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Accelerated Liming Process Using Phase Transfer Catalyst
by
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Abstract
In the present work, effect of using phase transfer catalysts (PTC) was studied in liming and re-liming processes of goat skin, for decrease in the processing time, thereby increasing productivity. Three different Phase Transfer Catalysts; Tetramethylammonium Hydroxide (TMAH), Tetraethylammonium Hydroxide (TEAH) and Tetrabutylammonium Hydroxide (TBAH) were chosen and experiments were conducted on liming and re-liming of goat skin to select suitable catalyst in comparison with the conventional liming process. The monitoring parameters were ease of hair removal and increase in pelt weight to find the maximum swelling and plumping. After determining the optimal PTC amount, studies were also carried out on reuse of liquor containing PTC with replenishment. Use of TMAH in liming process was found to bring about significant time reduction and could bring improved swelling in liming and re-liming processes.

Introduction
Liming is an important unit operation in leather making where soaked hides/skins are treated with calcium hydroxide (Ca(OH)2) solution along with an unhairing agent, usually the sodium sulfide (Na2S). It is a slow process and depending upon the type of leathers made from skins/hides, the process time varies between 5 to 48 hours. Liming process is carried out in the pit/drum/paddle where interfibrillary soluble proteins and keratinous matter get removed in addition to opening up of fiber bundles. After the unhairing process, the hides/skins are treated with Ca(OH)2 solution to achieve required degree of swelling and also to facilitate flesh removal. This process is also time consuming and takes nearly 14 hours to 72 hours for completion.

Phase transfer catalysis was first applied to reactions involving a water-soluble nucleophilic reagent and an organic soluble electrophilic reagent.1 By using a PTC in a chemical reaction, one can achieve faster reactions and obtain higher conversions or yields. PTC is not only limited to systems with hydrophilic and hydrophobic reactants, it is also employed in liquid/solid and liquid/gas reactions. PTC has been widely used for the synthesis of organic compounds for many decades. PTC can also be used in the production of pharmaceuticals, agricultural chemicals, fine chemicals and other specialty chemicals.2-5 There are many types of PTCs, such as Quaternary Ammonium Salts and Phosphonium Salts, Crown Ethers, etc. Among these, the Quaternary Ammonium Salts are most widely used in the industry because of the low cost. Several research initiatives have been made in the past to speedup liming process and to minimize the toxic waste generation. A detailed literature survey reveals the following. A very rapid liming and subsequent tanning process was reported by treating hides with sodium sulfide solution by painting followed by treatment with sodium peroxide treatment and neutralization led to subsequent tanning of hides in short span of time.6 Another method of very rapid liming and subsequent tanning process without effluent by dipping in sodium sulfide solution for 4 min followed by treatment with 10% sodium peroxide solution for 1 hour.7 A continuous automatic beamhouse processing was reported by rapid soaking of brine cured hides and unhairing using 4-6% sodium sulphide solution for 10 minutes.8 A lime free unhairing system has been reported by using 3% caustic soda, 1% salt, 1% DMAS, 1-2% sodium sulfhydrate.9 Other reports include oxidative unhairing of leathers using hydrogen peroxide, amine, enzyme,10 sulphide free unhairing using ozone,11 oxidative unhairing with hydrogen peroxide,12 rapid oxidative unhairing using calcium peroxide to avoid using sodium sulphide in unhairing process.13 There are few reports for optimal chemicals and reuse of chemicals during the liming process. Dima W. Nazer et al.14 proposed modification of the method where the un-hairing-liming liquids were reused several times after being recharged by reduced quantities of chemicals. Thanikaivelan et al.15 studied an approach to apply the beam-house chemicals with optimal requirement.

In the present study, an attempt has been made to use PTC to transfer ions from liquid to solid phase during the liming process, to decrease the processing time. Three different PTC’s, TMAH, TBAH and TEAH were chosen and experiments on liming of goat skin were carried out to compare the effect of PTC in comparison with the conventional liming process.

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Manuscript received August 23, 2015, accepted for publication November 23, 2015.
Experimental

Materials
Wet salted skins were used for the studies. TMAH (10% Aqueous Solution), TBAH (10% Aqueous Solution) and Tetraethylammonium Hydroxide (25% Aqueous Solution) used were purchased from Lab chemicals supplier, Chennai. Other chemicals used are calcium hydroxide (LR), sodium sulphide (LR) were purchased from SD fine chemicals, Mumbai, India.

Method
The wet salted goat skins were washed once with 300% water (on the weight of the skins) to remove the salt, blood stains, dirt etc. and soaked overnight in 300% water. The weight of the skin after soaking was chosen as basis for chemical addition. The skins were treated with 100% water, 10% lime, 2% sodium sulphide. The above process method is referred here as a conventional liming process. In PTC aided liming process the PTCs of required amount was added to the lime liquor containing 100% water, 10% lime, 2% sodium sulfate. The hair removal ability and increase in weight of limed skin was measured periodically with time to identify the one showing maximum swelling and plumping in comparison to conventional process.

Liming of Goat Skin Using Three Different Phase Transfer Catalysts
All experiments were repeated for thrice to check the reproducibility. A set of four soaked goat skin samples weighing about 500 g were taken in separate plastic trays. In all the four experiments 10% of lime, 100% of water and 2% of sodium sulphide was used. Three different PTCs TMAH, TEAH, TBAH were added to an extent of 2.5% to three samples and the fourth one was a conventional liming process without PTC. The solution was applied uniformly all over the skin and the skins are placed in the solution. The hair removal ability was checked for every one hour and the weight gain after each hour was measured for a period of 5 hours and percentage weight increase was calculated. Among the three PTCs based on their performance, TMAH was chosen and further experiments were conducted with TMAH only.

Optimization of Amount of TMAH Required for Liming Process
A set of four samples was taken and each was separately treated with 10% lime, 100% water and 2% sodium sulphide. In three samples different quantities of TMAH added (0.75, 1.0, 1.25) and the fourth one was a conventional liming process without TMAH. Experiments were conducted in the same manner as mentioned above and repeated thrice to check reproducibility. The hair removal ability was checked for every one hour and the weight gain after each hour was recorded for a period of 5 hours.

Reusing of Lime Liquor with Additional TMAH Replenishment
A total of two samples were taken in separately. In one sample, the lime liquor of 1% TMAH aided liming process from previous process was taken and 0.5% of TMAH was added. Additionally, 3% lime, 1.5% sulphide and 100% water was added. The sample 2 is a conventional process using 10% of lime, 100% water and 2%sodium sulphide were used. The hair removal ability was checked for every one hour and the weight gain after each hour was recorded for 5 hours.

Figure 1. Flow chart showing conventional and PTC aided liming process for reuse.
The above procedure was repeated for one more subsequent batch of water soaked goat skins to study the reusability of used lime liquor containing PTC with the additional make up of 0.5% TMAH. The experimental details are schematically shown as flow chart in Figure 1.

### The Effect of TMAH in Re-liming of Goat Skin

In order to study the effect of TMAH in re-liming process, a similar procedure was adopted as mentioned above, but using 200% water, 5% lime along with 0.5, 0.75, 1.0% TMAH and increase in weight was checked for every one hour for 7 hours. For comparison purpose a parallel experiment was conducted without the addition of TMAH.

### Reusing of Relime Liquor with Additional TMAH Replenishment

After establishing optimum quantity for re-liming process, in order to study the reusability of used relime liquor containing PTC, sets of two samples were taken in separately. In one sample, the lime liquor of 0.75% TMAH aided re-liming process from previous process was used and 0.5% of TMAH was added and additionally 2% lime, required amount of water was added to make 200% water. The sample 2 is a conventional process using 5% of Lime, required amount of water to make 200% Water. The weight gains after each hour and recorded for a period of 5 hours.

The above procedure was repeated for one more batch of limed goat skins to study the reusability of used relime liquor containing PTC, lime 2%, and required amount water to make up to 200% float. The details are also shown in Figure 1.

Then the limed skins were processed into full chrome goat upper leathers as per the standard process given in Appendix 1. Both control and PTC aided limed leathers were converted into chrome tanned crust leathers. They were tested for different physical and chemical analysis, and the organoleptic properties were evaluated by experts.

### Results and Discussion

Lime has the functional (OH) - Hydroxyl group. Since this being one of the groups in the reaction, specific PTC that has OH group for compatibility was chosen. Hence these three PTCs of Quaternary Ammonium salts, having the anion OH group were selected for this work.

It was found that PTC has considerable effect in the liming process in reducing process duration. It was found that not all the PTCs have the ability to reduce the liming time as shown in Figure 2.

**Figure 2.** Effect of time in increase in weight of limed goat skin for different phase transfer catalyst.

Among three PTCs, the TMAH produced better hair removal and swelling than other PTCs and conventional process as shown in Figure 1. Hair removal was achieved in 2 hours with TMAH and 3 hours in case of TEAH, TBAH aided liming processes. For conventional process it took 5 hours for hair removal. Application of PTC in the liming process results up to 60% time reduction for liming process. The flesh was removed easily in PTC aided liming process than the conventional liming process.

**Figure 3.** Effect of amount of TMAH on increase in weight of limed goat skin.

Figure 3 shows 1% and 1.25% PTC aided liming process gives almost equal hair removal ability and swelling. Hair removal was achieved in 2 hours. 0.75% PTC aided liming process achieved hair removal in 3 hours and in conventional liming process hair removal achieved in 5 hours. The flesh was removed easily in the PTC aided liming process.
First time reusing the lime liquor of the optimum amount of PTC aided the liming process with 0.5% PTC replenishment produced comparable results as the fresh optimum amount of PTC aided liming process and the results are shown in Figure 4. Hair removal achieved in 2 hours.

Second time reusing the lime liquor of the optimum amount of PTC aided the liming process with 0.5% PTC makeup produced similar results as the fresh optimum amount of PTC aided liming process. Hair removal was achieved in 2 hours. The reuse of PTC containing lime liquor reduced the amount of PTC required for each recycle process. For a set of three processes the TMAH used per process was reduced to 0.66% on soaked weight.

The TMAH assisted re-liming process gives better swelling than conventional re-liming process as shown in Figure 5. Application of PTC in the re-liming process results in more than 85% reduction of time needed for re-liming. The 0.75% of TMAH applied re-liming process provides better swelling than 0.5% and comparable swelling to 1% TMAH aided re-liming process. In the TMAH aided re-liming process, the flesh was easily removed than the conventional re-liming process.

First time reusing the relime liquor of optimum amount of PTC aided re-liming process with 0.5% PTC replenishment gives equal results as the fresh optimum amount of PTC aided re-liming process. It reduces the process time more than 85%. The results are shown in Figure 6.

Second time reusing the relime liquor of optimum amount of PTC aided re-liming process with 0.5% PTC makeup gives equal results as the fresh optimum amount of PTC aided re-liming process. The reuse of PTC relime liquor reduced the amount of PTC required for each process. For a set of three re-liming processes the TMAH used per process is reduced to 0.583% on soaked weight.

The effect of TMAH was also studied for re-liming process and TMAH had a similar effect. Studies on reuse of used lime liquor and re-lime liquor containing PTC with 0.5% of additional PTC make up shows that the used lime liquor can be used twice to have identical re-liming effect.

Chrome tanned crust leathers were tested for different physical and chemical analysis and the results are given in Table I. Results show that TMAH aided limed leathers has comparable properties as control leather is an additional proof that there is no adverse effect on the use of PTC during the liming process.
Average Value of Three Experiments
Table II shows the organoleptic properties of tanned leathers and the results reveal that control and experimental leathers possess similar characteristics.

Average Value of Three Evaluations
This study clearly shows that the liming and re-liming process time can be significantly reduced by employing TMAH, thereby leading to increased productivity without affecting the final leather quality.

<table>
<thead>
<tr>
<th>Table I</th>
<th>Physical and Chemical analysis of chrome tanned crust leather produced from conventional and TMAH aided liming process.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chrome content, % Cr₂O₃</td>
</tr>
<tr>
<td>Control</td>
<td>3.11±0.1</td>
</tr>
<tr>
<td>TMAH aided Liming</td>
<td>3.05±0.1</td>
</tr>
</tbody>
</table>

Average value of three experiments

<table>
<thead>
<tr>
<th>Table II</th>
<th>Organoleptic properties of chrome tanned crust leather produced from conventional and PTC aided liming process.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Softness</td>
</tr>
<tr>
<td>Control</td>
<td>6±1</td>
</tr>
<tr>
<td>TMAH aided Liming</td>
<td>7±1</td>
</tr>
</tbody>
</table>

0- poor, 10-Excellent

Average value of three evaluations

Conclusions
Preliminary experiment on use of PTC in the liming process of goat skin in comparison with conventional liming process reveals that PTC has considerable effect on unhairing and swelling during the liming process in reducing process duration. Among three catalysts the TMAH performs better. The conventional liming process took 5 hours for hair removal whereas TMAH aided liming process required just 2 hours and giving maximum weight gain due to swelling than the conventional liming process.

Similarly, studies carried out in re-liming process of goat skin showed that application of PTC in re-liming process results in more than 50% increase in swelling compared to conventional re-liming process. This study clearly shows that the liming and re-liming process time can be significantly reduced by employing Tetramethyammonium Hydroxide as a Phase Transfer Catalyst.

References


### Appendix

**Process description for processing cured goat skins into leather.**

<table>
<thead>
<tr>
<th>Process</th>
<th>Quantity</th>
<th>Product</th>
<th>Duration</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soaking I</td>
<td>300%</td>
<td>Water</td>
<td>30min</td>
<td></td>
</tr>
<tr>
<td>Soaking II</td>
<td>300%</td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1%</td>
<td>Preservative</td>
<td>Left overnight</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5%</td>
<td>Wetting agent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Next day washing</td>
<td>200%</td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liming</td>
<td></td>
<td></td>
<td></td>
<td>Process details given in experimental section</td>
</tr>
<tr>
<td>Reliming</td>
<td></td>
<td></td>
<td></td>
<td>Process details given in experimental section</td>
</tr>
<tr>
<td>Washing</td>
<td>200%</td>
<td>Water</td>
<td>10 min</td>
<td></td>
</tr>
<tr>
<td>Deliming</td>
<td>150%</td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>Ammonium chloride</td>
<td>Run for 1 h</td>
<td>Washed and drained pH 8-8.5</td>
</tr>
<tr>
<td></td>
<td>0.75%</td>
<td>Bating agent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Washing</td>
<td>100%</td>
<td>Water</td>
<td>10 min</td>
<td></td>
</tr>
<tr>
<td>Pickling</td>
<td>80%</td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8%</td>
<td>Sodium chloride</td>
<td>Run for 15 min</td>
<td>pH 2.8-3</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>Formic acid</td>
<td>3 x 10 min, Run for 10 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75%</td>
<td>Sulphuric acid</td>
<td>4 x 15 min, Run for 1 h</td>
<td></td>
</tr>
<tr>
<td>Next day the pelts drummed for 30 min pH at cross section adjusted to 2.8-3.0. Then 50% of pickle bath drained.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chrome tanning</td>
<td>8%</td>
<td>Basic chromium sulphate (BCS)</td>
<td>2 x 30 min</td>
<td>Check for penetration in cross section</td>
</tr>
<tr>
<td></td>
<td>1.0%</td>
<td>Sodium formate</td>
<td>10 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>Sodium bicarbonate</td>
<td>3 x 20 min, run for 1 h</td>
<td>Check the pH to be 3.8 to 4. Drain the bath and pile overnight.</td>
</tr>
</tbody>
</table>

Appendix continued on following page.
Appendix continued.

Next day sammed and shaved to 1.0 mm.

<table>
<thead>
<tr>
<th></th>
<th>Washing</th>
<th>Neutralization</th>
<th>Retanning and Fatliquoring</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200%</td>
<td>Water</td>
<td>10 min</td>
</tr>
<tr>
<td>Neutralization</td>
<td>150%</td>
<td>Water</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>0.5%</td>
<td>Sodium formate</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>0.5%</td>
<td>Sodium bicarbonate</td>
<td>3 x 15 min + 1 h</td>
</tr>
<tr>
<td>Washing</td>
<td>100%</td>
<td>Water</td>
<td>10 min</td>
</tr>
<tr>
<td>Retanning and Fatliquoring</td>
<td>100%</td>
<td>Water</td>
<td>pH 3.5</td>
</tr>
<tr>
<td></td>
<td>9%</td>
<td>Fatliquor</td>
<td>1 h</td>
</tr>
<tr>
<td></td>
<td>8%</td>
<td>Syntan</td>
<td>1 h</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>Formic acid</td>
<td>3 x 5 min + 40 min</td>
</tr>
</tbody>
</table>

Finally leathers were dried and then conditioned for testing and evaluation.
Looseness describes a structural fault in leather, which leads to the development of wrinkles on the surface when the leather is bent inwards. It causes up to 7% of hides processed to finished leather to be downgraded or rejected at final inspection, requiring replacement and causing delay in meeting orders. Fillers can fill the interstitial spaces in loose leathers and make the looseness less pronounced. Here, the effect of Cloisite Na+, a nanoclay filler, on loose cattle hides is investigated by electron microscopy and mechanical characterization. Whilst SEM studies show an apparent filling effect in the grain-corium boundary at increasing concentrations of filler, TEM images show that at an optimum concentration of 3% uniform dispersion of the filler along with good handle can be obtained. A gradual increase in tensile and tear strength is observed with increasing concentration of Cloisite Na+, however softness measurements correlated with microscopic observations in that only at optimum concentrations can both good handle and mechanical strength be achieved. We discuss a possible mechanism for the change in mechanical properties and handle of the loose leather after treating with Cloisite Na+. The mechanistic study of such treatments on low quality hides will result in the production of leathers with more uniform cutting area and added functionality.

Looseness is a well-known quality problem in the leather industry, reputed to cause up to 7% of bovine leather produced in New Zealand to be downgraded, at a significant expense to the tanner. From New Zealand hides alone, financial losses due to looseness in the finished leather are estimated to cost as much as $35 Million New Zealand per annum (23.1 Million USD). Leather is made of collagen fibers interwoven together into a network structure.2,3 Collagen molecules consist of three intertwined protein chains that polymerize to form fibrils of varying length and thickness. In turn, collagen fibers are made of bundles of these fibrils, where tearing, stretching or squeezing leather can disrupt or break the collagen fiber network.4-6 Looseness is a defect where the grain surface shows a wrinkly texture when it is subjected to compressive forces in the plane of the surface (Figure 1).7,8 This is an undesirable defect that can significantly downgrade the quality and value of leather.

The main components of animal hides are fibrillar and non-fibrillar proteins (mainly collagen), natural fatty materials (triglycerides, fatty acids), glycoproteins and water. When a hide is processed into leather, the glycoproteins, non-collagenous proteins and other materials are mostly removed and the remaining fibrous proteins are subsequently chemically modified by tanning agents to make the network structure permanent. During the early process stage of liming the fiber bundles are opened up (loosened) allowing most of the non-collagenous materials to be removed.9 The removal of these non-collagenous components creates open spaces, or voids, in the structure between fibrous layers. These open spaces, or voids, may be exacerbated or enlarged by a number of leather processing factors, such as the bacterial degradation of the raw stock,10 excessive opening up in the beamhouse, inadequate neutralization-post tanning, poor fatliquor distribution or inappropriate fatliquor selection, excessive mechanical stressing, especially at incorrect moisture levels, and excessive drying. The water content in the hide is significantly reduced as it is converted into leather. Removal of natural fats from the fiber network can also cause the collagen fibers to stick together as the leather dries, increasing its stiffness.
Very few studies on looseness have been conducted to date. Liu et al. used microscopy and mechanical characterization to investigate looseness and observed that the grain layer in loose leathers had a propensity to form sheet-like structures and had gaps between the interstitial and corium layers of the leathers. Mukhopadhyay et al. described a non-invasive technique using planar interdigital sensor to detect looseness in pickled pelts. Various fillers and retans have been developed with the specific aim of rectifying looseness, but to the best of our knowledge studies on their filling mechanism are yet to be reported. Layered silicate materials such as montmorillonite clays are used as inorganic fillers in polymer systems because of their ability to modify the mechanical properties of polymers at low cost.

Cloisite®Na+ is a naturally occurring montmorillonite nanoclay with the molecular formula \([\text{Na}_{0.75}(\text{Al}_{3.25}\text{Mg}_{0.75})_{8}\text{Si}_{20}\text{O}_{50}\text{(OH)}_{4}]\). It has gained much attention owing to its low weight ratio of filler to reinforcement properties, delivering lightweight yet resilient materials. Montmorillonite clay particles consist of stacks of 1 nm thick aluminosilicate layers (or platelets) with gaps in between them (interlayer). When dispersed in water they expand (swell) and exfoliate into stacks of platelets (called tactoids). Incorporation of the tactoids into a polymer matrix produces a composite structure with enhanced mechanical strength. When a load is applied to the material, the stress can be transferred from the polymer matrix to the clay particles. In leather making, montmorillonite clays and their composites have been used to impart characteristics such as flame retardancy, fat-liquoring, finish, and mechanical properties.

Here we investigate the effect of adding a natural nanoclay filler Cloisite®Na+ to a “fatliquor” emulsion to treat loose leathers. Fatliquoring is a leather process by which natural or synthetic oils are introduced into the skins to coat individual fibers uniformly, preventing fibers from sticking to each other through lubrication and thereby imparting softness to the final leather. Additionally properties such as handle, flexibility and water resistance can also be introduced through fatliquoring. Fatliquors are mostly oil-in-water emulsions and in our study we use a commercial anionic fatliquor Densodrin CD (BASF), which is a \(-50\%\text{ paraffin/polysiloxane emulsion. Clays such as montmorillonite are known to aggregate with oil drops and aid their dispersion in water. They may attach to the droplet surfaces, becoming partially immersed in the oil, and form a layer that encapsulates the drops to provide a barrier against drop coalescence. Clay particles may also enhance drop stability to coalescence by forming three-dimensional networks in water that surround and entrap the drops. We show that the mechanical properties of leathers treated with emulsions of oil-clay aggregates increase with clay concentration in the emulsions. This could be due to the clay particle/oil drop aggregates penetrating into the leather and dispersing within the collagen fiber network.}

**Experimental Section**

**Materials**
Cloisite®Na+ with a cationic exchange capacity (CEC) in the 80–95 mequiv/100 g range was obtained from Southern clay products (USA), stored at room temperature and used without further modification. Tanigan’ PAK-N was obtained from Lanxess, Tanicor PW was obtained from Clariant, Mimosa was obtained from Tanac SA and Densodrin CD was obtained from BASF. Bovine wet blue hide was purchased from a local tannery. All other chemicals and reagents were analytical grade and used as received. The wet blue hides from the local tannery were evaluated for loose grain and those identified as having poor quality were selected for treatment with Cloisite®Na+.

**Application of Cloisite®Na+ to Loose Leather**
A uniform dispersion of Cloisite®Na+ in water (50g in 1L) was formed using a stirrer and then introduced after the fat liquoring stages at offers of 1% wt/wt, 3% wt/wt and 6% wt/wt to study the effect of varying concentrations on the morphology and mechanical properties of the leather. Six samples (~300g each) collected from the official sampling position (OSP) areas of two loose wet blue hides were cut out and divided into treatment and control samples and processed in Dose drums. The processed leather samples were not finished and were stored as crust in a conditioned environment, at 20°C and 65% relative humidity for 3 days prior to physical testing.

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**Figure 1.** Photographic images of a normal and loose grain surface and their corresponding cross-sections.
Characterization

Samples for transmission electron microscopy were fixed with osmium tetroxide and embedded in an araldite resin and then carbon coated prior to imaging. Cloisite Na+ was imaged by preparing a dispersion in water and dropping the sample onto a carbon-coated copper grid. Low- and high-resolution TEM images were imaged and mapped using a JEOL 2100F Field Emission microscope operated at 200kV. EDX maps were recorded using a JEOL 2300 series SDD. For scanning electron microscopy studies, cross-sections from rectangular strips of leather crust were made by cutting from the grain surface to the flesh using a stainless steel blade and mounted on specimen stubs. The samples were then sputter-coated from a gold/palladium source and studied using a JEOL JSM 7000F field emission gun scanning electron microscope (Tokyo, Japan). The microscope was operated at 5.0 kV, and samples were viewed at a working distance of 15 mm.

Physical and Mechanical Characterization

Leather crust samples for physical tests were conditioned at 20±2°C and 65% relative humidity over a period of 3 days. The measurements were done parallel to the backbone and tests such as tensile strength, tear strength and elongation at break were examined as per standard ISO procedures using an Instron tensometer, model number 4467. Each test was conducted on five replicates from the six samples of the OSP region in each hide, and error bars were determined from the calculated mean and standard deviation. Leather softness was assessed using a BLC ST300 softness gauge.

Results and Discussion

Physical and Mechanical Studies of Cloisite Na+ Treated Leather

The mechanical properties of the treated loose leathers at increasing concentrations of Cloisite Na+ are listed in Table I. In general, an improvement in mechanical properties of the treated leathers was observed in comparison to the control loose leather. The tensile strength is the maximum load a material can withstand without breaking when being stretched to the original area of its cross-section and in leathers, is closely associated with the angle of weave, looseness and lubrication of the collagen fiber bundles. Tear strength is the maximum load that a material can endure whilst being stretched.

Both tensile (25.7-32 N/mm2) and tear strength (119-129 N/mm) of the leathers increased linearly with clay particle concentration which indicates that the Cloisite Na+ has impregnated through both grain and flesh regions of the loose leather acting as both a filler and reinforcing agent. The elongation at break further confirms this as a decrease from 60% for the control to 33% and 28% for the 3% and 6% treated Cloisite Na+ samples was observed, respectively, suggesting that the clay particles are placed in the inter-fibrillar gaps in the leather. Softness, in leathers is a very important characteristic of its quality and can be defined as the deformation response of the material to external forces. Softness measurements (ISO 17235) showed that the overall handle of the leathers is optimum at an offer of just 1% and then gradually decreases with increasing concentration of the nanoclay filler. While this is not marked in the 3% concentration (softness value of 22), in the case of the 6% there is a drastic decrease in softness (softness value of 15). This could be due to the nanoclay fillers flocculating in the fatliquor emulsions at high concentrations resulting in an uneven dispersion at the grain and corium surfaces, causing buildup of the filler on the surfaces of the leather as shown by microscopic characterization. Cross-sections of the Cloisite Na+ treated loose leathers were imaged using scanning electron microscopy to study the effect of filler concentration on the overall morphology of the loose leathers.

Microscopic Observations of Cloisite Na+ Treated Leather

There are two structurally distinct layers in the cross-section of the loose leather control (Figure 2A). An upper layer of densely

<table>
<thead>
<tr>
<th>Loose Samples</th>
<th>Tensile Strength [N/mm2]</th>
<th>Tear Strength [N/mm]</th>
<th>Elongation at break [%]</th>
<th>Softness (ISO 17235)</th>
</tr>
</thead>
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<tr>
<td>Control</td>
<td>25.7 ±6</td>
<td>119.9 ±1</td>
<td>60 ±2</td>
<td>21</td>
</tr>
<tr>
<td>Cloisite Na+ 1%</td>
<td>26.1 ±4</td>
<td>124.1 ±3</td>
<td>55 ±1</td>
<td>26</td>
</tr>
<tr>
<td>Cloisite Na+ 3%</td>
<td>30.3 ±8</td>
<td>126.3 ±1</td>
<td>33 ±3</td>
<td>22</td>
</tr>
<tr>
<td>Cloisite Na+ 6%</td>
<td>32.4 ±7</td>
<td>129.4 ±2</td>
<td>28 ±1</td>
<td>15</td>
</tr>
</tbody>
</table>
interwoven narrow (< 1 mm in diameter) collagen fibers (called the grain layer) and a lower layer of thicker bundles of fibers (corium). There is also a large zone (or junction) between the grain and the corium where the fiber structure is poorly defined. At a Cloisite Na+ offer level of 1% wt/wt (Figure 2B) no significant change in the structure was observed. However at concentrations of 3% wt/wt and 6% wt/wt (Figures 2C and D), an obvious filling effect was observed. Although a vast improvement in the fiber structure along with an apparent filling effect was also observed, with the fiber bundles well divided in the corium compared to the control (Figure 2A) for all concentrations of nanoclay fillers, it is not sufficient to guarantee remediation of the effects of looseness. Factors such as handle, breathability and mechanical strength also need to be considered to ensure that the aesthetic properties of the leather are also maintained. To further investigate the effect of Cloisite Na+ on the fibrous microstructure of the loose leathers transmission electron microscopy studies were undertaken.

Figure 3 is a low magnification TEM image of a loose section of a control leather displaying the grain layer, with the junction between the grain and corium showing large areas of voids and gaps ranging from a few hundred nanometres to micrometres in size. The lack of interconnect between the grain and corium layers causes the grain layer to move easily above the corium (flesh) layers, as it is no longer held firmly to the corium layer compared with normal or “tight” leathers, causing the grain surface to have a wrinkly appearance. At a concentration of 1% wt/wt the grain surface of the leather is observed to be coated with a thin layer (20-30 nm) of the nanoclay, as shown in Figure 4A.

Higher magnification images (Figure 4B) revealed that the clay particles exfoliate and orientate along the basal plane forming a continuous and smooth coating on the grain surface. However at this concentration the voids or spaces remained largely unfilled and vacant with very few areas showing penetration of the nanoclay filler. At a filler concentration of 3% the grain surface was found to be uniformly coated, with void spaces and gaps in the junction of the grain and corium layer also observed to be filled with the nanoclay fillers; most of the clay dispersed finely within the fiber network (Figure 5A). The clay particles also tended to exfoliate into smaller stacks (with high aspect ratios) that assemble around groups of fiber bundles (Figure 5B). Some of the clay particles that penetrate into the corium remain agglomerated as tactoids with sizes up to a few hundred nanometres and are able to fill void spaces in this layer (SI-3). STEM-EDS mapping images (not shown) of the 1% and 3% concentrations showed that the Cloisite Na+ nanoclay filler was coated evenly on the grain surface for the former and filled for the latter and, composed evenly of Al and Si.

At the highest concentration of 6% of nanoclay filler, very poor penetration of the clay particles into the leather microstructure was observed. Instead the fillers appear to flocculate and stack at the grain surface of the leather (Figure 6). This could be attributed to an unstable fatliquor emulsion caused by the higher concentration of nanoclay filler, which in turn leads to poor dispersion and coating of the nanoclay filler, a finding which is in agreement with the softness and handle measurements of the leather.
In summary, we have improved the mechanical strength of loose leather by altering the collagen fiber microstructure using oil-in-water emulsions containing clay nanoparticles. The clay nanoparticles aggregate with the oil drops in the emulsions and are transported into the collagen fiber network as the oil drops penetrate into the leather. The particles are dispersed within the collagen fiber matrix when the emulsions break and the oil drops wet and spread over the collagen fibers. The resulting fibrous network structures in the leather are characterized by the presence of clay tactoids, intercalated between bundles of collagen fibers.

Therefore, we speculate that the linear increase in the mechanical properties of the leathers with clay particle concentration indicates there are adhesive interactions between the clay tactoids and the collagen fibers. The clay particles deposited by

Figure 4. Low magnification TEM image of the grain surface of 1% Cloisite®Na+ treated loose leathers (B) higher magnification TEM image of rectangular section in A.

Figure 5. TEM image of the 3% Cloisite®Na+ nanoclay filler treated loose leathers showing (A) grain surface and grain-corium junction exhibiting filling, (B) areas of corium and flesh showing stacked nanoclay platelets filling void spaces.
the oil drops within the fiber network likely remain partially wetted by the oil. Adhesive interactions between the two solids would be mediated by the oil wetting both the clay particles and the fibers. Adhesion would improve the load transfer between the collagen matrix and the clay nanofillers when tensile stress is applied to the leather.

Although a vast improvement in the fiber structure along with an apparent filling effect, with the fiber bundles well divided in the corium compared to the control (Figure 5A) are observed for all concentrations of nanoclay fillers, it is not sufficient to guarantee remediation of looseness. This is due to the nanoclay fillers flocculating at high concentrations (6 wt%) at the grain and flesh surface resulting in uneven dispersion. It causes a buildup of the filler on the surfaces of the leather, as shown by microscopic characterization. This could be attributed to an unstable fatliquor emulsion caused by the high concentration of the nanoclay filler, which in turn leads to a poor dispersion and coating of the nanoclay filler and is in agreement with the softness and handle measurements of the leather.

Conclusions

We have shown here that emulsions of oil drop-clay particle aggregates are beneficial for reinforcing the mechanical properties of loose leather. At an offer of 3% wt/wt of nanoclay filler both mechanical strength and filler properties were optimized, demonstrating that an apparent filling of the leathers alone is not sufficient to guarantee remediation of looseness with factors such as handle, breathability and mechanical strength also needed to be taken into consideration. Fillers have an important role to play in the processing of leathers and can have a beneficial effect on the overall properties of the leather, if their mechanism of filling has been properly investigated and optimized.

Acknowledgment

S.P and G.H thank the MacDiarmid institute and the Ministry of Business, Innovation and Employment (MBIE) through grant LSRX-1301 for funding. S.P would like to thank Ms. Jordan Taylor of the Manawatu Microscopy & Imaging Centre, Massey University for Electron Microscopy analysis.

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Tara powder can be used to tan all kinds of hides and skins and to re-tan chrome tanned leathers to improve the grain tightening. The main application is in the manufacture of leather for car seats. The general specifications for commercial tara powder for tanning application are:

- Tannin content: min. 48%
- Water content: max. 13%

In our previous publication, the physical modification process of tara not gave an extract with high tannin content like obtained with the alternate aqueous extraction method (see Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara). But, as this current study showed, the physical modification of tara improved the penetration/fixation of its tannins into the leather, reduced the suspended matter and chemical oxygen demand in the spent floats. The best physical modification of tara was obtained by milling, sieving and using the particle size fraction of 50-40 microns (see Low carbon products to design innovative leather processes. Part II: determination of the optimal physical modification of tara).

An experimental design was developed in order to obtain an optimized innovative formulation based on tara for wet-white or metal free leather article, and to produce all kinds of final goods like shoe, apparel, upholstery, etc. (see Low carbon products to design innovative leather processes. Part III: optimization of an eco-friendly formulation using tara). By using this new modified product (milled and sieved tara) and a naphthalene sulphonic syntan dispersing agent we improved the penetration and distribution of the tara in the leather cross section. Another product we used in this innovative formulation is sodium acid pyrophosphate. It is a sequestering agent of iron, and further helped distribute the products in the leather cross section.

Abstract

In three previous studies, it has been used the fruit of the tara tree (Cæsalpinia Spinosa) as a pre-tanning agent. This new tailored tara product will be able to facilitate the penetration of the tannin molecules through the leather section, avoiding or reducing the use of aldehydes, syntans, common vegetable tannins and other mineral salts.

The aim of this part of the study is to manufacture final articles meeting the parameters set by different regulations, and assess if this modified tara can be marketed and used in the industry to replace some less sustainable products.

Introduction

The fruit of tara tree and its derivatives have high interest in a number of industries and, thus, a great worldwide economical potential for commerce. The properties of pods and seeds result in a sustainable and quality raw material for several applications.

The weight of the fruit of tara is composed by: 60-64% of pods, 34-38% of seeds and 2% of non-valuable residues. It is important to point out that tara powder is composed of 45- 50% tannins; tara gum can be obtained from 24% of the weight of the seeds.

Tara powder is obtained by simply mechanically milling and sifting the gross powder after threshing the pods and separate the seeds. The tara powder is a fine (100 to 200 mesh) yellowish "sawdust." Further than the leather industry, it is used, as well, in the chemical industry to obtain tara extract, also used in the leather industry and to other applications. The leather industry appreciates the tara powder as a source of vegetable tannins to obtain light colors, with good light fastness, and full and soft leather articles, with a firm and smooth grain. Tara is easily soluble in water and do not contain color substances like other vegetable tannins.
This new pre-tanning formulation using a 9% offer of tara is expected to give tanners a sustainable product, and further lower the offer of synthetic auxiliary products to a maximum of 2%. Additionally, a clear improvement in safeguards the environment was obtained by decreasing COD, suspended matter and the electrical conductivity (soluble salts) in the final spent floats of this innovative recipe.

**Materials and Methodology**

The aim of this part of the work is to obtain an optimized innovative formulation based on tara for wet-white or metal free article and able to produce automotive leather. By using the new modified product (milled and sieved tara) and a synthetic based on naphthalene sulphonfic syntan we will obtain a better penetration and distribution of the tara in leather section. Another product to consider is the sodium acid pyrophosphate that, besides of being a good sequestering of iron, it helps in the distribution of chemicals. This mix is called compact product.

In order to carry out a study of the feasibility of the new formulation, a comparison with a conventional formulation using glutaraldehyde was performed. The formulations of pre-tannage for each process, the new and the conventional, can be seen in Table I and II.a

After pretannage, leathers were re-tanned, dyed and fatliquored, following the formulations shown in Table III and IV. The leathers pre-tanned with modified tara were re-tanned using the formulation of Table III. The leathers pre-tanned with glutaraldehyde were re-tanned using the formulation of Table IV.

A final bath after pre-tanning and after re-tanning was taken and assessed to compare both processes. For the purpose of assessing the pollution in wastewaters, the following parameters were analyzed: Conductivity (μ/cm), Suspended solids (mg/L), COD (mg/L), N Kjeldahl (mg/L).

In order to determine the quality of the leathers and compare both systems, we carried out the physical tests set up by the IULTCS, which allowed us to assess the capacity of the leathers to withhold the wear and tear of automotive upholstery. The following official methods were used to this end:

- IUP 6 Measurement of tensile strength and percentage elongation (in accordance with EN ISO 3376).
- IUP 8 Measurement of tear load (in accordance with EN ISO 3377-2).

**Results and Discussion**

The aim of this part of the study is to assess whether the leathers processed with this new system present advantages over the conventional one. In addition, we will check that the leathers meet the demands required for automotive upholstery.

Table V shows the comparison of pollution in wastewaters between the pre-tannage using modified tara and the pre-tannage using glutaraldehyde.

The values show a clear decrease in almost every determination for the new pre-tanning process with modified Tara. In the case of COD there is a reduction of about 21%, which highlights the improvement using a natural product against the use of a

---

**Table I**

<table>
<thead>
<tr>
<th>%</th>
<th>PRODUCT</th>
<th>TIME</th>
<th>OBSERVATIONS</th>
</tr>
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<tr>
<td>50</td>
<td>Water + Salt 20°C</td>
<td>15’</td>
<td>6 °Bé</td>
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<tr>
<td>X</td>
<td>Compact product*</td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>Sulphited oil</td>
<td>Over night</td>
<td>Cut</td>
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<tr>
<td>0.8</td>
<td>Formic acid</td>
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<td>pH=3.75</td>
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</table>

*The compact product corresponds to the mix of milled and sieved tara (modified tara), naphthalene sulphonfic syntan and sodium acid pyrophosphate.

**Table II**

<table>
<thead>
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<th>%</th>
<th>PRODUCT</th>
<th>TIME</th>
<th>OBSERVATIONS</th>
</tr>
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<td>50</td>
<td>Water + Salt 20°C</td>
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<tr>
<td>2.5</td>
<td>Glutaraldehyde 50%, exempt from free formaldehyde</td>
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<tr>
<td>5</td>
<td>Sulfonic synthetic</td>
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<td>pH= 4.0-4.2</td>
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<tr>
<td>300</td>
<td>Water</td>
<td>20’</td>
<td>Drain Horse up. Sammy</td>
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Table III
Re-tanning, dyeing and fatliquoring for automotive leather using modified tara.

<table>
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<th>OPERATION</th>
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<th>TIME</th>
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<td></td>
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<td></td>
<td>Drain and wash</td>
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<td>Sodium Formate</td>
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<tr>
<td></td>
<td>0.5</td>
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<td>Sodium Bicarbonate</td>
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<td>2</td>
<td></td>
<td>Naphthalene sulphonic syntan</td>
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<td>3</td>
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<td>Sulphited synthetic oil</td>
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<td>4</td>
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<tr>
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<td>50</td>
<td>50</td>
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<td>5’</td>
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<td>Sulphated oil</td>
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Table III continued on following page.
Table III continued.

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<tr>
<th>45</th>
<th>150</th>
<th>Water At 45ºC</th>
<th>Drain</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>Sulphited synthetic oil</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Lecithin</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Sulphated oil 60'</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>Formic Acid 30' pH final = 3.50</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>200</td>
<td>Water At 30</td>
<td>Drain and wash</td>
</tr>
</tbody>
</table>

*The compact product refers to the combination of modified tara, synthetic naphthalene sulphonate and sodium acid pyrophosphate.

---

**Table IV**

Re-tanning, dyeing and fatliquoring for automotive leather using conventional tara.

<table>
<thead>
<tr>
<th>OPERATION</th>
<th>ºC</th>
<th>%</th>
<th>PRODUCT</th>
<th>TIME</th>
<th>OBSERVATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wash</td>
<td>30</td>
<td>200</td>
<td>Water</td>
<td>10'</td>
<td>Drain</td>
</tr>
<tr>
<td>Neutralizing</td>
<td>30</td>
<td>200</td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
<td>Sodium formate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td></td>
<td>Sodium bicarbonate</td>
<td>20'</td>
<td>pH= 5.0</td>
</tr>
<tr>
<td>Re-tanning</td>
<td>10</td>
<td></td>
<td>Phenol syntan</td>
<td>30'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>Tara</td>
<td>30'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>Resin syntan</td>
<td>40'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>Phenol syntan</td>
<td>30'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>Tara</td>
<td>30'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
<td>Dye</td>
<td>3h</td>
<td>Night</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
<td>Formic acid (1:10)</td>
<td>60'</td>
<td>pH= 3.8 Drain</td>
</tr>
<tr>
<td>Washing</td>
<td>50</td>
<td>200</td>
<td>Water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table IV continued on following page.
chemically synthesized product. The suspended solids also show a decrement in the value, as well a decrease in the conductivity. In addition, a determination of tannins has been made for the new process with modified tara, in order to determine the tannin exhaustion on final baths. The results can be seen in Table VI.

As can be see, there is a small value on tannin (0.8%), which makes us notice the great penetration of the tannins into the leather structure.

Table VII shows the comparison of pollution in wastewaters between the re-tanning process using modified tara and the conventional re-tanning process.

Once again, for these processes, there is a big difference in almost every determination. The use of naphthalene sulphonate syntan as auxiliary in the new re-tanning process, as well the use of the modified tara is a difference maker in terms of better penetration of the products into the leather and therefore a decrease in COD and suspended solids in the wastewater.

Table VIII shows the physical tests carried out on the tanned leathers.
The leathers have a very good appearance, with a uniform dye and acceptable smoothness; also the results from physical tests are within the parameters established for each item. As can be seen in Table 8 the leathers processed using the modified tara present similar results to those obtained using the conventional system.

**Conclusions**

The physical modification process does not allow for an extract with high tannin content as it was with the aqueous extraction (see Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara), but it improves the penetration of the extract into the leather and reduces the suspended matter and chemical oxygen demand of the residual floats.

The best physical modification is obtained by milling and sieving at particle size fraction of 50-40 microns (see Low carbon products to design innovative leather processes. Part II: determination of the optimal physical modification of tara).

By using the new pre-tanning formulation using modified tara, we can use a sustainable product and we can reduce the use of synthetic products. The new pre-tanning and re-tanning processes based on modified tara produce perfectly free-chromium leathers meeting all requirements for automotive upholstery. In addition, the new system is an environmentally friendly process due to the fact that reduces by 17-21% in COD in contrast with the glutaraldehyde system and reduces by 12-15% in suspended solids.

**Acknowledgement**

This work is part of the project "Low carbon products to design leather processes based on sustainable tannins to improve leather manufacture.” E! 6565 LOWEST (Eurostars Project).

**References**


---

### Table VII

**Pollution in wastewaters of re-tanning.**

<table>
<thead>
<tr>
<th>Determination</th>
<th>Tara</th>
<th>Conventional</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.7</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Suspended solids</td>
<td>2245</td>
<td>2641</td>
<td>mg/L</td>
</tr>
<tr>
<td>Chemical Oxygen Demands</td>
<td>29852</td>
<td>35120</td>
<td>mgO₂/L</td>
</tr>
<tr>
<td>Organic Nitrogen Ammonia</td>
<td>314.5</td>
<td>370</td>
<td>mgN/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>15667</td>
<td>14702</td>
<td>μS/cm</td>
</tr>
</tbody>
</table>

---

### Table VIII

**Automotive upholstery physical tests.**

<table>
<thead>
<tr>
<th>Determination</th>
<th>Tara</th>
<th>Conventional</th>
<th>Minimum Recommendations</th>
<th>Unit</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
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<td></td>
<td></td>
<td></td>
<td>IUP-6 / ISO 3376</td>
</tr>
<tr>
<td>Strength</td>
<td>259.90</td>
<td>249.90</td>
<td>100</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>Elongation at break</td>
<td>46.70</td>
<td>44.40</td>
<td>35-60</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Tear Resistance</td>
<td>107.10</td>
<td>61.90</td>
<td>40</td>
<td>N/mm</td>
<td>IUP -8/ ISO377</td>
</tr>
<tr>
<td>Softness test</td>
<td>3</td>
<td>3</td>
<td></td>
<td>mm</td>
<td>IUP -36/ EN ISO 17235</td>
</tr>
</tbody>
</table>
12. UK REACH Competent Authority Information Leaflet Number 8 – Exemptions - Nov 2012.
Preparation of Biobased Sponges from Un-tanned Hides
by
Aisha Siddique, Nicholas P. Latona, Maryann M. Taylor and Cheng-Kung Liu

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Abstract
One of our research endeavors to address ongoing challenges faced by the U.S. hide and leather industries is to develop innovative uses and novel biobased products from hides to improve prospective markets and to secure a viable future for hides and leather industries. We had previously investigated the production of nonwoven, green composites, and films from collagen fiber networks, which were extracted from un-tanned hides and from tannery solid wastes, such as splits or trimmings. Recently, we investigated the preparation of biobased sponges from un-tanned, specifically limed hides, which have potential commercial applications in medical care. We also investigated the effects of processing steps such as bating and alkaline treatments using sodium hydroxide (NaOH) on the morphology and viscoelasticity of resultant sponges from un-tanned hides. Results showed that the treatments of fiber networks have significant effects on the properties of resultant sponges. The dynamic mechanical analysis showed stiffer sponges than limed and bated samples. SDS-PAGE analysis showed the molecular weights of sponges were maintained in the range as those of commercial collagen samples. Lastly the resultant sponges are in the desirable apparent density range for a potential application as a medical sponge.

Introduction
Improving utilization of waste is one of major challenges that the U.S. hides and leather industries are currently facing. We have addressed this challenge by developing innovative uses and novel biobased products from the solid fibrous wastes generated from tanneries. We hypothesized that those solid fibrous wastes from a tannery can be purified into collagen fiber networks and utilized in making useful biobased products such as green (i.e. renewable and degradable) composites and biobased films, all of which have great market potential. Earlier studies were devoted to understanding the effects of dehydration on the morphology and physical properties of the fiber networks derived from un-tanned hides, which will be the starting material for constructing nonwoven and green composites. Five dehydration methods were investigated and observation showed solvent- and freeze-drying yielded the lowest apparent density indicating a higher degree of separation in the fibrous networks that will be favorable for further processing into useful products. The results from comparisons showed that samples frozen and then followed by vacuum drying offer many advantages over those from the other dehydration methods in terms of economic and open fibrous structure.

Further study investigated the use of crosslinking with glutaraldehyde and other treatments to improve the integrity of fibrous structures that offer better stability and physical properties. Crosslinking is a process to apply a chemical agent - like glutaraldehyde to bridge molecular chains, thereby providing stability and improved physical properties to collagen matrices. There are various crosslinking treatments currently being used today for collagen materials. Two of the most common methods, i.e. transglutaminase and glutaraldehyde, were used to treat the collagen fiber networks. Results showed that glutaraldehyde treatment yielded a highly open structure, in which the fibers are well separated from each other.

Research was carried out for preparations of nonwoven and green composites derived from fiber networks extracted from hides. Nonwoven sheets were prepared using paper-making technology. They were then used as reinforced components to make composites that used gelatin as the matrix. Test results showed that finer size fibers and higher portions of gelatin yielded better tensile strength and higher stiffness of nonwoven and composites. The results of this research are useful to the production of high quality fibrous products such as high efficiency air filters or green composites. Another potential

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product that can be derived from un-tanned hides or tannery solid wastes is biobased films. Many reports have shown the important applications of biobased films in medical care such as wound dressing and skin repair because of the excellent biocompatibility.9-12 Beside medical applications, recently, there is a great interest in using biobased films for food packaging.13-18 In a recent study, matrix biopolymer collagen obtained from tannery waste combined with guar gum was incorporated with varying proportions of carbon nanotubes to form flexible and electrically conducting carbon nano-biocomposites for potential wide applications in biosensors and electronic devices.19

We recently reported that the most important step for preparing a collagen film or fiber is its dissolution.20-26 Acid extractions using acetic acid followed by enzymatic treatments mostly by pepsin are the most popular methods for extraction of soluble and insoluble collagen from different biological sources.21-23

We modified a dissolution method by Nishihara, which was very effective in digesting hide fibers to make collagen solutions, and it was less detrimental to the environment.20 The dissolution system utilized a commonly used protease, pepsin at a suitable pH as described later. A study focused on preparations of biobased films from un-tanned hides, including limed hides and delimed-bated hides, which correspond with their actual tannery waste of limed splits and their trimmings. These films could be used in the field of medicine because of their good compatibility with living tissue, and in packaging of food due to their excellent mechanical properties, and accepted edibility. The aqueous concentration of collagen extracted from the hides and the timing of the addition of glutaraldehyde during the preparation of films had significant positive effects on their mechanical properties.

To further exploit the utilization of tannery solid wastes, we recently carried out an investigation to prepare a biobased sponge from collagen solutions derived from un-tanned hides. Collagen sponges have many unique properties that are desirable in medical applications.27-30 Theoretical as well as practical-clinical applications of collagen sponge as a biodegradable material was reviewed by Chvapil.31 Sponges are used to stop coagulating material such as thrombin. Collagen sponges have an important advantage in that they may remain in the body cavity since they are non-antigenic and absorbable.28-30 It was reported that the collagen sponges of uniform porosity will quickly absorb about 70 times their weight in water.30 The variables we studied which affected sponge formation were the treatments (e.g. liming, bating and alkaline) of hide fiber networks before dissolving into a collagen solution. This report presents the preparation of collagen sponges, their resultant viscoelasticity, and their structure and morphology by examination with SEM.

Experimental

Materials and Procedures

Fleshed fresh steer hides, purchased from JBS (Souderton, PA), were processed to the lime, bate, and limed and soaked in a NaOH solution, where the soluble collagen was then extracted as previously reported.1 In summary, the fleshed hides were sided and soaked for 1 h in 150% float with 0.15% Borron TS (TFL, The Woodlands, TX) and 0.1% Proxel (Chemtan Co. Inc., Exeter, NH) with a drum speed of 6 rpm. The float was drained and the hide was washed for 5 min; 2% sodium sulfide, 2% lime, and 1% soda ash were added in addition to 100% float. The drum was run for total of 4 h with a run time of 10 min per hour. After 4 h the float was drained, 100% float was added and washed for 5 min and then drained. A 200% float was then added to the drum with 2% lime and 1% sodium sulfide and run for 20 h at 6 rpm for 3 min per hour. After 20 h the float was drained, 100% float was added and the hide was washed for 5 min, then drained again. This step was repeated for a total of two times. Pieces were cut out of the limed hide (12” x 12”), and were either stored in a refrigerator or delimed, bated and then stored in a refrigerator. For the delimed and bated hides, after the liming step the hides were refloated to 125% with 3% ammonium sulfate, 0.15% Rohapon 6000 (TFL, The Woodlands, TX), and 0.10% Borron TS, and run for 90 min at a drum speed of 6 rpm. The float was drained, the hide was washed in a 100% float, and drained again. Samples treated with NaOH, were added in a 5% solution with 200% float and let run for 24 h, then drained. Pieces from the delimed only, delimed-bated treatments and NaOH were cut into approximately 1.5” to 2” squares and allowed to air dry fully in a fume hood. They were then ground in a Wiley Mill (Thomas Scientific, Swedesboro, NJ) and sieved through a 4 mm circular screen. The collagen fibers were then stored in sealed plastic bags until the preparation of their solutions.

The process we used to extract soluble collagen from delimed only, and delimed-bated hides into collagen solutions was modified from that reported by Nishihara.20 Ground (4 mm) collagen fibers (~ 2 g) were added to 30 times their weight of water in a beaker (600 mL) to rehydrate them on a stir plate. The pH of this mixture was then lowered to 2 – 2.5 by using 2N HCl. A 50 to 1 weight ratio of the sample (2 g) to pepsin (0.04 g) was added to the rehydrated collagen mixture. Two to three drops of sodium azide were next added to this mixture in order to prevent future mold growth. Several such samples were stirred for 48 to 72 h so as to solubilize the collagen fiber networks. The progress of solubilizing collagen was monitored visually as evidenced by an increase in the viscosity of its solutions. Then, 33 times the weight of the samples of 0.005N HCl (66 g) was added to the beakers, and the mixture was stirred continuously for 24 h. Additional 0.005N HCl was added so as to decrease the viscosity, and render it easier to stir. After 24 h of stirring, the collagen
solutions were filtered using a fine plastic mesh screen, then neutralized using 5N or 2N NaOH to a pH of 6-7. The mixture was centrifuged, and the collagen concentrate (precipitate) was collected, washed with water, and the mixture was centrifuged again. This collagen concentrate (precipitate) was then separated from the supernatant (wash-water), and stored in a glass jar in a refrigerator until needed for film formation studies.

Instead of using the dried ground hides for making collagen solutions, freshly limed hides can also be used. However, the limed hides will dissolve better if they are ground rather than left whole. Limed only and delimed-bated hides (~ 70% moisture) were cut into 0.5” x 0.5” squares and then ground by using a Hamilton Beach Co. (Racine, WI) Model 222 meat grinder. The delimed-bated pieces were too soft to be ground thoroughly, unlike their precursor limed hides, which were readily ground in the meat grinder, and most of their ground pieces digested with pepsin. Consequently, freshly ground limed hides were the starting material for our studies, and by extension, tanneries could utilize their waste lime trimmings as a starting material to make biobased films. The delimed-bated samples were also prepared using the ground lime stock, performed in a beaker using the same formula above. The NaOH treated ground lime stock was also prepared in a beaker and treated the same as above in a 5% solution based on the weight of the ground lime stock.

Ground lime, delimed-bated, and NaOH treated stock (2 to 10 g), and 10 times the weight in the amount of water (20 to 100 mL) were added to separate beakers (600 to 2000 mL) and these mixtures were stirred using a stir plate. A collagen solution was thus prepared from these ground stocks by using the modified pepsin dissolution method which was described above, and which was initiated by lowering the pH of this mixture to 2.0 -2.5. Collagen sponges are prepared from the collagen concentrate stored in the refrigerator; the final concentration of collagen solution was 2%. The collagen concentrate was added to freezer flasks and DI water was added to make it less viscous. The freezer flasks were then dipped and turned constantly in a bowl of dry ice and acetone to rapidly freeze the concentrates. The flasks were attached to a Labconco Freezone 1 (Kansas City, MS) lyophilizer until fully dry. After the samples were completely dry, they were then stored in sealed plastic bags and stored in a desiccator. Typical percentage yield ranged from 83 to 95% for the lime and bated samples. The NaOH samples absorbed NaCl and therefore the recovery was calculated to be over 100%.

Dynamic Mechanical Analysis
Dynamic mechanical analysis was performed on a DMA1 (Mettler-Toledo, LLC., Columbus, OH) in compression mode. Storage modulus (E’) and loss modulus (E”) were measured as the function of temperature. All samples were tested using a 1 Hz frequency. A 6.35 mm (1/4 in) die was used to cut out cylindrical samples from the sponge. The sample was then mounted into the compression holder with a gage length of 1 mm and amplitude of 10 μm. The samples were then tested from -50°C to 200°C at a heating rate of 10°C/min.

Molecular Weight Distribution
Protein molecular weights were estimated as described by Taylor, et al. A small portion of the lyophilized sponges were dissolved in sample buffer (10 mM Tris-HCl at pH 8.0 containing 1 mM EDTA, 2.5% SDS, 5% β-mercaptoethanol and 0.01% bromophenol blue) and were then heated at 40°C for 4 h. Separation was achieved using a Phast-Gel System (Pharmacia Biotech Inc., Piscataway, NJ). Gels were stained with Coomassie Blue (Pharmacia). Polyacrylamide gel electrophoresis in sodium dodecyl sulfate (SDS-PAGE) was run using precast 4-15% gradient gels. A broad range (BRS) calibration standard (Bio-Rad, Hercules, CA) as Reference, ranging in size from 6,500 to 200,000 Da, was used.

Microscopic Observations
A scanning electron microscope (SEM) was used to compare the structural difference among the different collagen sponges. The samples were freeze fractured, and then glued to specimen holders using Duco cement. They were sputter-coated once for 30 seconds with a thin layer of gold using an EMS Q150R sputter coater (Quorum Technologies, Ltd., Laughton, East Sussex, England). Images were collected using a FEI Quanta 200F scanning electron microscope (Hillsboro, OR), and operated in the secondary electron imaging mode.

Water Absorption Capacity
A 6.35-mm (1/4 in) diameter punch was used to stamp out pieces of the different collagen type sponge structures. The 6.35-mm pieces were stored in a sealed plastic zip-lock bag and stored in a desiccator until needed. A piece of sponge from each treatment (i.e. liming, bating, NaOH) was weighed dry and then placed in a half full 150-ml beaker with deionized water for 20 to 120 seconds. After the desired time the 6.35-mm piece was taken out from the beaker and put directly onto a scale and weighed again. The water absorption capacity was calculated by dividing the wet weight over the dry weight.

Results and Discussion
Porosity is an important property in a sponge structure, which is directly correlated with its apparent density. This data provides insight into the effect of preparation methods on the sponge structure. For the sake of achieving better liquid absorption, the lower the apparent density the more desirable the structure will be. Figure 1 demonstrates that the bated fiber networks yielded the lowest apparent density of sponges, indicating this treatment method provided the most open sponge structure compared to the other two treatments. Leather’s typical apparent density
ranges from 0.60 to 0.90 g/cm³, however, the apparent density of the collagen sponges ranged from 0.01 to 0.05 g/cm³. It is desirable to be in the range 0.02 to 0.03 g/cm³ such as those obtained from bating and NaOH treatments as shown in Figure 1.30

A cross section cut from the entire collagen sponge is demonstrated in Figure 2. It looks like similar collagen sponges reported in literature.31 One can also observe the different layers making up the sponge caused by the shell drying before the samples were put on the lyophilizer. Figure 3 shows a closer look at the cross section of the collagen sponges demonstrating a porous structure with many voids distributed in the structure. As reported previously, porous collagen scaffolds have broad applications in tissue engineering and regenerative medicine.27-30 The open and interconnected porous structure of the collagen sponge are required for smooth cell seeding, cell penetration, and uniform cell distribution throughout a scaffold, and accelerated cell proliferation and regeneration of new tissue. From Figure 3, the different treatments look similar; however, the average pore size was measured for each sample and resulted in bated, 92.6 µm, lime, 135.7 µm and NaOH 108.1 µm. There is some difference between the different treatments and the pore

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Figure 1. Collagen sponge density.

Figure 2. Stereomicroscopic view of the cross section of a limed sponge.

Figure 3. Stereomicroscopic view of a cross-section of collagen sponges prepared from the concentrated solution of ground hide fibers (a) limed, (b) bated, and (c) further treated with NaOH.
size can change depending on the different drying conditions and the type of drying. Further research would need to be done to match a specific application to the desired pore size needed.

The more detailed internal structure is shown in the SEM micrographs, Figure 4. It appears that the sponge is composed of both membrane and fibrous components. It is interesting to note that the sponge obtained from NaOH treatment has less of a membrane structure than those from the other two treatments. This is probably because the collagen solution from NaOH treatment has the presence of salt and this lead to a poor membrane forming ability, consequently the resultant collagen structure is dominated by the fibers. This is further confirmed in that the NaOH samples contained around 70% ash compared to the limed and bated samples which contained 1.3 and 1.2% ash respectfully.

Because the molecular weight is pivotal to the mechanical properties and dimensional stability, it is important to maintain a sufficient molecular weight of collagen during treatments of the fiber network and solution preparation. The resultant collagen sponges were nearly pure type I collagen as demonstrated in Figure 5 by SDS-PAGE analysis, comparing the limed, bated and NaOH samples to the profile of a commercial Type 1 collagen (Bovine Achilles Tendon, Sigma, St. Louis, MO) sample as

![Figure 4. SEM micrographs of collagen sponge structure obtained from concentrated solution of ground hide fibers (a) limed, (b) bated, and (c) further treated with NaOH.](image)

![Figure 5. SDS-PAGE gels for collagen sponges prepared from lime, bate and NaOH treated collagen fiber networks compared to a commercial collagen sample and standard protein calibration.](image)

![Figure 6. Water absorption Capacity as a function of time.](image)
described previously. The bands for collagen sponges produced match the bands for the commercial collagen (marked as Collagen in the far right of Figure 5) very well, which indicates that there is little degradation occurring in the dissolution process to make the collagen sponges. In addition, we are forming aggregated collagen with no low molecular weight hydrolysates.

**Water Absorption Capacity**
One of the most important criteria of surgical sponges is the absorption capacity of aqueous liquids. The sponges have to soak up blood and other physiological fluids during their use as fast as possible. Therefore, absorption capacity should be as high as possible. Beside the surface structure, the hydrophilicity of the collagen component in the sponge may influence its absorbing capacity, which can be affected by various treatments for fiber networks. It was reported that during liming, the amide groups (Gln, Asn) are transferred into the corresponding carboxyl groups (Glu, Asp) leading to a decrease of the isoelectric point of the collagen.\(^{33}\) Furthermore, long-term alkaline treatment induces the topochemical hydrolysis of some natural crosslinks.\(^{34}\) The starting material in this investigation was limed hides. But, it is reasonable to expect that the additional treatments of bating and alkaline will affect the properties of biobased sponges. Bating is a further step to purify the hide before tanning in the leathermaking process by digesting undesired proteins. Figure 6, shows that water absorption increased with time for limed and bated treatments. But the NaOH treatment demonstrated a small decrease in absorption capacity with time. A reason for this phenomenon is the collagen was bound to the salt (NaCl) produced from the reaction of NaOH and HCl in the process. The salt aided in the quicker water absorption and as the NaOH sample is left in the water, the salt diffused out of the collagen and into water, therefore resulting in a decrease in the absorption capacity over time. Therefore further processing to remove the excess salt would be needed for the NaOH treated sample.

**Dynamic Mechanical Behavior**
A sponge needs some degree of stiffness for use in a load bearing application. The stiffness can be evaluated by measuring the storage modulus for the sponge samples using a dynamic mechanical analyzer (DMA). Polymeric materials such as sponges generally demonstrate a mechanical behavior that may incorporate a blend of both elastic and viscous characteristics; this is referred to as viscoelasticity.\(^{35-38}\) We previously reported that besides the elasticity, the viscous component or viscosity plays an important role in determining the stress-strain curves even at the very beginning of the leather deformation.\(^{39}\) The viscoelasticity is commonly measured by either dynamic or static tests.\(^{35}\) In the dynamic tests as conducted in the current study, a sinusoidal variation of strain is imposed on the material and a variation of the responding stress is observed. As to the static tests (as reported in our previous papers), a constant strain or a constant stress is imposed, and the variation of the stress (relaxation) or the strain (creep) as a function of time is observed.\(^{40}\) The storage modulus (E’) and loss modulus (E”) in viscoelastic solids such as sponges measure the stored energy (E’), representing the elastic portion, and the energy dissipated as heat (E”), representing the viscous portion. Storage modulus is known to be associated with the stiffness of materials, whereas loss modulus is linked to the plasticity of materials. The ratio of E”/E’ is defined as the tangent delta or damping, which is a measure of the ability of a material to dissipate the energy. It usually peaks at the glass-transition temperature of a material, where it becomes rubber-like. The relationship between the storage and loss moduli are as follows:

\[
E = E' + iE''
\]

(1)

Where, E is a complex modulus (also named dynamic modulus) and i is the square root of -1.

DMA tests showed the curves of E’ vs. temperature look very similar for all three sponge samples as shown in Figure 7. In the beginning, the E’ decreases with temperature until around 50°C, hereafter the E’ increases with temperature. Probably at 50°C, the collagen sponge starts to shrink and induced a tension and resulted in the increase of E’. It appears that limed samples show the lowest E’ and further treatment by bating and NaOH increase E’ significantly. A similar behavior was also observed for E”, as demonstrated in Figure 8. It is worthy to note, however, that E” is much smaller than E’, indicating that the elastic component in the collagen sponge is the dominant factor in governing the mechanical properties. Figure 9 demonstrates the relationship of the tangent delta vs. temperature plot to have a reversed pattern to that of the E’ vs. temperature profile in Figure 7. Peak of tangent delta indicates the glass transition point, where the molecular chains start to soften up for moving. All three samples were characterized by two peak points within 10 degrees of each other.

![Figure 7. Storage modulus vs. temperature in Dynamic Mechanical Testing.](image)
the first peak for the lime, bate and NaOH sponges occurred at 55.3, 57.1, and 54.1°C respectively. Although the peak temperatures may not be significantly different from one another, it does show that the treatments had a slight shift in the tangent delta curves. This data also correlates to the absorption data, in which the limed samples had the lowest absorption capacity probably due to the fibers were more tightly compact together and resulted in a higher tangent delta. Whereas the NaOH treated sample had the lowest tangent delta and highest absorption rate.

Conclusions

This study focused on preparations of biobased sponges from un-tanned hides, including limed hides and delimed-bated hides, which correspond with their actual tannery waste of limed splits and their trimmings. Observations showed that the treatments of fiber networks have significant effects on the properties of resultant sponges. Bating has a positive effect on reducing the apparent density of sponges, which are in the desirable apparent density ranges. The dynamic mechanic analysis showed alkaline treatments yielded stiffer sponges, thus indicating NaOH treatment of fiber networks is not a desirable processing step for preparing collagen sponges, in addition to the further processing that would be needed to reduce the added salt. SDS-PAGE analysis showed the resultant molecular weights were maintained in the range as a commercial Type 1 collagen. These sponges could be used in the field of medicine because of their good compatibility with living tissue.

Acknowledgments

We thank ARS, ERRC scientists: Joseph Uknalis for SEM photos, Lorelie Bumanlag and Joe Lee for sample preparations.

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Life Lines

N. Vedaraman, see JALCA 107, 435, 2012

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Sujay Prabakar received his PhD in materials chemistry from Victoria University of Wellington in 2010 and is currently a Scientist at New Zealand Leather Research and an Associate Investigator with the MacDiarmid Institute for Advanced Materials & Nanotechnology. His expertise is on the synthesis and characterization of inorganic based functional nanomaterials for applications such as leather processing/coatings and collagen based biomaterials.

Catherine Whitby was appointed a Senior Lecturer in Chemistry at Massey University in late October 2014. Prior to this she was an ARC Future Fellow and Senior Research Fellow at the Ian Wark Research Institute at the University of South Australia. She is a physical chemist with expertise in using nanomaterials to modify the structure and mechanical properties of materials.

Anna Henning received her PhD in Chemistry in 2013, specializing in the synthesis and characterization of nanoparticles. Employed at Boutiq Science Ltd. in Wellington NZ as product development manager, Anna manages R&D for new materials and applications, focusing on the biomedical space.

Geoff Holmes, see JALCA 110, 379, 2015

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Jorge Diaz, see JALCA 108, 401, 2013

C. Casas, see JALCA 109, 32, 2014

Anna Bacardit, see JALCA 101, 284, 2006

Aisha Siddique is doing her Ph.D. in Department Of Microbiology at Quaid-i-Azam University, Islamabad, Pakistan. She joined USDA in March 2015 as visiting research scientist as a part of her PhD program. She is working in Biobased and Other Animal Co-Products (BOAC) under the supervision of Dr. Cheng-Kung Liu. She has been working in research project of environment friendly leather making and recovery of value added products from solid tannery waste. Her major interests include applications and use of microbial enzymes in leather industry.

Nicholas P. Latona, see JALCA 96, 401, 2001

Maryann M. Taylor, see JALCA 93, 328, 1998

Cheng-Kung Liu, see JALCA 94, 158, 1999
Welcome to an exciting venue of events that will be unfolding for us from June 22 to June 25, 2016. We will host the 112th Annual Convention at the beautiful Oglebay Resort & Conference Center in Wheeling, West Virginia. It is a first class facility. You can learn more about Oglebay by logging on to their website at http://www.oglebay-resort.com.

In mid March we e-mail all ALCA members advising that the brochure is online with all details about the convention. Voting for our Slate of Candidates will be done via email in late April. The online convention registration form will be updated as soon as possible if you wish to print it out and use it. Log into: leatherchemists.org/2016 ALCA Registration Form.pdf for the convention registration form. Continue checking this website for new information and announcements about the 112th Annual Convention.

Prior to the official opening of the convention, the annual golf tournament will be held at the Speidel Golf Club, Palmer Course, beginning at 1 pm. Pre-registration for golfers is a must to facilitate the start of the tournament. Further information on the golf outing can be found under this section as well as our online brochure available in mid-March 2016.

The official opening of the convention will begin with Registration on Wednesday, June 22, from 5 – 7 pm in the Glessner Lobby followed by a Cocktail Reception from 7 – 8 pm at the West Terrace. A dinner and conversations with old and new associates of the leather industry will complete the evening.

ALCA President Sarah Drayna will open the Technical Program at 9 am on Thursday, June 23. This year’s technical program is being organized by Vice-President David Peters and will offer a wide array of leather technologies covering tanning to finishing to environmental issues and can be viewed in the coming months under this section of our website. The 57th John Arthur Wilson Lecture will feature Rachel Garwood, Director of the Institute for Creative Leather Technologies (ICLT) in Northampton, UK. Her title will be “Leather Education - Preserving the Past... Protecting the Future.” The technical sessions will end at 4:45 pm followed by the Fun Run at 5:15 pm. Again this year Buckman is sponsoring their golf swing analyzer, Larry Shaver, from 7 to 10 pm in Banquet 3. Thursday’s activities will be capped off by a cocktail reception from 7:15 pm to 8 pm in the Courtyard followed by dinner and Monte Carlo Night in Banquet 1-2 from 8 pm – 11 pm. This will be an exciting evening that you won’t want to miss.

Technical papers will resume Friday morning at 9 am with the Annual Business Meeting ending the morning sessions at 11:15 am. At noon everyone is invited to attend the Activities Awards Luncheon in Banquet Rooms 1-2, where prizes will be awarded for the Fun Run and golf outing. Technical papers will resume in the afternoon at 1:30 pm until 4:15 pm with the Awards Banquet Social Hour beginning at 6:30 pm in Banquet Rooms 1-2. Dinner will follow at 7:30 with the awards presentations afterwards. The convention will close with check out on Saturday.

Please make plans now to join us for a wonderful time at Oglebay!

Doug Morrison
Convention Chair
112th ALCA Annual Meeting  
June 22-25, 2016  
Oglebay Resort & Conference Center  
Wheeling, West Virginia, USA

Tentative Technical Program starting Thursday, June 23

John Arthur Wilson Memorial Lecture
“Leather Education - Preserving the Past...Investing in the Future” by Rachel Garwood
Director of the Institute for Creative Leather Technologies (ICLT), Northampton, UK

Other Papers to be Presented on Thursday and Friday:

Global Trade with China by Su Chaoying, Chinese Leather Industry Association (CLIA), China
Most Recent Advancement in Clean Beaming Technologies by Jurgen Christner, TFL Ledertechnik AG, Basel Switzerland
Traceability and Protocols by Adam Hughes, LWG, UK
Trends in Automotive and Impacts on Leather by Andreas Kinderman, Wollsdorf Leder, Schmidt & Co Ges.m.b.H., Austria
The Over-Engineering of Nature’s Most Beautiful Product by Steve Lange, Leather Research Laboratory, University of Cincinnati, Cincinnati, OH
The Physical Properties, Morphology and Viscoelasticity of Biobased Sponges Prepared from Un-tanned Hides by Cheng-Kung Liu, United States Department of Agriculture, Eastern Regional Research Center, Wyndmoor, PA
New Technologies for Leather Production by Marc Oomens, IM, Holland
The Process and Technology of Collagen Treatment by Juan Luis Salmeron, IPAP, Spain
Modified Smart Collagen Biomaterials for Biomedical, Pharmacy, Cosmetic and Adhesive Applications by Jan Sedliacik, Technical University in Zvolen, Slovak Republic
Update on U.S. Hide Trade by Stephen Sothmann, U.S. Hide, Skin & Leather Association (USHSLA), Washington, D.C.
Complexing Agents and Their Practical Influence in Pickling, Chrome Penetration and Basification by Marcelo Fraga de Sousa, Buckman North America, Memphis, TN
Brazilian Global Leather Trade by Rogerio de Souza Cunha, CICB, Brazil
Is Tanning without Effluent Discharge Still Far from Us? by Jiasheng Su, Biosk (SQ) Chemicals Co. Limited, China
Utilization of Water-Soluble Carbodiimides in the Modification of Gelatin and Chitosan by Maryann M. Taylor, United States Department of Agriculture, ERRC, Wyndmoor, PA
Green Crust Technology: A Game Changing Chemical Solution for Wet End Processing by Dietrich Tegtmeier, LANXESS Deutschland GmbH, Germany
Automation for Hide Handling by Luca Tisato, Feltre, Italy
Barnini - Preserving the Technology of Quality...Protecting the Quality of Technology by Tieko Tuijnman, Barnini, Italy
Tanning Technologies and Equipment Offered by the Italian Industry by Roberto Vago, ASSOMAC, Italy
The 57th John Arthur Wilson Memorial Lecture
by Rachel Garwood, BSc MSc

Rachel Garwood, Director of the Institute for Creative Leather Technologies (ICLT), Northampton, UK, will present the 57th John Arthur Wilson Memorial Lecture at our Annual Meeting at 9 am Thursday, June 23, 2016. The title of his presentation is:

**Leather Education — Preserving the Past... Investing in the Future**

“Challenges facing the leather industry” is often a topic for discussion: these commonly include environmental legislation; the need for green chemistry, traceability, ethical sourcing and the list goes on. One issue that is crucial for the sustainability of the global leather industry and is often overlooked is “succession planning.” With large cohorts of employees due for retirement between now and 2020, the demand for quality leather graduates is ever increasing, placing a larger reliance on higher education.

The importance of leather education is clearly demonstrated by the success of John Arthur Wilson himself. During his two years study at the University of Leeds he became an award-winning student under the renowned Professor Henry Richardson Proctor, both of whom made significant contributions in the field of leather science and are still referred to in modern leather science education today.

In this review, the history, the present and the future of leather education are explored. What has driven the transition from “chalk and talk” to delivery via virtual space? With advanced information technology we are also facing a changing student and today’s student does not expect to be spoon-fed the facts. Today, they have ready access to information on the internet, so classroom delivery takes on a very different picture. Modes of delivery now incorporate social media, discussion boards, blogs alongside tutorials and seminars.

The ability within education to address these changing demands and an understanding of the ever-changing market pressures will support the sustainability of our high value industry.
Call For Papers
for the 112th Annual Meeting of the
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Oglebay Resort, Wheeling, West Virginia
June 22-25, 2016

If you have recently completed or will shortly be completing research studies relevant to hide preservation, hide and leather defects, leather manufacturing technology, new product development, tannery equipment development, leather properties and specifications, tannery environmental management, or other related subjects, you are encouraged to present the results of this research at the next annual convention of the Association to be held at the Oglebay Resort, Wheeling, West Virginia, June 22-25, 2016

Abstracts must be received by May 15, 2016.

They are to be submitted by e-mail to the ALCA Vice-President and Chair of the Technical Program:

David Peters
DLP Advisors
Phone: +1 240 490 9007
E-mail: DLPeters99@gmail.com

The Abstract should begin with the title in capital letters, followed by the authors’ names. An asterisk should denote the name of the speaker, and contact information should be provided that includes an e-mail address. The abstract should be no longer than 300 English words, and in the Microsoft Word format.

Full Presentations at the convention will be limited to 25 minutes. In accordance with the Association Bylaws, all presentations are considered for publication by The Journal of the American Leather Chemists Association. They are not to be published elsewhere, other than in abstract form, without permission of the Journal Editor. For further paper preparation guidelines please refer to the JALCA Publication Policy on our website: leatherchemists.org

Full Presentations are due by June 15, 2016.

They are to be submitted by e-mail to the JALCA editor:

Robert F. White
Journal Editor
The American Leather Chemists Association
E-mail: jalcaeditor@prodigy.net
Mobile Phone (616) 540-2469

In accordance with the Association Bylaws, all presentations are considered for publication by The Journal of the American Leather Chemists Association.
The Leather Research Laboratory at the University of Cincinnati will be hosting several educational opportunities in 2016:

**Leather Orientation Course**
This popular 2-Day course will take place at the Leather Research Laboratory on the campus of the University of Cincinnati and will cover a wide range of leather related issues such as physical structure, species identification, hide supply, wet-end and finishing operations, regulations, testing and customer acceptance issues. Attendees will also be given an in-depth tour of the Leather Research Laboratory.

The cost of this course is $925 per person with a discounted price of $830 for additional participants from the same company. Dates: August 17 – 18.

**Quality Assurance for Leather Workshop**
This new course is designed for individuals working in the leather industry that need a comprehensive understanding of the best quality control methods for quality leather production. This course will be a blend of classroom instruction along with significant time for hands on application in the laboratory. Participants will be able to perform many of these quality tests and techniques on the provided leather samples or on their own samples. Course materials will include a copy of the book: *Skin, Hide and Leather Defects* by Jean Tancous.

The cost of this course is $1050 per person with a discounted price of $945 for additional participants from the same company. Dates: May 18 – 19 and September 14 – 15.

**Leather Buyers Conference**
This 1.5-day conference is intended for individuals responsible for sourcing decisions within their organization. Attendees will learn the key skills necessary to intelligently source leather and avoid common pitfalls that can cost your company money. This conference will have presentations by representatives from the Leather Research Laboratory, the Washington DC based law firm, Kelley Drye & Warren LLP, Stephan Sothmann from the U.S. Hide, Skin and Leather Association and seasoned industry professional David Peters.

The cost of this 1.5 day conference is $625 per person. Date: July 26-27.

Contact: Rhonda Price at 513 242-6300 or email pricerf@uc.edu for further information or to register for one of these courses. A more detailed agenda for these programs can be found on our website: www.leatherusa.org under the Lab News button.
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112th ANNUAL MEETING
AMERICAN LEATHER CHEMISTS ASSOCIATION

June 22-25, 2016
Oglebay Resort & Conference Center, Wheeling, WV

Presenting the 57th John Arthur Wilson Memorial Lecture
By Rachel Garwood, Director,
Institute for Creative Leather Technologies (ICLT)

Title: Leather Education - Preserving the Past...Investing in the Future

Schedule
Wednesday, June 22
Golf Tournament
Opening Reception, Dinner

Thursday, June 23
John Arthur Wilson Memorial Lecture
Technical Sessions, Fun Run,
Golf Swing Analyzer, Reception,
Dinner and Monte Carlo Night

Friday, June 24
Technical Sessions, Annual Business Meeting
Sports Activities Awards Luncheon
Social Hour & Awards Banquet

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