# A Modified Leather Processing Method for Water and Pollution Reduction in Tannery

*by*

S. Saravanabhavan, J. Raghavar Rao*, Balachandran Unni Nair
*Chemical Laboratory, Central Leather Research Institute*
Adyar, Chennai 600 020, India


## Abstract

Current practice of leather manufacture subjects the hides/skins to repeated acid and alkali treatments. Conventional process protocol results in high total dissolved solid (TDS) and chemical oxygen demand (COD) in the wastewater. Further, the process employs huge amount of water and subsequently discharges the same as wastewater. The cost for the treatment of wastewater is directly proportional to the volume of wastewater generated. In this study, the leather processing sequence has been modified for water and pollution reductions as well as better quality leather production. The modified process treats the delimed pelt with post-tanning chemicals first followed by chrome tanning salt. This is possible due to appropriate choice of charge of the hide matrix and post tanning chemicals and pH profiles of leather processing. This process logic eventually eliminates several acid and alkali treatment and washing steps that are followed in the conventional process. The percentage offer of post tanning chemicals is determined based on pelt weight to split weight relation. The leather from modified process is characterized through stratigraphic distribution of chromium, percentage oils and fats, scanning electron microscopy, softness and physical testing. The performance of the leathers is found to be on par with that of conventionally processed leathers through hand and physical evaluation. The modified process significantly reduces the usage and discharge of water by 62 and 62%, respectively. It also enjoys the reduction in COD and TS loads by 49 and 70%, respectively. Further, the process reduces the usage of chemicals by 41% by avoiding acid and alkali treatment steps. The modified process appears to be technically feasible and economically viable.

## Resumen

Las presentes prácticas de fabricación del cuero someten a las pieles a repetidos tratamientos con ácido y álcali. El protocolo convencional resulta en altos valores de sólidos solubles totales (SST) y demanda química de oxígeno (DQO) en los efluentes. Más aun, el proceso utiliza enormes cantidades de agua que subsecuentemente se descargan en las aguas residuales. El costo de tratamiento del agua residual es proporcional al volumen del agua residual generado. En este estudio, la secuencia de procesamiento del cuero se ha modificado para así reducir la generación de agua y contaminación como también para producir una mejor calidad de cuero. El proceso modificado trata la piel ya desencalada con agentes químicos recurtientes luego de ser tratada con sal de cromo curtiente. Esto es posible dada la acertada carga seleccionada para la matriz de la piel y los recurtientes que le siguen en términos de los perfiles del pH en el proceso. La lógica tras el proceso permite eliminar varios tratamientos con ácido y álcali y los lavados posteriores que siguen en el proceso convencional. El porcentaje de recurtientes ofrecidos se determina por la relación basada en los pesos de la piel desencalada a la piel ya dividida. El cuero obtenido en el proceso modificado es caracterizado a través de la distribución estratigráfica del cromo, porcentaje de aceites y grasas, microscopía electrónica por barrido, blandura y pruebas físicas. Los rendimientos del cuero se encontraron ser a la par con cueros convencionalmente procesados tanto por tacto como por evaluación física. El proceso modificado reduce el uso y la descarga de agua en 62 y 62% respectivamente. También goza de una reducción de la carga en DQO y SST del 49 y 70%, respectivamente. Adicionalmente, el proceso reduce el consumo de de agentes químicos en un 41% evitando tratamientos concurrentes ácidos y alcalinos. El proceso modificado aparenta ser técnicamente factible y económicamente viable.


## Introduction

Conventional method of leather making involves 14-15 steps of unit processes. It comprises a combination of single and multi-step operations that use as well as discharge various organic and inorganic substances.[1] Water is the main medium of transport for the chemicals. Conventional leather processing employs about 30-40 L of water per kg of hide processed and subsequently discharges them as wastewater along with pollutants.[2] Globally, the liquid effluent from leather processing accounts to 300-500 billion L. This gives rise to two major problems for the leather industry, viz., the availability of good quality water and the need for treatment of such large quantities of effluents, which requires major investments in effluent treatment plants. Pollutants in wastewater discharged from the leather processing contribute to biochemical oxygen demand (BOD), chemical oxygen demand and total dissolved solids. These are primarily due to the fact that the conventional leather processing employs 'do-undo' process schemes such as liming-deliming (swell-deswell), pickle-depickle (acidification-basification), rechroming-basification (acidification-basification) and neutralization-fixing (basification-acidification).[3] In other words, conventional methods employed in leather processing subjects the skin/hide to several acidification and deacidification steps.[4] Such steps demand the use of acids and alkalis, which results in the generation of salts. This results in a net increase of TDS, chlorides, sulfates and other minerals in tannery wastewaters.[5,6]

Conventional chrome tanning generally involves pickling and tanning using basic chromium sulfate (BCS) followed by basification processes. Conventional method of post-tanning process involves[7,8] major steps comprising rechroming, basification, neutralization, washing, retanning, dyeing, fatliquoring and fixing. Tanning and post-tanning processes employ a pH range of 2.8-6.5 and a variety of chemicals. Several attempts have been made to reduce or prevent the pollution at source through in-process control measures.[7-16] This has gained importance in global leather industry. However, these improvements are specific to a unit operation. Implementation of all the advanced technologies and eco-friendly chemicals involves financial input and machinery requirements as well. This calls for the development of integrated leather processing methods for pollution reduction.

Very few attempts have been made to integrate the whole or part of leather processing steps for water and pollution reductions.[17-20] Recently, integrated one-step wet finishing and one-step tanning and post tanning processes have been developed.[21-24] Further, reversed leather process for making upper leathers from goatskins and glove leathers from hair sheepskins has been developed.[25-27] Reverse leather process uses the pH condition of the delimed/bated pelt, which is 7.5-8.0, for the application of post tanning chemicals, because the pelt is partially anionic in nature. After the penetration of post tanning auxiliaries, pH of the pelt decreased to a level of 3.0-3.2. At this stage, the tanning is performed using basic chromium sulfate. The final pH of leather is adjusted to 3.8-4.0 using sodium bicarbonate. A schematic representation for the comparison of process steps of conventional and modified leather process is shown in Figure 1. The detailed mechanism of the process has already been reported.[26]

Although the reverse process was possible on skins, it is necessary to investigate the application of this process on cowhides due to its high thickness. In this study, the reverse leather processing sequence has been applied for making upper leathers from cowhides. The pH of the chrome tanning in the reverse process has been chosen as 3.0-3.2, instead of 5.0-5.2 for complete penetration of chromium in thick hides. The percentage offer of post tanning chemicals for the modified process has been determined by evolving a relationship between pelt and split tanned weight. Material balance for chemicals and water has been carried out for both the conventional and modified leather processes. The pollution parameters such as COD and

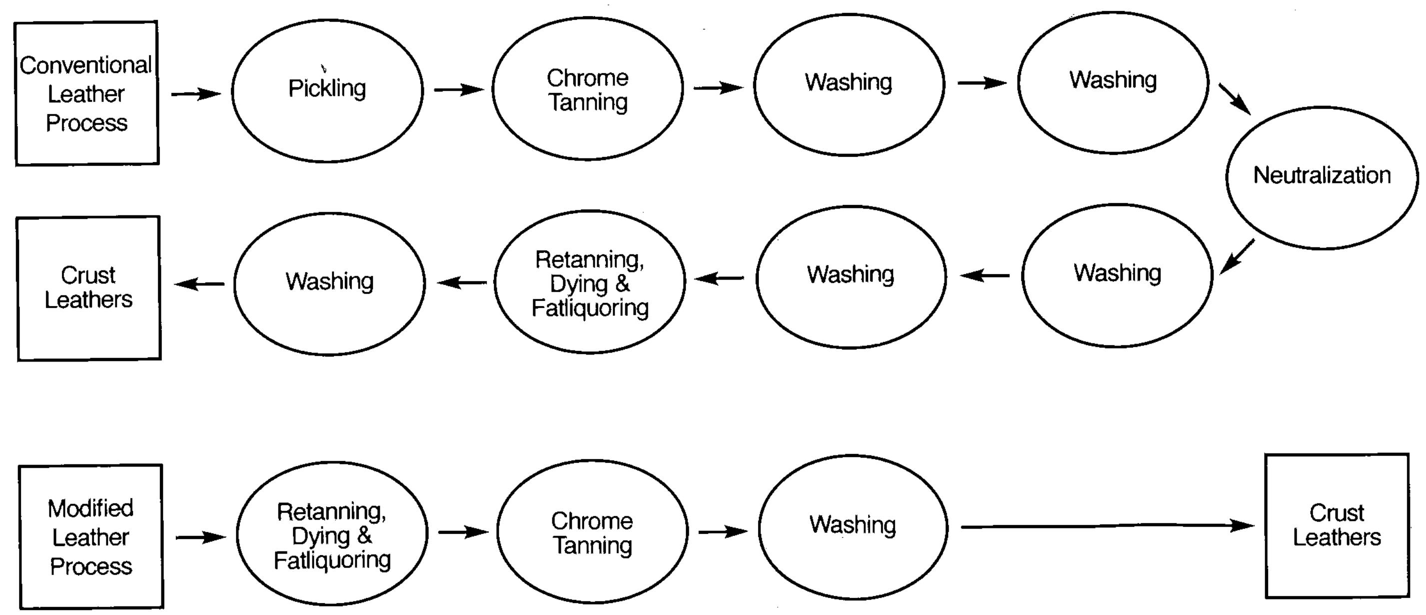


Figure 1: Schematic representation of conventional *Vs* modified process.

* Author for correspondence - Email: clrichem@mailcity.com, chemlab@clrim.org
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## Conventional Leather Process (C)
## (Ten delimed/bated cow sides were used; Pelt weight - 75 kg; % based on pelt weight)

| Process/chemicals | % | Duration | Remarks |
|---|---|---|---|
| **Pickling** | | | |
| Water | 100 | | |
| Sodium chloride | 10 | 10 min | |
| Formic acid | 0.5 | | |
| Water for dilution | 10 | 30 min | |
| Sulfuric acid | 1 | | |
| Water for dilution | 10 | 3 x 15 min + 4h | The pH of the cross section of the pelt was found to be 3.0. 50% bath was drained. |
| **Chrome tanning** | | | |
| Basic chromium sulfate | 8 | 3h | |
| Water | 50 | 2h | |
| Sodium formate | 1 | | |
| Sodium bicarbonate | 1 | | |
| Water for dilution | 10 | 3 x 10 min + 3h | The pH of the cross section of the tanned leathers was found to be 3.8. Bath was drained. |
| **Washing** | | | |
| Water | 200 | 10 min | Bath was drained. |

The leathers were piled for 24 h. The leathers were then sammed, split and shaved to a uniform thickness (1.1±0.1mm). The weight of the leathers was noted and termed as shaved weight. Rechroming was not done. Percentages of the following chemicals were based on shaved weight.

| Process/chemicals | % | Duration | Remarks |
|---|---|---|---|
| **Post-tanning** | | | |
| **Washing** | | | |
| Water | 200 | 10 min | Bath was drained. |
| **Neutralization** | | | |
| Water | 100 | | |
| Sodium formate | 1 | | |
| Sodium bicarbonate | 1 | | |
| Water for dilution | 10 | 3 x 10 min + 2.5h | pH was found to be 5.0-5.2. |
| Acrylic syntan | 2 | 45 min | Bath was drained. |
| **Washing I** | | | |
| Water | 200 | 10 min | Bath was drained. |
| **Washing II** | | | |
| Water | 200 | 10 min | Bath was drained. |
| **Retanning, dyeing and fatliquoring** | | | |
| Water | 100 | | |
| Phenolic syntan | 3 | 60 min | |
| Phenolic syntan | 2 | 30 min | |
| Natural oil based fatliquor | 2 | 30 min | Fatliquor was emulsified using 10% hot water at 60°C |
| Urea-melamine based syntan | 4 | 45 min | |
| Acid black dye | 3 | 45 min | The complete penetration of dye was checked. |
| Urea-melamine based syntan | 2 | 30 min | |
| Synthetic fatliquor | 2 | | |
| Semi-synthetic fatliquor | 2 | | |
| Natural oil based fatliquor | 3 | 120 min | Fatliquors were emulsified using 10% hot water at 60°C |





| Process/chemicals | % | Duration | Remarks |
|---|---|---|---|
| Phenolic syntan | 2 | 45 min | |
| **Fixing** | | | |
| Formic acid | 2 | | |
| Water for dilution | 20 | 3 x 10 min + 2h | Bath was drained. |
| **Washing** | | | |
| Water | 200 | 10 min | Bath was drained. |

The leathers were set and hooked for drying. The dried leathers were conditioned, staked, trimmed and toggled.

## Modified Leather Process (E)
## (Ten delimed/bated cow sides were used; Pelt weight - 78 kg; % based on pelt weight)

| Process/chemicals | % | Duration | Remarks |
|---|---|---|---|
| Water | 50 | | |
| Acrylic syntan | 0.7 | 30 min | |
| Phenolic syntan | 1.05 | 60 min | |
| Phenolic syntan | 0.7 | 30 min | |
| Natural oil based fatliquor | 0.7 | 30 min | Fatliquor was emulsified using 10% hot water at 60°C |
| Urea-melamine based syntan | 1.4 | 45 min | |
| Acid black dye | 1.05 | 45 min | The complete penetration of dye was checked. |
| Urea-melamine based syntan | 0.7 | 30 min | |
| Synthetic fatliquor | 0.7 | | |
| Semi-synthetic fatliquor | 0.7 | | |
| Natural oil based fatliquor | 1.05 | 120 min | Fatliquors were emulsified using 10% hot water at 60°C |
| Phenolic syntan | 0.7 | 45 min | |
| Formic acid | 1.0 | | |
| Water for dilution | 10 | 3 x 10 min + 90 min | The pH of the cross section of the matrix was found to be 3.0-3.2. |
| Basic chromium sulfate | 8.0 | 4 h | |
| Sodium bicarbonate | 1.0 | | |
| Water for dilution | 10 | 3 x 10 min + 2 h | The pH of the cross section of the leather was found to be 3.8-4.0. |
| **Washing** | | | |
| Water | 200 | 10 min | Bath was drained. |

The leathers were sammed, split to 1.2 mm, set and hooked for drying.
The dried leathers were conditioned, staked, dry shaved to a uniform thickness (1.1 mm), trimmed and toggled.

TS loads have been quantified and analyzed. The performance of the final leathers has been evaluated in terms of physical as well as organoleptic properties. Softness of the leathers has been quantified and compared with conventionally processed leathers. Scanning electron microscopic analysis has been carried out for crust leathers. Techno-economic viability of the modified process has also been discussed.

## EXPERIMENTAL MENTHODS

### Materials

Conventionally delimed/bated cow sides were chosen as the raw material. The chemicals employed for leather processing were of commercial grade. The chemicals used for analytical techniques were of reagent grade.

### Relation Between Pelt and Shaved/Split Weight: For Post Tanning Chemicals Offer

Post tanning chemicals are offered based on shaved weight of chrome tanned leathers. However, the modified leather processing involves application of post tanning chemicals on delimed pelt. Hence, it is necessary to establish the relation between pelt and shaved weight. Fifteen fleshed cow pelts of different weight ranges were taken; weight of each pelt was noted and conventionally processed into chrome tanned leathers. The tanned leathers

**TABLE I**
**Comparison of Layer-Wise Distribution of Chromium Content and Shrinkage Temperature of Leathers and Percentage Exhaustion of Chromium from Conventional (C) and Modified (E) Processes**

| Sample | % $Cr_2O_3$ [b] (dry weight basis[a]) Grain | Middle | Flesh | % Uptake of chromium[b] | Ts°C |
|---|---|---|---|---|---|
| C | 3.73±0.02 | 3.65±0.04 | 3.75±0.02 | 71±2 | >120 |
| E | 3.90±0.04 | 3.87±0.02 | 3.91±0.02 | 87±2 | >120 |

[a] Moisture free tanned leather weight
[b] Average of three measurements

**TABLE II**
**Comparison of Oil and Fats, Water Soluble and Inorganic Ash Content in Leathers from Control and Modified Process[a]**

| Parameters | Control | Experimental |
|---|---|---|
| % oils and fats[b] | 5.12±0.2 | 4.98±0.1 |
| % water soluble[b] | 5.25±0.1 | 2.52±0.1 |
| % total ash[b] | 3.72±0.1 | 3.12±0.1 |

[a] Moisture free crust leather weight
[b] Average of three measurements

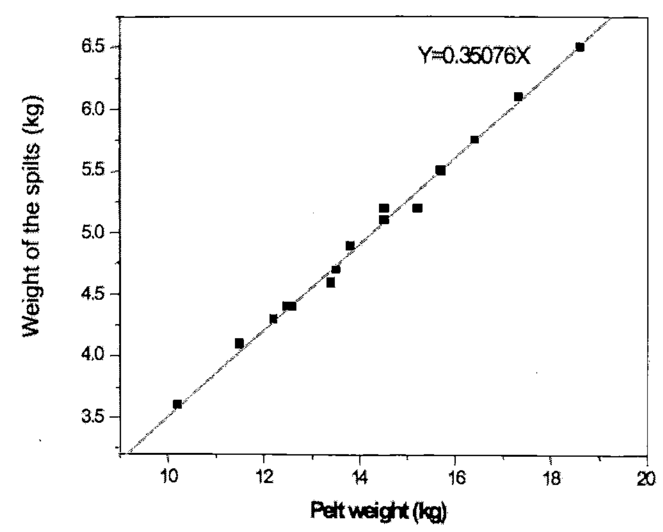


Figure 2: Plot of pelt weight *Vs* splits weight

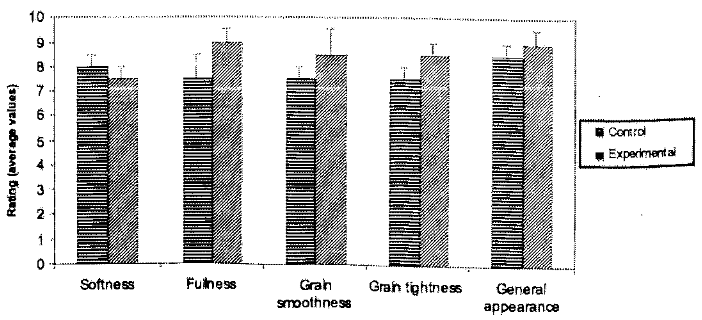


Figure 3: Evaluation of organoleptic properties of crust leathers obtained from control (C) and experimental (E) process

were split to 1.2 mm and shaved to uniform thickness of 1.1 mm. The shaved weight of grain split and bottom split weight (flesh split) of the each tanned leathers were noted. The ratio of the sum of the two tanned weights to the delimed/bated pelt weight would be used to determine the percentage offer of post tanning chemicals for the modified process.

### Process Details

In this study, delimed/bated cow sides were chosen as the starting material for conventional and modified leather process. Twenty matched pair delimed/bated cow sides were converted into shoe upper leathers through conventional and modified process in stainless steel drum with the size of 140x60 cm.

### Material Balance Analysis

A comprehensive material balance for the water and chemicals and other reaction products was carried out for the conventional and modified leather processes excluding soaking, liming and deliming. The material balance for the acid and alkali was not calculated because they remain in the effluent in the form of reaction products. Similarly, auditing for post tanning chemicals such as syntans, dye and fatliquors were not carried out as they are principally fixed to the matrix and it is difficult to analyze them in a mixed form. The amount of chromium in the wastewater from chrome tanning was analyzed as per the standard procedure[28].

### Stratigraphic Chrome Distribution Analysis

Samples from the official sampling position[29] of control and experimental wet blue leathers were split into three uniform layers using a Camoga splitting machine and analyzed for layer wise chromium content. A known weight (~1g) of the samples was taken and the amount of chromium was estimated as per standard procedure.[30] Samples were initially analyzed for moisture content[31] and chrome content was expressed on dry weight basis of leather. The shrinkage temperature of the leathers was measured using a Theis shrinkage tester.[32]

### Characterization of Crust Leathers

A known weight (~5g) of the samples from the official butt position of control and experimental crust leathers was taken.[29] Samples were estimated for oils and fats, water solubles and total inorganic ash as per the standard procedures.[33-35] Samples were initially analyzed for moisture content[31] and all the values were expressed on dry weight basis of crust leather.





**TABLE III**
**Physical Strength Data of Control (C) and Experimental (E) Leathers**

| Sample | Tensile strength ($kg/cm^2$) Average value[a] | % elongation at break Average value[a] | Tear strength (kg/cm) Average value[a] | Grain crack strength (average value[b]) Load (kg) | Distension (mm) |
|---|---|---|---|---|---|
| C | 258±6 | 63±2 | 38±2 | 42±1 | 9.2±0.4 |
| E | 282±4 | 68±2 | 42±4 | 55±2 | 10.2±0.2 |

[a] Average of mean of five measurements of along and across backbone values
[b] Average of five measurements of load and distension values

**TABLE IV**
**Comparison of Water Consumption and Discharge for Conventional (C) and Modified (E) Leather Process for Processing of 1 Kg Raw Cow Hides[a]**

| Unit processes | C Input (L) | C Output (L) | E Input (L) | E Output (L) |
|---|---|---|---|---|
| Pickling | 1.000 | 0.500 | - | - |
| Chrome tanning/modified process | 0.500 | 0.980 | 0.500 | 0.400 |
| Washing | 2.000 | 1.980 | 2.000 | 1.980 |
| Washing | 0.700 | 0.400 | | |
| Neutralization | 0.350 | 0.340 | | |
| Washing I | 0.700 | 0.690 | | |
| Washing II | 0.700 | 0.700 | | |
| Retanning, dyeing and fatliquoring | 0.350 | 0.340 | | |
| Washing | 0.700 | 0.690 | | |
| Dilution of acids/alkalis and emulsification of fatliquors | 0.436 | 0.384 | 0.300 | 0.285 |
| Total | 7.436 | 7.004 | 2.800 | 2.665 |

[a] weight of hides before soaking; water audit was not made from soaking to deliming because they were constant for both conventional and modified process.

### Quantitative Assessment of Softness

Softness of the leather can be quantified based on their Young's modulus and initial strain energy at 10% initial strain.[36,37] Specimens for tensile test were cut from butt and belly regions of the one matched pair leather at different angles (30, 45, 90 and 180° angle to the backbone).[38] Totally, eight specimens were used for the determination of softness. Before testing, the specimens were conditioned at 80± 4°F and 65±2% relative humidity over a period of 48 h. An Instron Universal Tensile Tester, Model 4501 was used for the measurements. The strain rate (crosshead speed) was set at 100 mm/min. The stress and strain values of all the specimen were measured. Based on these values Young's modulus and initial strain energy were calculated.[36]

### Physical Testing and Hand Evaluation of Leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method.[39] Specimens were conditioned at 80±4°F and 65±2% relative humidity over a period of 48 h. Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures.[38,40,41] Crust leathers from control as well as experiment were assessed for softness, fullness, grain tightness, grain smoothness and general appearance by hand examination. The leathers were rated on a scale of 0-10 points for each functional property by two experienced tanners, where higher points indicate better property.

### Analysis of Chromium in Spent Liquors

Chrome liquor collected from the control chrome tanning process was analyzed for chromium content as per the standard procedure.[28] In the case of modified leather process, the final liquor was collected and used for the chromium analysis. Finally, the uptake of the chromium was calculated based on the amount of chromium present in the spent liquor and the amount chromium offered for processing.

### Analysis of Composite Waste Liquor

Composite liquors from control and experimental processes were collected from all the unit processes except pre-tanning

**TABLE V**
**Emission Loads of Control (C) and Experimental (E) Processes**

| Process | COD (ppm)[b] | TS(ppm)[b] | Volume of effluent (L/metric ton of raw hides[c]) | Emission load (kg/metric ton of raw hides[c] processed) COD | TS |
|---|---|---|---|---|---|
| Control | 4390±12 | 24996±32 | 7004 | 30.7 | 175 |
| Experimental | 5852±8 | 19864±24 | 2665 | 15.6 | 53 |

[a] Composite liquors were collected from all the unit operations expect from soaking and liming
[b] Average of three measurements
[c] Weight of cow hides before soaking

processes (soaking to deliming) and analyzed for COD and TS (dried at 103-105°C for 1 h) as per the standard procedures.[42] From this, emission loads were calculated by multiplying concentration (mg/L) with volume of effluent (L) per metric ton of raw hides processed.

### Scanning Electron Microscopic Analysis

Samples from the control (C) and experimental (E) crust leathers were cut from the official sampling position.[39] The crust leather samples from both experimental and control process with uniform thickness were directly taken for analysis without any pre-treatment. All specimens were then coated with gold using Edwards E306 sputter coater. Quanta 200 series scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at high vacuum and an accelerating voltage of 12 KV with different magnification levels.

## Results and Discussion

### Relation between Pelt and Split Weight to Determine the Percentage Offer of Post tanning Chemicals for Modified Leather Process

The pelt weight of various weight ranges of cowhides is plotted against the weight of the leathers after splitting (sum of weight of shaved grain split and flesh split) as shown in Figure 2. It exhibits a liner fit passing through zero. The corresponding equation of the line was obtained and given in eq. (1). The shaved weight of the hides can be calculated from the desired equation, Y=0.35076X, by substituting 'X' value as pelt weight of the hides. In other words, the percentage offer of post tanning chemicals for modified leather process can be determined by substituting 'X' value with the percentage offer of post tanning chemicals for conventional leather process.

### Chromium in Leather and Spent Tan Liquor

The amount of chromium present in the leather at layer wise and spent tan liquor has been analyzed to assess the chromium distribution and uptake behavior of the modified leather process. The amount of distribution of chromium present in the leathers at layer-wise is given in Table I. It is seen that the leathers from control and modified process exhibit uniform chromium distribution along the entire cross section. The leathers from modified process possess higher amount of chromium compared to the control leathers in all the three layers. This may be due to the presence of organic materials during the chrome tanning process. It is seen that the uptake of chromium is slightly increased in the modified process compared to the conventional process. This is in accordance with the trend observed in the chrome content of the leathers. The shrinkage temperature of leathers from both control and modified processes is more than 120°C.

### Chemical Characteristics of Leathers

It is important to characterize the leathers from modified process in comparison to the conventional process due to the reduction in the number of process steps, water and chemical usage. The amount of oil and fats, water solubles and ash content in control and experimental leathers is given in Table II. The percentage oils and fats present in the leathers obtained from modified process is comparable to the conventionally processed leathers. It indicates that the conversion factor used to calculate the offer of the fatliquor, post tanning chemicals in general, based on the pelt weight is technically valid compared to the offer of fatliquor on shaved weight. Further, the modified process involves post tanning followed by tanning in a single step thereby avoids several washing steps. Hence, there is a possibility of presence of more water solubles materials in the leather. Table II shows that the modified process possess lower amount of water solubles compared to conventionally processed leathers.

### Physical Characteristics and Hand Evaluation of Leathers

The average strength values of five leathers each from conventional and modified process are given in Table III along with standard deviation. It is seen that the strength properties of the leathers obtained from the modified process are better compared to conventionally processed leathers. The average of the rating for the five leathers from control and experiment, evaluated by two independent tanners, were calculated for each bulk property and given in Figure 3 along with standard error. Fullness, grain smoothness and grain tightness of the leathers from modified process are better than the conventionally processed leathers. This may be due to the improved uptake of post tanning and tanning chemicals. Softness and general appearance of the leathers from modified process are comparable to the conventionally processed leathers.





**TABLE VI**
**Material Audit for Control and Experimental Process for Processing 1 Metric Ton of Raw Cow Hides[a]**

| Process | Chemicals | Control Input (kg) | Control Output (kg) | Experimental Input (kg) | Experimental Output (kg) |
|---|---|---|---|---|---|
| Pickling/retanning dyeing and fatliquoring | Water | 1000 | 500 | 500 | 400 |
| | Syntan | - | - | 49 | N.E |
| | Dye | - | - | 10.5 | N.E |
| | Fatliquor | - | - | 31.5 | N.E |
| | Formic acid | 5 | R.P | 10 | R.P |
| | Salt | 100 | R.P | - | - |
| | $H_2SO_4$ | 10 | R.P | - | - |
| | Water for dilution | 200 | 190 | 200 | 190 |
| Chrome tanning | Water | 500 | 980 | - | - |
| | Basic chromium sulfate[b] (BCS) | 80 | 31.2 | 80 | 29.5 |
| | Sodium formate | 10 | R.P | - | - |
| | Sodium bicarbonate | 15 | R.P | 10 | R.P |
| | Water for dilution | 100 | 95 | 100 | 95 |
| Washing | Water | 2000 | 1980 | 2000 | 1980 |
| Post tanning | Shaved leathers and tanned splits | 350 | N.E | - | - |
| Washing | Water | 700 | 400 | - | - |
| Neutralization | Water | 350 | 340 | - | - |
| | Sodium formate | 3.5 | R.P | - | - |
| | Sodium bicarbonate | 3.5 | R.P | - | - |
| | Water for dilution | 35 | 33 | - | - |
| | Acrylic syntan | 7 | N.E | - | - |
| Washing I | Water | 700 | 690 | - | - |
| Washing II | Water | 700 | 700 | - | - |
| Retanning, dyeing and fatliquoring | Water | 350 | 340 | - | - |
| | Syntan | 42 | N.E | - | - |
| | Dye | 10.5 | N.E | - | - |
| | Fatliquor | 31.5 | N.E | - | - |
| | Water for dilution | 35 | 33 | - | - |
| Fixing | Formic acid | 7 | R.P | - | - |
| | Water for dilution | 35 | 33 | - | - |
| Washing | Water | 700 | 690 | - | - |

[a] Raw weight of hides
[b] BCS contains 35% sodium sulfate salt, which is included in the output of BCS
R.P = reaction product; N.E = not estimated

### Scanning Electron Microscopic Analysis

The scanning electron micrographs of crust leather samples from conventional and modified processes showing the grain surface at a magnification of x80 are given in Figures 4a and 4b. There is no change in the surface characteristics of experimental sample compared to control sample. In other words, reversing the order of conventional process does not lead to any change in the grain characteristics of leathers. Scanning electron micrographs of crust leather samples showing the cross section at a magnification (x100) are given in Figs. 5a and 5b. The orientation of fibers is uniform and regular in the experimental sample compared to the control sample. Further, it is interesting to note that the experimental sample exhibits a well-ordered and compact structure in especially between the grain layer and corium major junction. Further, the fiber structure of the experimental crust leather seems to be more compact and uniformly relaxed throughout the cross section compared to the control leather. This may be due to higher absorption of post tanning chemicals in general and synthetic tanning agent in particular by the untanned matrix (delimed pelt) compared to the tanned matrix. Higher magnification (x250) scanning electron micrographs (Figs. 5c and 5d) show a uniformly opened fiber structure in the experimental sample compared to the control sample.

### Softness Measurements

Softness can be quantitatively measured based on two physical quantities such as initial strain energy and Young's modulus at 10% initial strain as described by Liu *et al.*[36,37] Figure 6 shows a linear relationship between initial strain energy and Young's modulus for leathers obtained from both conventional and modified process. The each point on the graph (Figure 6) represents a single measurement. The correlation co-efficient (r2) for both the linear fits are found to be more than 0.998. Young's modulus generally represents the stiffness of the material. However, softness is a opposite property of stiffness, hence the lower the Young's modulus the higher the softness. Initial strain energy on the other hand represents the stiffness of the material on account of non-linear viscoelasticity of leather. Higher initial strain energy signifies the softness of the material. Control leathers show slightly lower Young's modulus and higher initial strain energy compared to the experimental leathers. This indicates that the softness of the leather from control process is slightly higher than that from modified process. This is in accordance with the results from hand evaluation (Figure 3). Further, it has been shown that the fiber structure of the experimental crust leather is more compact and rigid (Figure 5b). Hence, it is obvious that the experimental leather has slightly lower softness. In principle, the softness of leathers from experimental process can be slightly increased by reducing the compactness of the fiber structure. This can be achieved by reducing the offer of synthetic tanning agents.

### Exploitation of Water for Processing

Water use minimization in the leather processing assumes greater significance due to increasing wastewater treatment costs and decreasing availability of water. It is expected that the modified leather process would enable significant reduction in water usage since the process avoids several acidification, deacidification and washing steps. Hence, the water consumption and discharge audit for conventional and modified process has been carried out. The quantity of water consumption and discharge for processing 1 kg of cow hide pelt through conventional and modified process is given in Table IV. It is apparent that the modified process enjoys a reduction in water consumption and effluent discharge by 62% for processing 1 kg cowhide pelt. The leather processing with the recycle/optimization approach provides a saving in the amount of water used for only pre-tanning and tanning operations by 67%.[43] However, the

**TABLE VII**
**Time and Power Consumption for the Conventional (C) and Modified (E) Processes**

| Unit operations | Time (h) C | Time (h) E |
|---|---|---|
| Pickling | 5.16 | - |
| Chrome tanning/ modified process | 8.33 | 15.41 |
| Washing | 0.16 | 0.16 |
| Washing | 0.16 | - |
| Neutralization | 3.58 | - |
| Washing I | 0.16 | - |
| Washing II | 0.16 | - |
| Retanning, dyeing and fatliquoring | 6.75 | - |
| Fixing | 2.33 | - |
| Washing | 0.16 | - |
| Total | 26.95 | 15.57 |
| Total power consumption (KWh) | 808.5 | 467.1 |
| Cost (US$) | 80.8 | 46.7 |

@1 h running = 30 KWh; 1 KWh = US$ 0.1

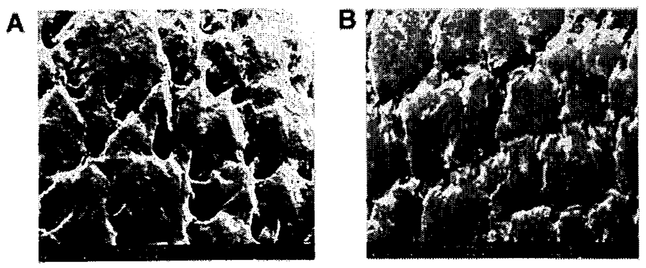


Figure 4: Scanning electron micrographs of crust leather samples showing the grain surface at x80 magnification
a) control and b) experiment

modified process reduces the water usage for processing pickling pelt to crust leather by 62% without employing recycle/reuse approach, which is a pioneering achievement. It has been reported that, by 2025 AD, 1.8 billion people will live in countries or regions with absolute water scarcity.[44] In this perspective, the modified process is able to reduce the water consumption remarkably.

### Environmental Benefits

The composite liquors were collected from all the unit processes except from soaking, liming and deliming. Two environmental parameters such as COD and TS have been chosen to analyze the environmental impact of the conventional and modified leather processes. A direct comparison of the observed COD and TS values may not give proper result on the environmental





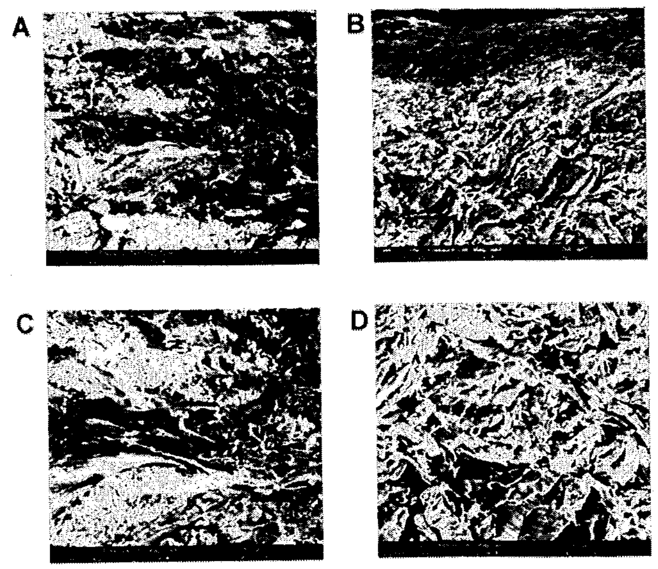


Figure 5: Scanning electron micrographs of crust leather samples showing the cross section at lower and higher magnifications
a) control (x100) b) experiment (x100)
c) control (x250) and d) experiment (x250)

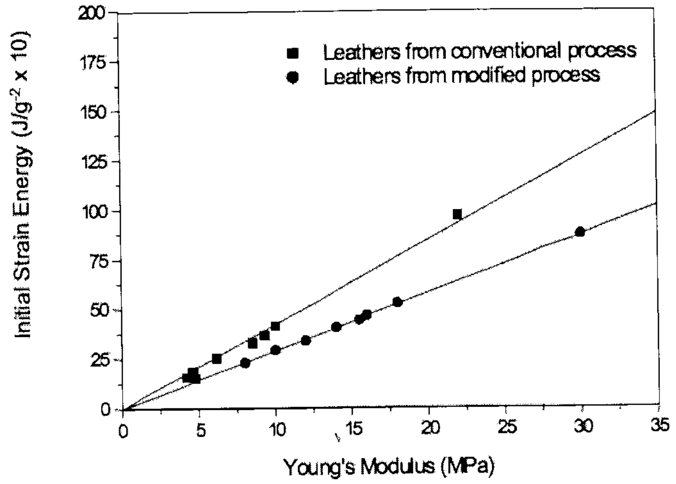


Figure 6: Plot of Young's modulus *Vs* initial strain energy

impact. Hence, these values have been converted into emission loads. The COD and TS values and the corresponding calculated emission loads are given in Table V. It is interesting to note that the concentration of TS is significantly lower in the effluent from modified process compared to the conventional process, in spite of the low volume of effluent generation. This is primarily due to the fact that the modified process avoids the several acidification-deacidification steps that are followed in the conventional leather processing. It is known that acidification-deacidification steps would lead to the formation of neutral salts that contribute to dissolved or total solids. It is seen that the COD value of the effluent from the modified process is higher than the conventional process. This is due to the presence of pollutants in significantly low amount of effluent. However, there is a significant reduction in the COD and TS parameters when they are converted into emission loads. The reduction in COD and TS loads are 49 and 70%, respectively. These reductions are not only due to the elimination of several processes but also due to the better uptake of chemicals such as chromium, syntans, dyes and fatliquors. It is intriguing to note that these reductions are possible without changing the process chemicals or using any specialty chemicals.

### Material Audit

The input-output audit in leather manufacture is to assess the efficiency of existing operations. The input and output of the chemicals and water has been monitored for the control and experimental process. The observed values have been calculated for processing 1 metric ton of cow hide pelts and are given in Table VI. Conventional process practices the pickling, which leads to chemical usage of 100 kg sodium chloride and 10 kg of sulfuric acid and subsequent discharge in the effluent. In the case of modified process, pickling process was completely eliminated from the conventional sequence. Further, the conventional process employs 32 and 7 kg of chemicals for deacidification (basification and neutralization) and acidification (fixing), respectively. However, the modified process employs 10 and 10 kg for acidification and deacidification, respectively. The chemicals used for the acidification and deacidification steps result in the formation of neutral salts in the discharged wastewater. Chrome tanning has been carried out for control after pickling and for experimental after post tanning. The chromium uptake for the control and experimental processes are 71 and 87% of the applied basic chromium sulfate. Basic chromium sulfate used in this study contains 14% chromium(III), 33-35% neutral salts, 5% moisture and remaining 45% water bound to the chromium complex. The amount of chromium, neutral salts discharged from conventional and modified processes are 3.24, 28 and 1.46, 28 kg, respectively. The quantity of syntans, dye and fatliquors employed for both the control and experimental processes are similar. The total amount of chemicals consumed for conventional and experimental leather processing is 325 and 191 kg, respectively. This means that the modified leather process enjoys a reduction in total chemical consumption by 41% compared to conventional leather processing. Of the total chemicals used, chromium and post tanning chemicals are predominantly fixed to the hide matrix and remaining chemicals are discharged into the wastewater. The control and experimental leather processing release about 185 and 50 kg materials, respectively (in to the effluent), which means a 73% reduction is possible.

### Techno-Economic Viability

Commercialization of any newly developed process in the industry generally demands the technical feasibility and cost effectiveness. In this work, modified leather process has been explored to achieve reductions in water, time, power as well as better quality of leather and effluent. It is already shown (Table IV) that the modified leather process enjoys a reduction in water consumption by 62% compared to the control process, which provides savings in water cost. This reduction in water consumption lowers the hydraulic load by 62%, thereby reduces the operating cost of ETP. The consumption of process time and power for the control and experimental processes is given in Table VII. Time consumption of the modified process (drumming time) is 42% lower than the control process. Further, there is also a significant reduction in the time lag between conventional chrome tanning and wet finishing, which is usually a minimum of 12 hours (overnight ageing). The reduction in the energy consumption for the modified process is about 42% compared to the control process, which leads to a saving of about US$ 34 for processing 1 metric ton of cow hide pelts. The total reduction in chemical consumption is about 41% for processing 1 metric ton of cow hide pelt through the experimental process. The chemical costing was not carried out for BCS, syntans, dyes and fatliquors because there is no change in the type and percentage offer of chemicals between the two processes. However, the modified process provides a considerable reduction in chemical cost by about US $15 for processing 1 metric ton of raw hides by avoiding acids and alkalis required for several acidification and deacidification processes. Hence, it is evident that there is a significant reduction in the consumption of water, time, energy and chemicals. This would provide an overall reduction in the cost of leather processing.

## Conclusion

The leather industry, world over, is glimpsing for the sustenance through newer leather processing methods. In this work, a modified leather processing method has been developed for making upper leathers from cowhides. The percentage offer of post tanning for modified process has been determined based on the pelt to shaved weight relationship. A significant increase in the chromium uptake and a uniform distribution of chromium in the leather are observed for the modified process. The chemical analysis of experimental leathers shows comparable amount of oils and fats, lower percentage of water solubles and ash in the leather, in relation to conventionally processed leathers. Softness measurements show that the experimental leathers have slightly lower softness and higher stiffness compared to the control leather. Leathers obtained from modified process possess better physical and comparable bulk properties to that of leathers from conventional process. Scanning electron micrograph reveals that leathers from modified process seem to be more compact and rigid compared to the conventionally processed leathers. More particularly, the water usage is reduced by nearly 62% for processing one metric ton of raw hides from delimed to crust stage, which is one of the pioneering achievements. Further, the modified process technique results in remarkable reduction in pollution loads such as COD and TS by 49 and 70%, respectively. Material audit study reveals that the modified process reduces the chemical consumption by 41% and eliminates the 73% discharge of chemicals into the wastewater. Techno-economic viability study shows that there is a considerable reduction in the cost of leather production and the process is commercially viable.

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