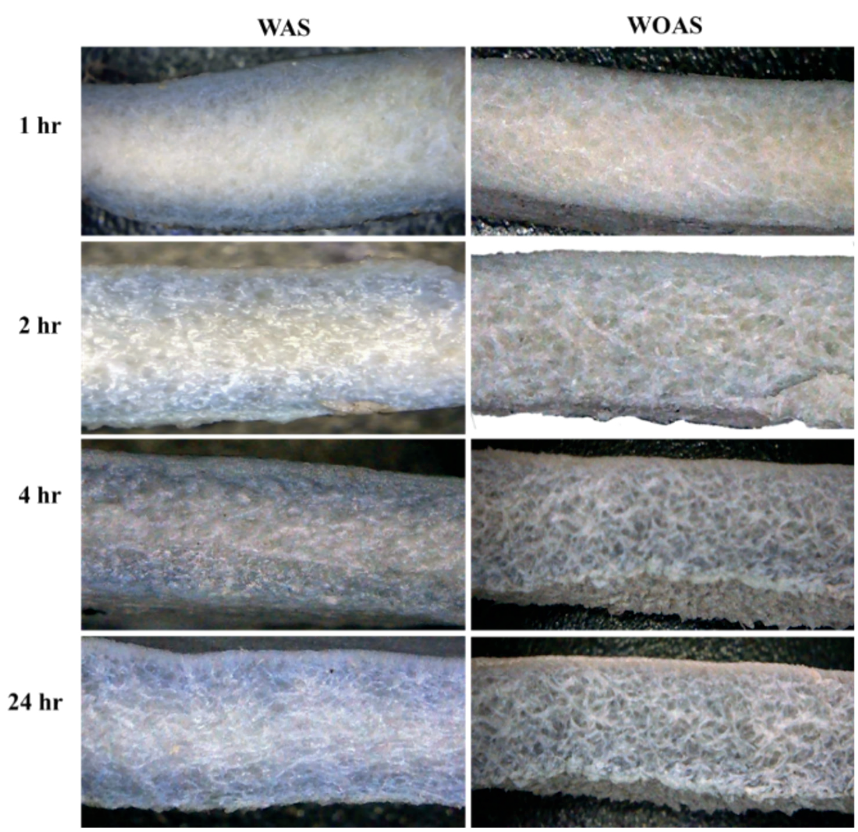

Figure 2. Micrographs taken at different time interval of chromium tanning

Table V

Hydrothermal shrinkage temperature at different processing stages

Processing Stage	WAS (°C)	WOAS (°C)
Deliming	59 ± 1	59 ± 1
Acid swelling/*Pickling	40 ± 2	55 ± 1
Chrome tanning (after basification)	98 ± 1	101 ± 1
After 48 hrs ageing	100 ± 1	105 ± 1

* Saline water (10% NaCl solution) used for shrinkage temperature measurement of pickled pelt

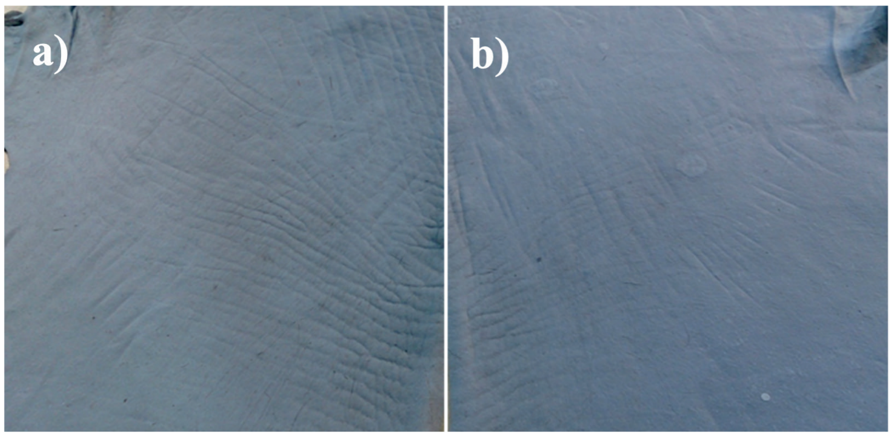

Figure 3. Photographic image of **(a)** WAS wet-blue and **(b)** WOAS wet-blue

Further, the shrinkage temperature of the wet-blue leather obtained from WAS is 98°C whereas it is 101°C for WOAS system. It may be due to the synergetic effect of improper chromium diffusion and change in inter-molecular interaction due to the acid swelling. However, shrinkage temperature is marginally improved after the ageing (48 hrs) process. Nevertheless, it is not comparable to the level of wet-blue obtained from the WOAS system.

Characteristics of Wet-Blue

The wet-blue leather obtained from WAS system is rubbery in nature. In addition, the color of chrome tanned leather is green with pronounced growth marks (Figure 3a). In the case of the WOAS system, grain pattern is uniform in nature (Figure 3b).

The wet-blue leathers obtained from both WAS/WOAS systems were stored at room temperature and continuously monitored. It is evident from Figure 4a that the fungal growth was observed on WAS-wet-blue within 7 days whereas no such growth noted in WOAS system. Besides, the wet-blue of WAS system loses its moisture content faster than the conventional wet-blue. After 30 days, the moisture content of the WAS wet-blue was 42% w/w whereas it was 60% w/w for WOAS wet-blue. The reason for faster fungal growth formation and drying of WAS wet-blue may be due to the lower salinity concentration.

It is demonstrated that the salinity inhibits the growth of fungal formation and the inhibition potential is directly proportional to the salinity concentration.[18] The presence of salinity limits the hyphae and mycelium growth of fungi. Further, the presence of salt decreases the vapor pressure of water and thereby avoids faster dehydration.[19] In addition, commercial sodium chloride contains some amount of potassium chloride which is hygroscopic in nature.

Hence, the decrease in vapor pressure of water and the presence of hygroscopic salt in wet-blue leather may prevent the faster dehydration of wet-blue leather.

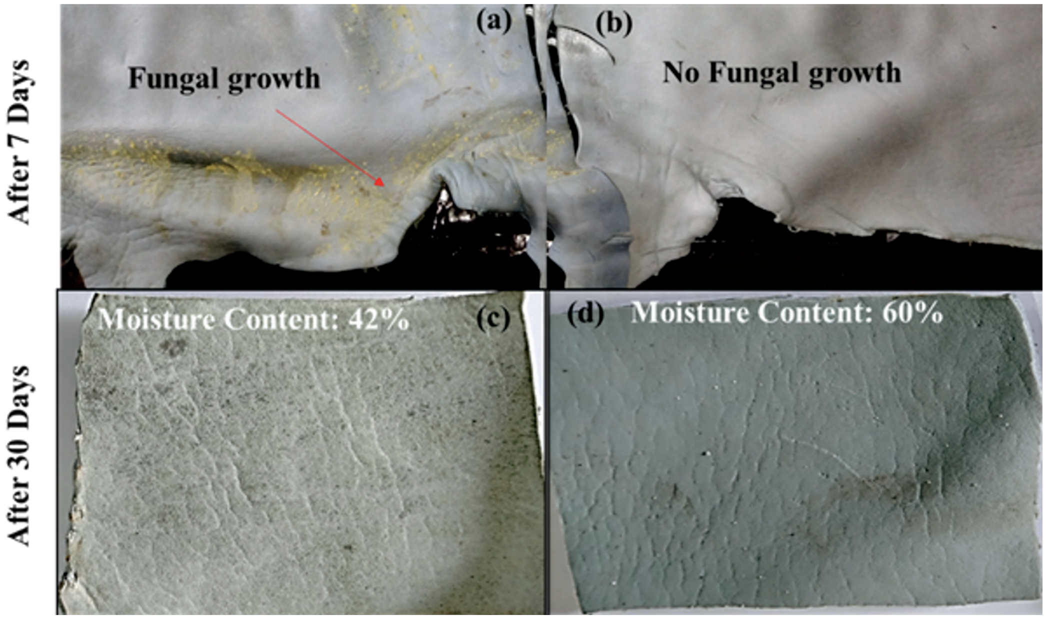

Figure 4. Wet-blue leather obtained from WAS system **(a and c)**, and WOAS system **(b and d)** after ageing for 7 and 30 days

Evaluation of Crust Leather – Industrial glove

The wet-blue leathers obtained from the WAS/WOAS system were processed into industrial glove leather and subsequently, the properties of matched pair crust leathers were analyzed.

In order to avoid the interference of collagen stabilization by synthetic tanning agents employed in the post-tanning process, the industrial glove leather process (without any synthetic tanning agents) was adopted. The process recipe was collected from a commercial industrial glove leather manufacturing unit in Kolkata, West Bengal, India. The physical strength characteristics of crust leather obtained from WAS/WOAS system are given in Table VI. It is evident from Table VI that all the physical strength characteristics of WOAS crust leather are superior to that of WAS system. Acid swelling reduces the tensile and tear strength of the final leather by about 15% and 17%, respectively. However, negligible difference was observed for % elongation. Further, about 20% reduction in both grain crack and bursting strength is observed. On the other hand, the grain crack and bursting distance are high for WOAS-crust leather. The results clearly indicate that the fiber bundle of the grain layer is well lubricated/dispersed and stronger in nature for WOAS crust leather.

Table VI

Physical properties of crust leathers

Characteristics	WAS	WOAS	% Variation w.r.t. WOAS
Average Thickness (mm)	0.9 ± 0.1	1.0 ± 0.1	-10.0
Tensile strength (MPa)	12.8 ± 1.6	15.1 ± 1.5	-15.2
Elongation (%)	50.5 ± 5.6	50.1 ± 4.7	-0.1
Tear Strength (N/mm)	73 ± 7.7	88.4 ± 10.0	-17.4
Grain crack load (kgf)	23 ± 1.3	29 ± 0.3	-20.7
Grain crack distance (mm)	8 ± 0.7	8.7 ± 1.7	-8
Bursting load (kgf)	26 ± 2	33 ± 2	-21
Bursting distance (mm)	9.6 ± 0.5	10.7 ± 1.1	-10.2
Softness (mm) – Neck	4.5 ± 0.4	5.1 ± 0.6	-11.8
Softness (mm) – OSP	5.0 ± 0.3	5.5 ± 0.3	-9

OSP – Official Sampling Position; All the specimens were taken from OSP

Table VII
Organoleptic properties of crust leathers

Properties	WAS	WOAS
Softness	Softness is lower than the WOAS-crust leather. The degree of heterogeneity in softness is high	Good softness with low heterogeneity
Stretchiness	Stretchiness is on par with the WOAS crust leather (both along and across the backbone) at OSP. However, the neck region is hard and tight	Good stretchiness
Grain smoothness	Grain is not smoother as like WOAS crust	Good smoothness with less heterogeneity
Uniformity	Non-uniform and patchy grain	Uniform grain
Internal softness	Internally empty	Good internal softness
Looseness	More looseness	No looseness with good body
Touch	Papery touch	Leathery touch

Note: The methodology for the analysis of organoleptic properties is described in Materials and Methods section

In addition, acid swelling reduces the softness of the final leather and a detailed investigation is required to understand the phenomena. The organoleptic properties of crust leathers have been analyzed and compared in Table VII.

Morphology Analysis

Generally, acid swelling leads to a reduction in fiber length and also induces differential strain at various layers. Subsequently, the induced strain may alter the surface morphology of the final leather. It is evident from Figure 5 that the neck portion of the WAS-crust leather is non-uniform in nature and also the enhanced growth mark is observed, whereas it is uniform in WOAS-crust leather. However, the grain pattern of WAS and WAOS crust leathers is uniform at OSP. It is also evident from Figure 6 that the uneven patches have been observed on neck portions of WAS crust leathers, whereas uniform coloration is seen in other places. No such issues were found in WOAS crust leather. The cross-sectional morphology of the crust leathers (WAS/WOAS) is visualized through scanning electron microscope and the same is shown in Figure 7.

It is evident from Figure 7 that the fiber bundles of WAS-crust leather (Neck/OSP) are more highly separated than the WOAS leather. Whereas the fiber bundles are thicker in WOAS system but

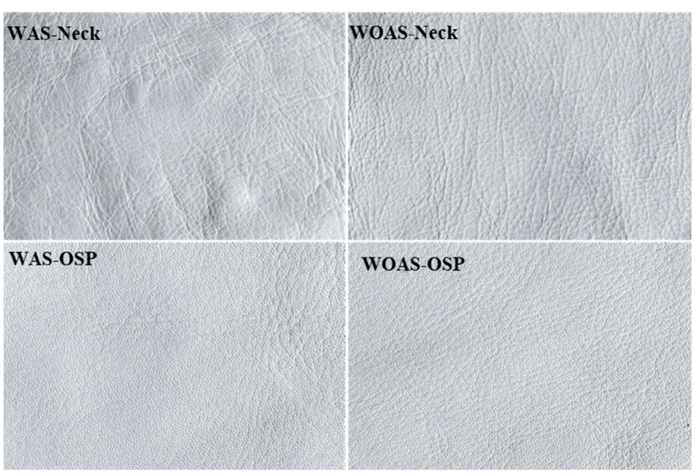

Figure 5. Photographic images of crust leathers

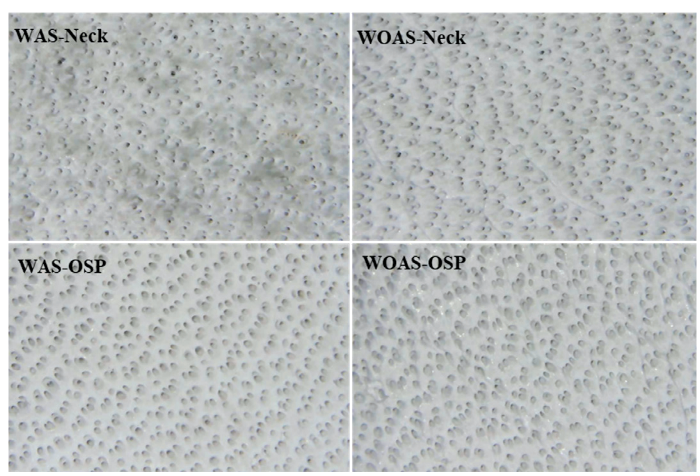

Figure 6. Microscopic images of crust leathers

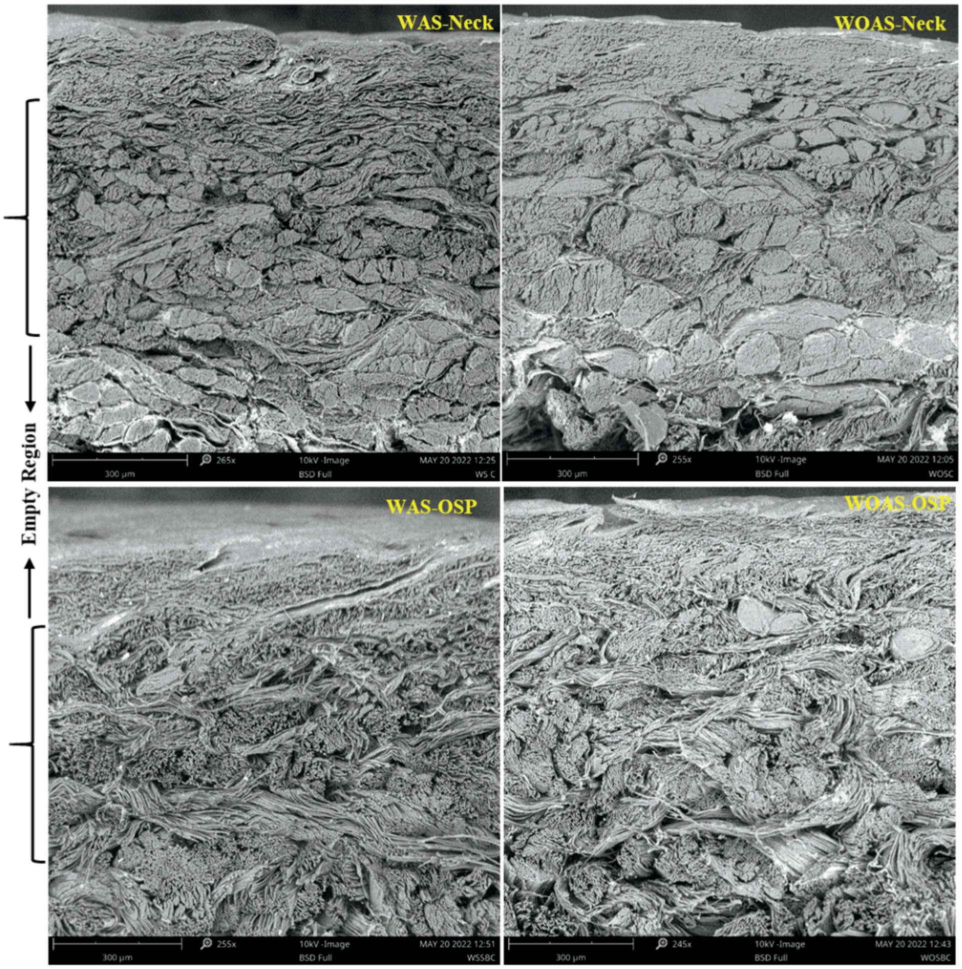

Figure 7. Scanning electron micrographs showing the cross-sectional view of crust leathers

not cemented in nature (cemented fibers make the leather harder). The extensive sub-division of fiber bundles may be the reason for the production of empty/loose leather in WAS system.

Color value measurements

The color coordinates of the wet-blue/crust leathers obtained from both WAS and WOAS systems have been measured and given in Table VIII. The lightness value of both wet-blue and crust leather obtained from WOAS system is higher than the WAS leather. This clearly indicates that the leather obtained from WOAS system is lighter blue (after chrome tanning) and whiter (after crusting process) than the WAS leather. Similarly, the high a* value indicates that WAS wet-blue leather is slightly greener than WOAS leather.

Table VIII

Color value measurement of wet-blue and crust leather

Name	L	a*	b*
WAS-WB	52.90	-6.40	3.37
WOAS-WB	59.97	-3.87	5.36
WAS-Crust	75.32	-4.22	1.87
WOAS-Crust	81.39	-3.43	1.83

L – Lightness (0-Black, 100-White); a* - (-ve value toward green/+ve value towards Red), b* - (-ve value toward blue/+ve value toward yellow)

Conclusions

It may be concluded from the present investigation that the acid swelling increases the delimed pelt weight by about 17% w/w and the addition of tanning salt reverses the swelling state to a maximum extent. Further, the diffusion of chromium is greatly affected by acid swelling and the time taken for chromium diffusion up to the cross-section is about 4 hrs in WOAS system whereas in the case of WAS system it is incomplete even after 24 hrs. The wet-blue leather obtained from WAS system has enhanced growth marks, dehydrates faster and is also more prone to fungal attack than the WOAS system. Acid swelling reduced the physical strength characteristics of the leathers and also makes the leather tight especially in neck area and empty (looseness) in other areas. Finally, the crust leather obtained from WAS system was slighter greener than the WAS system. The study provides avenues for commercial exploitation of salt-free chrome tanning systems.

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