A Systematic Study on the Role of Chilling Temperatures on the Curing Efficacy of Hides and Skins

by

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Abstract

Chilling is considered an alternative curing method for salt-free short-term preservation of hides and skins, but no systematic studies has been carried out with this method. In the present study, an attempt was made to investigate the role of chilling temperatures on the preservation efficacy. The experiments were done in a cold temperature cabinet using goat skins and cow hides. The samples of the hides and skins, chilled to different temperatures, were analyzed for the bacterial count, soluble nitrogen and hydroxyproline. The data suggested that 4°C is the optimum temperature for 7 days storage. The results of the chilling profile study indicate the need for a blast chiller to chill down to the target temperature in less than 2 hours in order to minimize the chance for bacterial damage. The optical microscopic studies of the chilled hides and skins at different temperatures show that the fiber compaction increases with the decrease in temperature compared to the skins preserved with common salt. The leathers produced had also the required qualities and strength properties to fulfill the trade requirements as evidenced from the organoleptic assessment, physical testing and scanning electron microscopic studies.

Resumen

La refrigeración se considera un método alternativo de curado para la conservación sin sal a corto plazo de pieles grandes o chicas, pero no hay estudios sistemáticos realizados con este método. En el presente estudio, se llevó a cabo un intento para investigar el papel de las temperaturas de refrigeración sobre la eficacia de la conservación. Los experimentos se realizaron en una cabina de temperatura fría usando pieles de cabra y pieles de vaca. Las muestras de las pieles, refrigeradas a temperaturas diferentes, se analizaron para el recuento de bacterias, nitrógeno soluble e hidroxiprolina. Los datos sugirieron que 4°C es la temperatura óptima para 7 días de almacenamiento. Los resultados del estudio del perfil de enfriamiento indican la necesidad de un equipo de refrigeración rápida para enfriar hasta la temperatura objetivo en menos de 2hrs. con el fin de reducir al mínimo la posibilidad de daños bacterianos. Los estudios ópticos microscópicos de las pieles refrigeradas a temperaturas diferentes muestran que la compactación de las fibras aumenta con la disminución de la temperatura en comparación con las pieles conservadas con sal común. Los cueros producidos tenían también las cualidades requeridas y las propiedades de resistencia para cumplir con las exigencias comerciales como evidenciado por la evaluación organoléptica, los ensayo físicos y los estudios con microscopio electrónico de barrido.

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INTRODUCTION

Common salt (NaCl) is most popularly used for the preservation of hides and skins, the major byproducts of meat industry in many parts of the world. Sodium chloride based curing methods rely on the dehydrating and bacteriostatic properties of the salt and are very effective in preserving the hides and skins for long storage periods. Though, salting method is cost effective and easy to practice, it suffers heavily from the environmental perspective. The spent soak liquor is characterized by high Total Dissolved Solids (TDS), sodium and chloride contents.[1,2] The discharge of untreated spent soak liquor into land leads to significant addition of salinity to the soil.[3] The transport of salt through ground water affects the water bodies in the region posing a major environmental challenge. The effect of salinity from tanning sector on the ground water and fertility of the soil has been reviewed in detail.[4]

Since the discharge limit for TDS is quite stringent in many parts of the world,[5] the wastewater from the soaking operation needs to be segregated and evaporated in specially constructed solar pans. The constraints are the space available for constructing the solar pans and the efficiency is poor due to prevailing climatic conditions. Moreover, there is also a problem associated with the safe disposal of the salt recovered from the solar pans. Hence, there is a tremendous pressure on the tanners to avoid the use of salts for preservation as well as in processing. The long lasting solution to the problem may rest on the development and adoption of alternative curing methods based on salt-free preservation methods, which will not affect the quality of the resultant leathers adversely.[6-8] The various factors to be considered in the development of new curing methods are (a) bacteriological aspects of curing, (b) water content in the skins, (c) temperature, (d) humidity and (e) pH condition.[9]

Preservation of hides and skins by chilling is a good alternative to salt, as there is no pollution, no contamination of by-products and it is suitable for all raw materials and there is no hair-loosening.[10] The chilling is achieved in a unit, where the required low temperature is maintained. The temperature at which hides and skins should be chilled depends on the required time of preservation. Chilling is popular in the developed countries including Australia for situations, where the chilled hides from slaughter house/abattoirs can be transported in insulated containers by overnight journey.[11] This option is being widely used in many countries totally based on the conventional knowledge available to them. However perusal of literature on the chilling method indicates the need for a systematic study to understand the effect of different chilling temperatures on the curing efficacy for the storage of the hides and its effect on the structure of the preserved skins and hides as well as the resultant leathers.

The process of preservation by chilling consists of cooling down the temperature of the skin to a particular point. The parameters, which determine the quality of the chilled skin is the final temperature of the skin, how quickly the temperature is reached and the time for which it remains at that particular temperature after the chiller is switched off. Skin, being a non-heat conducting material, it is also important to know how long does it take for the skin to return to the room temperature, once the chilling source has been removed. This information is necessary for safety reasons, once there is a failure in the chilling system and also for deciding about the time of transportation of the chilled skins in an insulated container. In some countries, where chilling method is practiced for short-term preservation of hides, refrigerated trucks are employed for longer transportation period to avoid any possible damage to the stock. Cold temperature cabinets with good thermostat control were used in the present investigation to understand the effect of chilling temperature on the curing efficacy of fresh cowhides and goatskins.

MATERIALS AND METHODS

Cow hides of weight range 10-12 kg and area range of 25-30 sq. ft. and goats skins weighing about 1 kg/piece were obtained fresh within the duration of 2 h after flaying from local slaughterhouse and used in the study without washing in tune with commercial practice. The skins received in the form of sleeves were cut open and used in the experiments.

Effect of Chilling Temperature on the Curing Efficacy

Each cow hide was cut into two sides along the backbone and right sides were used for chilling experiments whereas the left sides were cured with 40% common salt on the green weight of the sides to act as control in this study. The batch size used per experiment was 1 side whereas in the case of goatskins, 5 pieces have been used per batch with a possibility for matched pair comparison with control. The experimental sides and skins were folded and kept in the low temperature cabinets adjusted to different temperatures, *viz.*, 0°, 2°, 4°, 7° and 10°C. In the case of hides, a Data Logger instrument was placed inside the fold to measure the rate of chilling of materials. The Data Logger has been programmed to measure the temperature and humidity at a time interval of 10 min for a total duration of 10 days. The materials were kept in the cold storage for 7 days after which the quality of preservation was assessed for any hair slip, change in the color and appearance and foul odor.

Determination of Bacterial Count

The standard plate count method, which is an indirect measurement of cell density revealing information related only to live bacteria, was used for the determination of bacterial count in the skins and sides chilled to different temperatures.[12] 5 g of the preserved samples were soaked in 50

mL sterile water and the extract was prepared by shaking in the arbitral shaker at 200 rpm for 30 min. 1mL of the extract was taken in 9 mL of sterile water and shaken well to get uniform suspension of the bacteria. 0.1 mL of the respective diluted solution was taken in sterile petri plates and molten nutrient agar at 40°C was poured and shaken gently to get uniform distribution of the bacteria. The plates were incubated at 37°C for 48 h. The number of colonies on the agar medium was counted using Quebec colony counter. The colony forming units (cfu) per g of the sample of skin was calculated.

Determination of Soluble Nitrogen Content in Chilled Hides and Skins

The nitrogen content in an aliquot of 25 mL of the water extract of the chill cured material prepared as for the bacterial count analysis was determined by Kjeldahl method.[13]

Determination of Soluble Hydroxyproline Content in Chilled Hides and Skins

The hydroxyproline content in the water extract was estimated by the Woessner method.[14] This method is based on the oxidation of hydroxyproline to pyrrole-2-carboxylic acid with peroxide. This is then condensed with p-dimethylamino benzaldehyde (PDAB) to form a red chromogen.

Determination of Shrinkage Temperature

The hydrothermal stability of the skins and hides was measured using a digital Theis shrinkage meter. The test sample of dimension 20 mm x 3 mm was cut from the side and fixed between the two clamps of the instrument. The sample was immersed in water and glycerol mixture taken in a beaker and the instrument was started. The rate of heating was kept at 2°C per min. The temperature at which the test specimen shrank was noted as the shrinkage temperature.

Histological Studies on Chilled Hides and Skins

The histological studies for the chill cured goatskins and cow sides were carried out. The samples from the preserved goat skins and cow sides were cut from butt region, treated with 10% neutral buffered formalin and aged for 24 h at 4°C. The fixed samples were dehydrated in a series of solutions of alcohol of different concentrations (50 to 100%) and then cleared in xylene. They were finally embedded in paraffin wax into moulds. The moulds were labeled and stored until use. The skin samples were sectioned at a thickness of 10 mm and deparaffinised. They were stained with hematoxylin and again counterstained with eosine.

Processing of Chilled Hides and Skins into Leathers

Skins and sides chilled to selected temperature were processed into dyed crust upper leathers along with the corresponding control using a standard process recipe. The recipes followed are described in Appendix 1.

SEM Studies on Leathers

The samples measuring 5mm x 2mm were cut from the official butt portion of the leathers as per IUP 2 (International Union for Physical Testing) sampling procedures. The samples were mounted on aluminium stubs using an adhesive, coated with gold using an Edwards E-306 sputter coater. Thickness of coating was adjusted to minimum level required to prevent charging. The micrographs for the grain surface and the cross section were obtained using FEI-Quanta 200 scanning electron microscope by operating at accelerating voltage of 12.0 kV.

Physical Testing and Organoleptic Assessment of the Leathers

The effect of chilling method of preservation on the strength properties of the leathers produced was studied in comparison with the leather from salt cured skins and sides. The samples for physical testing were cut from the experimental and control leathers as per the official sampling procedure IUP 2.[15] The samples were conditioned at 20±2° C and 65±4% relative humidity for 48 h. The tensile strength, and tear strength were determined as per the IUP 6 and 8 methods respectively.[16,17] Lastometer test was carried out as per the method SLP 9.[18] The leathers in the crust stage were assessed for their organoleptic properties by an experienced leather technologist.

RESULTS AND DISCUSSION

Assessment of Curing Efficacy of Chilling Method

The curing efficacy of the skins and hides chilled to different temperatures has been assessed after 7 days of storage period by a subjective assessment, soluble nitrogen and hydroxyproline contents and bacterial count in the skins and hides. Any loss in hydrothermal stability of the stock was also checked by shrinkage temperature (T_s) measurement

Subjective Assessment of Preserved Hides and Skins

Table 1 presents the results of the subjective assessment of the hides and skins after 7 days of storage period. It is evident from the results that no hair slip or bad odor has been noticed in the case of materials chilled to 2° and 4°C. The materials looked as fresh as it was obtained from the slaughter house. In the case of 7°C, no hair slip or bad odor was observed with goatskins but the skins were bit slimy with slight change in the color of flesh side. With cow sides, hair slip was seen in bellies and the side was also a bit slimy. These observations indicate that there is growth of bacteria in the skin but the extent of damage is seen only in some places. In the case of 10°C, hair slip was noticed especially in looser areas of both the substrates studied in this experiment. There was also slight bad odor emanating and also the condition of the skins and cow side was a bit slimy. It is evident that it may not be safer to operate at 7 and 10°C for 7 days storage. Hence, it is inferred from the results that 4°C is the optimum temperature suitable for 7 days short-term preservation of hides and skins.

TABLE I
Subjective assessment of curing efficacy for chilled goat skins after 7 days of storage.

Substrate	Hair slip	Smell	Condition of the skin
Goat skins			
Control	Nil	No bad odor	Dry
2°C	Nil	No bad odor	Fresh and wet
4°C	Nil	No bad odor	Fresh and wet
7°C	Nil	No bad odor	Bit slimy
10°C	Hair slip in looser areas	Slight odor	Wet and slimy
Cow hides			
Control	Nil	No bad odor	Dry
2°C	Nil	No bad odor	Fresh and wet
4°C	Nil	No bad odor	Fresh and wet
7°C	Slight hair slip in bellies	No bad odor	Bit slimy
10°C	Hair slip in looser areas	Bad odor	Wet and slimy

TABLE II
Soluble nitrogen and hydroxyproline in skins and hides after 7 days of storage.

Substrate	Nitrogen g of N_2/g of skin	Hydroxyproline µg/g of skin
Goat skins		
Control	$1.5x10^{-3}$	Nil
2°C	$2.0x10^{-3}$	Nil
4°C	$3.3x10^{-3}$	Nil
7°C	$2.8x10^{-2}$	Nil
10°C	$9.5x10^{-2}$	9.37
Cow hides		
Control	$3.4x10^{-3}$	Nil
2°C	$2.6x10^{-3}$	Nil
4°C	$3.8x10^{-3}$	Nil
7°C	$9.1x10^{-3}$	Nil
10°C	$7.6x10^{-2}$	15.94

Soluble Nitrogen and Hydroxyproline Contents in the Hides and Skins

The degradation if any of the proteinous components of the skins and hides was assessed by the determination of the soluble nitrogen in water extracts. The degradation of collagen was checked by hydroxyproline assay for the water solubles from the chilled hides. The results of the study for goat skins and cow sides are given in Table 2. The values for soluble nitrogen in the water solubles for skins and hides chilled to 2°C and 4°C are similar to the control salt cured stock and there was no hydroxyproline detected in the water solubles either. In the case of 7°C, the water extractable nitrogen registered a small but significant increase with both the substrates, whereas in the case of 10°C, the value is about 40 fold more for goat skins and about 20 fold more for cow side compared to the corresponding values for the respective control. No hydroxyproline was found with 7°C whereas small quantities of hydroxyproline were detected, *viz.,* 9.37 µg/g and 15.9 µg/g for goat skin and cow side chilled at 10°C respectively. This may mean that there is some degradation of non-collagenous proteins whereas the collagen degradation is absent at 7°C, whereas at 10°C, some amount of collagen degradation is seen. The results are in agreement with organoleptic assessment too.

Assessment of Curing Efficacy by Bacterial Count

Bacterial count data for the control and experimental skins and hides are set out in Table 3. It is seen that the bacterial count in the chilled goat skins were $5.9x10^5$ and $6.8x10^5$ cfu/g at 2 and 4°C respectively, which are of the same order as in the case of salt cured skins. Similarly the bacterial count in cow sides chilled to 2 and 4°C are also in the order as found for salt cured hide. But further increase in temperature results in steady increase in bacterial count in the skins and hides. In the case of chilling at 10°C, the bacterial count increases many fold compared to that in control skin and hide. The values are $4.5x10^8$ and $3.4x10^9$ cfu/g for goat skin and cow side respectively. It is evident from these results that temperatures 7° and 10°C are not able to completely arrest the growth of bacteria in 7 days storage.

The Effect of Chilling on the Hydrothermal Stability

The shrinkage temperature is the measurement of breakdown of stabilizing linkages existing in the collagen matrix.[19] The

TABLE III
Bacterial count (cfu/g)
(After 7 days storage).

Substrate	2°C	4°C	7°C	10°C	Control
Goat Skins	Initial $5.5x10^5$	$5.5x10^5$	$5.5x10^5$	$5.5x10^5$	$5.5x10^5$
	After 7 days $5.9x10^5$	$6.8x10^5$	$9.1x10^7$	$4.5x10^8$	$5.37x10^5$
Cow hides	Initial $3.6x10^5$	$3.6x10^5$	$3.6x10^5$	$3.6x10^5$	$3.6x10^5$
	After 7 days $6.3x10^5$	$9.3x10^5$	$6.8x10^7$	$3.4x10^9$	$9.6x10^5$

TABLE IV
Shrinkage temperature data for chilled goat skins and cow sides.

Substrate	T_s °C*
Goat skins	
Control	65.3±0.58
2°C	66±0.0
4°C	65.3±0.58
7°C	65±1.0
10°C	65.3±0.58
Cow hides	
Control	66±0.0
2°C	67±1.0
4°C	66±1.0
7°C	66±0.0
10°C	66±1.0

* Mean of 3 values

effect of chilling if any on hydrothermal stability of the skins and sides has been studied by the measurement of shrinkage temperature (T_s). The data for goat skins and cow sides are given in Table 4. From the results, it is evident that T_s is not affected by the chilling method of preservation. This reveals that the chilling has not brought about any disruption of inter-fibrillar crosslinks in the matrix. Even with chilling at 10°C, the shrinkage temperature is similar to that for control even though the materials seem to have undergone some damage due to growth of microorganisms as evidenced by hair slip and increase in bacterial count. This indicates that the damage has happened only at the surface level and there is no disruption of fiber stabilizing forces.

Chilling and Warming (Natural) Profiles of Cow Sides for Different Temperatures

The chilling and warming profiles for the cow sides chilled to different temperatures, viz., 2, 4, 7 and 10°C have been studied by using the programmable Data Loggers. The results obtained in the study were summarized in the Table 5 for cow sides. From Table 5, it can be seen that the time taken to reach 2°C for cow hide was more than 13 h whereas the time taken to warm from 2 to 20°C was 7 h and 10 min. Similar data for chilling to 4°C are 7 h and 40 min and close to 7 h. For 7°C, it took 6.5 h to cool down to the target temperature and 3.5 h to warm from that point to 20°C. For 10°C chilling, the pulling down time to reach 10° C was close to 6 h whereas warming to 20° from 10°C took only 2 h. For all these three temperatures, the pulling down time is too long and this may result in bacterial growth especially if the chilling process is scaled up. Usually, it is considered that the skins and hides are to be preserved within the duration of 2-4 h after their removal from the body of the dead animal. Hence, it is necessary to bring down the pulling down time to less than 2 h from material safety point of view by resorting to accelerated chilling procedure as there will be delay in bringing the material to the chilling plant from the slaughter houses or primary collection centers. So the chiller designed for the purpose should have a blast chiller facility to achieve such a low pulling down time. Another feature to be considered is the provision for hooking the skins and hides to achieve faster and uniform cooling. Hides and skins being good insulating materials, getting the temperature inside the fold will take longer time even with a blast chiller facility and hence hooking them will give a better chance to achieve the target chilling temperature all over the material quickly.

It is seen from the warming profile for chilling temperatures 2 and 4°C that it takes 7 h and 40 min and 6 h and 50 min respectively for the temperature of the material to go up to 20°C. It appears from these data that the duration of transportation of hides/skins in an insulated container from the slaughter houses/collection centers to the tanneries should be less than 7 h so as to avoid any bacterial damage. 20°C is taken as the benchmark based on the experience reported by various research papers that at this temperature, the stock can be held for at least 24 h.[20] However, this conclusion has to be corroborated by the data for the bacterial count. Moreover, this has also to be checked in larger scale trials. For 7° and 10°C chilling, the time taken to warm to 20°C was 3.5 h and 2 h respectively, which might be too short for the safe transportation of the material.

TABLE V
Chilling and warming profiles for cow sides.

Temperature (°C)		Time Taken (min)	% Relative humidity
From	To		
Chilling and warming profile for 2°C			
30	-	0	67.0
30	10	170	78.8
30	7	285	80.9
30	4	400	82.6
30	2	800	85.0
2	4	40	87.0
2	7	80	89.6
2	10	140	90.2
2	15	265	91.8
2	20	430	93.2
Chilling and warming profile for 4°C			
30	-	0	66.0
30	10	190	81.8
30	7	330	82.4
30	4	460	85.6
4	7	35	87.4
4	10	90	89.2
4	15	200	90.8
4	20	410	91.4
Chilling and warming profile for 7°C			
30	10	190	80.1
30	7	330	82.3
7	15	160	86.7
7	20	210	90.7
Chilling and warming profile for 10°C			
30	10	230	81.1
10	15	40	85.3
10	20	120	89.5

The percent relative humidity (% RH) during chilling and warming was also recorded for cow sides and the same has been included in the table. It is evident that % RH increased both during chilling and warming for all the temperatures studied.

It appears from various aspects studied to assess the curing efficacy as well as from the warming profile that 4°C may be the optimum temperature. However, an accelerated chilling may be necessary to reduce the cooling time.

Histological Studies on Chilled Skins and Sides

The optical microscopic studies have been carried out on goatskins and cow sides chilled to different temperatures and compared with the salt cured counterparts. The microphotographs for the goatskins and cowhides are set out in Figure 1. It is evident from the figure that the chilled skins and hides have more compact fiber bundles compared to control and the compactness increases with decreasing temperature. In the case of control, the fiber bundles appeared to have delineated probably due to dehydration. The small dots seen in the case of control skins and hides may be due to the splitting up of fiber bundles and this is absent in the case of chilled skins and hides. The inference from the study is that the structure of chilled skins and hides remain unchanged whereas that of salt cured stock undergoes changes due to dehydration brought about by the high concentration of the salt used in curing.

Effect of Chilling on the Fiber Structure of Leather

Scanning electron micrographs for the surface (100x magnification) and cross section (200x magnification) are

TABLE VI
Organoleptic assessment data for goat and cow leathers

Properties	Goat Leathers		Cow Leathers	
	Control	Chilling at 4°C	Control	Chilling at 4°C
General appearance	9	9	7	8
Softness	7	7	8	8
Fullness	8	8	7	8
Grain tightness	7	8	6	8
Grain smoothness	8	8	8	8

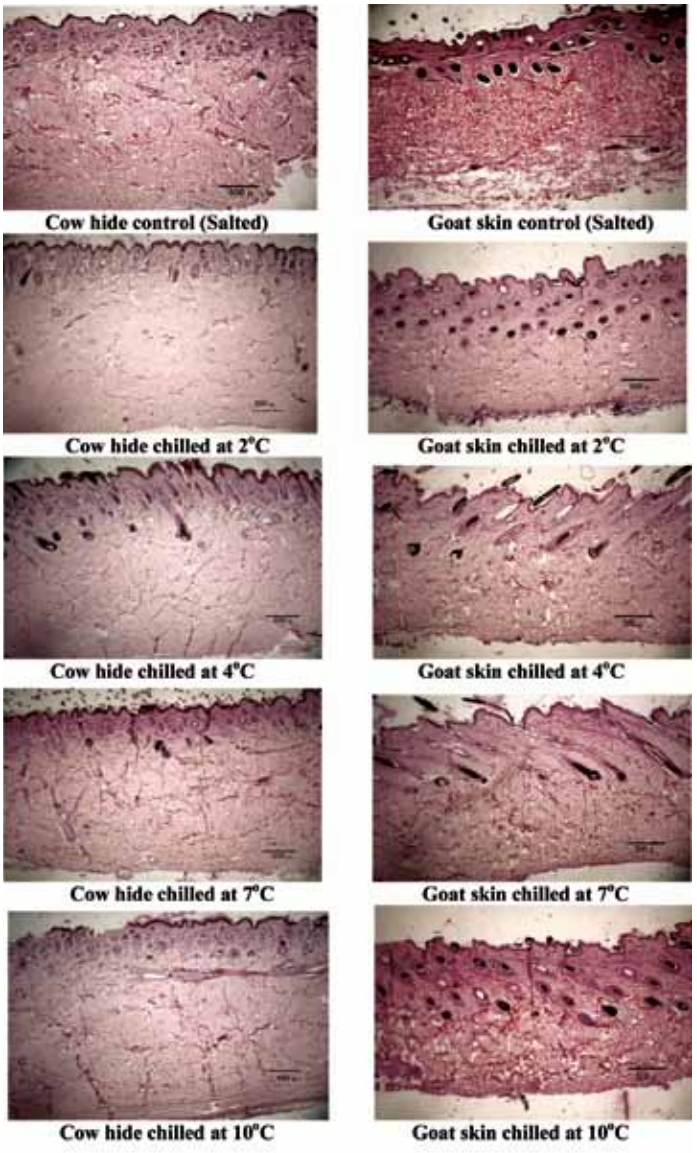

Figure 1. Optical microscopic images for preserved cow and goat skins.

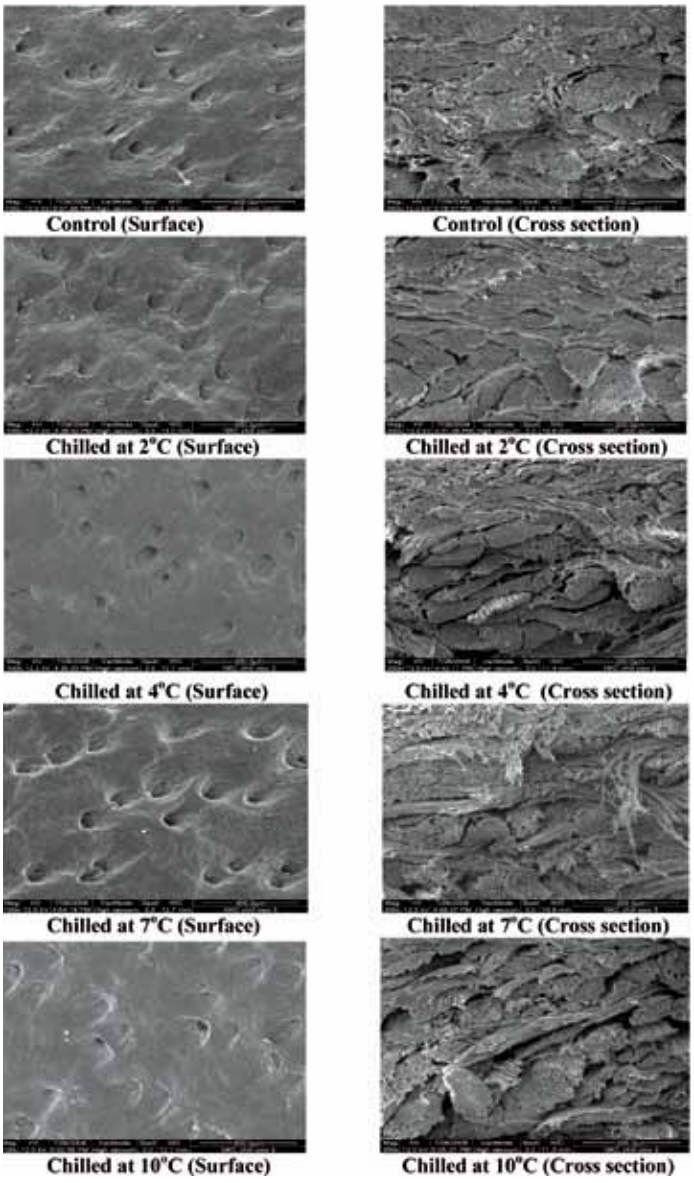

Figure 2. Scanning electron micrographs of preserved cow crust leathers.

TABLE VII
Physical testing data for goat and cow leathers.

Parameter	Goat Leathers		Cow Leathers	
	Control	Chilling at 4°C	Control	Chilling at 4°C
Tensile Strength (kg/cm^2)	215 ± 20.5*	210 ± 16.5	228 ± 20.5*	231± 9.9
Elongation at Break (%)	53±4.2%	52±5.7%	50 ± 2.8%	50.5±6.4%
Tear Strength (kg/cm)	29 ± 3	32 ± 5	41 ± 4.2	42 ± 1.4
Load at Grain Crack (kg)	34 ± 1.4	35 ±2	34 ± 1.4	36 ±2
Distention at Grain Crack (mm)	8 ±0.2	7.5±0.3	7.7 ± 0.2	7.5 ± 0.14

*Mean of 2 values

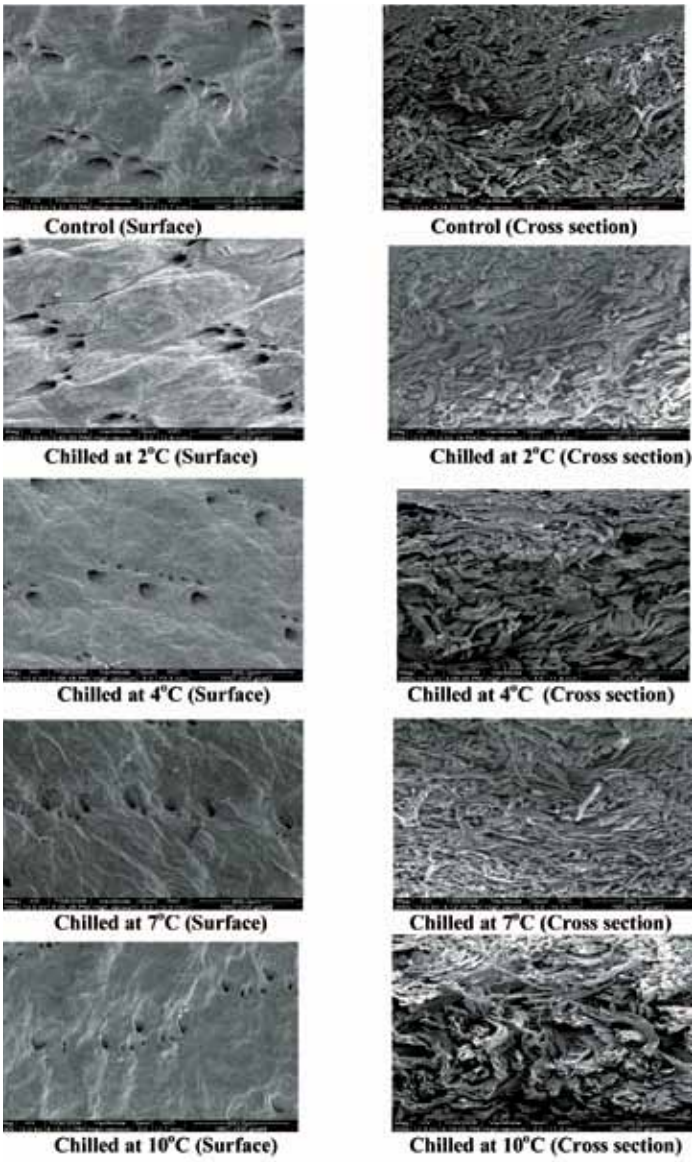

Figure 3. Scanning electron micrographs of preserved goat crust leathers.

given in Figure 2 for cow leathers and in Figure 3 for goat leathers. No grain damage or loss of fiber or distortion in the fiber weave has been noticed for leathers from chilled skins and hides indicating that the stocks did not suffer any bacterial damage during the storage. However, in the case of goatskins, except for 4°C, there seems to be some sort of distortion of the grain in the experimental leathers. The fiber structures of experimental goat and cow upper leathers are seen to be comparable with that of their control counterparts except that they are more compact. In addition, there appears to be a gradual decrease in the compactness as the chilling temperature is varied from 2° to 10°C. This observation corroborates with the organoleptic assessment that the experimental leathers are more compact than control leathers. This aspect can be taken advantage of in the case of Indian cowhides, which are commonly affected by looseness in the fiber structure as they are mostly from old and fallen animals.

Effect of Chilling Method on the Quality of the Leathers

The organoleptic assessment data for the upper leathers produced from control and chilled (4°C) skins and sides are given in Table 6. The results indicate that the leathers produced from chilled skins and sides are fuller and much more compact in fiber structure as compared to the control leathers. The grain tightness with experimental cow upper leathers seems to have improved markedly by the chilling treatment. The softness and grain smoothness properties are comparable.

The physical testing data for the matched pairs of control and experimental leathers are presented in Table 7. It is evident from the results that the chilling method has not adversely affected the strength properties and the strength properties of the experimental leathers are comparable to that of salt cured leathers. Generally it is believed that putrefaction results in decrease in tear strength of the leathers. It is evident from the table that with both the substrates, the tear strength was found to be comparable if not slightly better in the case of leathers from chill cured stock.

CONCLUSION

From the results of the study, it has been concluded that 4°C is the optimum temperature for 7 days storage period. However, the chilling profiles inform that a blast chiller and hooking arrangements might be necessary for bringing down the temperature to 4° C in less than 2 h to avoid bacterial damage for the commercial exploitation of the process. The optical microscopic study indicates that there is no adverse effect noticed on the chilled goatskin and cow hides. In the chilled skins and hides, the fiber bundles seemed to be more compact compared to control and the extent of compaction increases with the decrease in temperature. The quality of the leathers processed from skins and hides chilled at 4°C was found to be comparable to the control leathers and fulfill all the trade requirements in terms of both organoleptic assessment and strength characteristics. The improved fiber compaction and grain tightness noticed with chilled material can be beneficial especially in the case of Indian cow hides, which are mostly from old and fallen animals.

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APPENDIX I
RECIPES FOR THE PROCESSING OF PRESERVED HIDES AND SKINS
Process for Goat Upper Leather.

Process	Material	%	Time	pH
Soaking (Pit) I Soak Drain II Soak Drain	 Water Water N. I. (Non ionic) Wetting agent Soaking enzyme	 300 200 0.1 0.2	 1 h 3 h	
Liming	Water Lime Sodium sulphide	15 10 3		
Make a paste and apply on the flesh side and leave overnight. Next day, dehair and relime.				
Reliming (Paddle)	Water Lime	250 8		
Run initially for 15 min, run 5 min/h for 48 h				
Flesh, wash				
Washing (Drum)	Water	150	20 min	
Deliming and Bating (Drum)	Water Ammonium sulphate	100 1.0	 45 min	
Check completion of deliming with phenolphtahlein				
Add Drain Washing Drain; wash	Microbate Water N. I. wetting agent Sodium bisulphite	1.0 150 0.1 0.3	60 min 15 min	
Pickling	Water Salt Formic acid Sulphuric acid	80 8.0 0.3 1.0	 15 min 20 min	
Add in 3 feeds at 15 min intervals. Finally run for 1 h. Check pH Leave overnight. Next day, run for 30 min. Drain half the bath.				2.5-3.0
Chrome tanning	Pickle Float BCS (Basic Chromium Sulphate) Cationic fatliquor	50 8 0.5		
Check penetration. Add water 75% run for 45 min.				
Basification	Sodium formate Sodium bicarbonate	1.0 0.75	20 min	
Added in 3 feeds at 15 min interval and finally run for 2 h. Check pH. Drain, wash, pile overnight.				3.8-4.0
The leathers were sammed, shaved to 0.7-0.8 mm thickness and the shaved weight was noted.				

Appendix I continued on thefollowing page.

Appendix I continued.

Acid wash Drain	Water Acetic acid Fat dispersing agent	200 0.25 0.5	30 min	
Rechroming	Water Chrome syntan Basyntan AN (Aromatic syntan)	100 5.0 4.0	45 min	
Basification	Sodium formate Sodium bicarbonate Check pH.	0.5 0.5	45 min.	4.0-4.2
Wash, Drain; pile overnight. Next day, wash and neutralize.				
Neutralization	Water Sodium formate Sodium bicarbonate	150 1 0.5	15 min	
Added in 2 feeds at 15 min interval, finally run for 30 min.				5.0-5.2
Wet finishing	Water Relugan RE (Acrylic syntan) Basyntan DI(Phenolic syntan)	100 2.0 2.0	45 min 30 min	
Add	Vernaminol ASN(synthetic fatliquor	2.0	30 min	
Add	Dye	3.0	30 min	
Check penetration				
Add	Vernatan OS(phenolic syntan) Basyntan DI Basyntan FB6 (Resin syntan)	3 4 3	60 min 30 min	
Add	Balmol SX 20 (synthetic fatliquor) Lipoderm Liquor FBII (vegetable fatliquor)	4.0 3.0	45 min	
	Vernatan R7 (Resin syntan) GS Powder (Mimosa) Basyntan FB6	4.0 2.0 2.0	45 min 30 min	
Fixing	Formic acid	2.0		
Add in 3 feeds at 10 min intervals and finally run for 30 min.				
Next day, set, hook to dry, stake, buff, trim and toggle.				

APPENDIX I
RECIPES FOR THE PROCESSING OF PRESERVED HIDES AND SKINS
Process for Cow Softy Upper.

Process	Material	%	Duration	pH
Soaking (Pit) I Soak Drain II soak	Water Water N.I. Wetting agent Soaking enzyme	300 300 0.1 0.3	1 h 3 h	
Liming (Paddle)	Water Lime Sodium sulphide	250 10 3.0	24h	
Run Initially for 15 min and then 5 min/h for 24h. Drain; Flesh and wash thoroughly in the drum				
Deliming & Bating	Water Ammonium sulphate Sodium bisulphite	100 2.5 0.3	2 h	
Check completion of deliming with phenopthalein. Drain, wash and drain.				
Add	Microbate	0.5	45 min	
Drain, wash, Drain.				
Washing Drain, wash.	Water Sodium bisulphite N.I. wetting agent	100 0.5 0.2	20 min	
Pickling	Water Salt Formic acid Sulphuric acid	80 8 0.3 1.5	20 min 15 min	
4 feeds at 10 min interval. Finally run for 2 h. Check pH; leave overnight. Next day, run for 30 min. Drain half the bath				2.8-3.0
Chrome tanning	Pickle float BCS Cationic fatliquor	50 8 0.5	2 h	
Check penetration. Flood with 50% water				
Basification	Sodium formate Sodium bicarbonate	0.5 1.25	15 min	
4 feeds at 10 min interval. Finally run for 120 min. Check pH. Drain, wash and pile for 2 days.				
The leathers were sammed, shaved to 1.2-1.4 mm thickness and the shaved weight was noted.				

Appendix II continued on the following page.

Appendix II continued.

Acid wash Drain	Water Acetic acid Fat dispersing agent	200 0.25 0.3	30 min	
Rechroming	Water Chrome syntan Oratan 540 (Acrylic syntan) Sodium formate Check pH	100 4.0 4.0 0.5	45 min 30 min	4.0
Wash, Drain; pile overnight. Next day, wash and neutralize.				
Neutralization	Water Vernatan AKM (Neutralizing syntan) Sodium bicarbanate	100 1.5 0.3	20 min	
2 feeds at 10 min interval. Finally run for 30 min. Check pH Wash/drain and wash/drain.				5-5.2
Retanning Dyeing and Fatliquoring	Water Relugan RE Vernaminol ASN Basyntan DI GS powder	100 3 2 2 2	30 min 15 min 60 min	
	Dye	3	30 min	
Check penetration.				
	Balmol SLW (semi synthetic fatliquor) Balmol BL II (semi synthetic) Balmol SX 20 Preservative	3 3 2 0.2	 30 min 15 min	
	Basyntan DI Basyntan FB6	4 3	45 min	
Fixing	Formic acid	1.5		
3 feeds at 10 min interval. Finally run for 30 min. Drain, wash and dry, pile over night. Next day, set, hook to dry, stake, buff, toggle and trim				