Salinity reduction in the production of nappa skins by using agents with non-swelling capacity in pickling/tanning.

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Introduction

In previous papers, the behaviour of four commercial products with non-swelling capacity in the pickling/tanning processes of hides\textsuperscript{1,2} and sheepskins\textsuperscript{3,4} was studied. The application of these products gave a significant reduction in salinity.

In the case of sheepskins, it was found that the best results in terms of non-swelling capacity, shrinkage temperature, conductivity and Chemical Oxygen Demand of the residual baths corresponded to the pickling treatments carried out at a salinity of 2º Bé with a 2\% offer of naphtol 3-6 disulphonic acid, or with a 2\% offer of p-hydroxydiphenil sulphonic acid, or with a 4\% offer of polyacrylic acid.

Aim of the work

The objective of this work is to study the influence of the naphtol 3-6 disulphonic acid and the p-hydroxydiphenil sulphonic acid applied in the pickling process of sheepskins on their final chemical, physical and sensorial properties. The results of the study will be compared to those obtained by applying a 6 ºBé conventional pickling process without the addition of any auxiliary agent.

The application of the polyacrylic acid has not been investigated because in the previous work their best results were obtained using an offer as high as 4\% of the commercial product, double quantity of the other two alternatives.

Experimental

Starting material. Pickling and Tanning operations

Sixteen lambskins from Catalonia (Spain) were conventionally processed until the bating operation. Once bated, each skin was cut in two halves along the backbone. The left sides were subjected to a conventional pickling/tanning process adjusting the salinity to 6 ºBé. The sixteen right sides were divided in two groups of eight sides each, which were pickled using non-swelling capacity agents at a salinity of 2 ºBé.

One of these two groups, referenced as “NA” was treated with a 2\% offer of naphtol 3-6 disulphonic acid and the other one (reference “p-H”) with an offer of 2\% p-hydroxydiphenil sulphonic acid. Table I summarizes the processes applied to the three groups.
It is important to emphasize that a 2% of NaCl was sufficient to obtain a salinity of 2ºBé, but a 8% of NaCl was required to reach a salinity of 6ºBé.

Therefore, each alternative method saves the 75% of the NaCl employed in the conventional pickling operation.

<table>
<thead>
<tr>
<th>Process</th>
<th>Conventional</th>
<th>Group “NA”</th>
<th>Group “p-H”</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conditioning</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>80 %</td>
<td>80 %</td>
<td>80 %</td>
<td>25 ºC</td>
</tr>
<tr>
<td>NaCl</td>
<td>6 º Bé</td>
<td>2 ºBé</td>
<td>2 ºBé</td>
<td></td>
</tr>
<tr>
<td>naphtol 3-6 disulphonic acid</td>
<td>-</td>
<td>2 %</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>p-hydroxydiphenil s. acid</td>
<td>-</td>
<td>-</td>
<td>2 %</td>
<td></td>
</tr>
<tr>
<td><strong>Pickling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formic acid (1:10)</td>
<td>1 %</td>
<td>1 %</td>
<td>1 %</td>
<td>Drum 15 min</td>
</tr>
<tr>
<td>Sulphuric acid (1:10)</td>
<td>0.7 %</td>
<td>0.7 %</td>
<td>0.7 %</td>
<td>Drum 2 h</td>
</tr>
<tr>
<td>Adjust pH</td>
<td></td>
<td></td>
<td></td>
<td>pH 3.0 - 3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Drum 1 h</td>
</tr>
<tr>
<td><strong>Tanning</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium salt 33 ºSc</td>
<td>6 %</td>
<td>6 %</td>
<td>6 %</td>
<td>Drum 2 h</td>
</tr>
<tr>
<td>Basifying agent</td>
<td>0.7 %</td>
<td>0.7 %</td>
<td>0.7 %</td>
<td>Drum 8 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>41 - 42 ºC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH 3.8 - 4.2</td>
</tr>
</tbody>
</table>

Table I. Processes carried out after bating (offers on delimed weight)

**Post-Tanning Processes**

Eight of the sixteen “conventional” wet-blue sides were processed to produce nappa skins for clothing, and the other eight were processed to obtain nappa for footwear. Exactly the same processes were applied to the wet blue sides obtained from the two “alternative” pickling methods.

Tables II and III show the post-tanning processes applied for clothing nappa and for footwear nappa, respectively. The skins were shaved to a final thickness of 0.7 mm (clothing) and 1.1 mm (footwear).

All the obtained nappa skins were systematically evaluated for physical resistances, some chemical parameters, and organoleptic properties.

The results of side skins obtained under low salinity conditions were compared to those of the side skins obtained conventionally.
**Wetting**
250 % water at 35°C
0.1 % acetic acid
0.1 % wetting agent
Drum 10 min
Drain

**Retanning**
100 % water at 45°C
2.5 % acrylic resin (with lubricating effect) diluted 1:5 with water
Drum 20 min
2.0 % organo-chromium syntan 12.0 % Cr₂O₃
Drum 90 min  pH around 4.
Drain
200 % water
Drum 15 min
Drain

**Neutralisation**
100 % water at 25°C
1 % sodium formate. Drum 15 min
1.1 % sodium bicarbonate diluted 1:12 with water
Drum approx. 1.5 – 2 hours. pH: 5.9 – 6.3.
Penetration control with bromocresol green
Drain
200 % water at 25°C
Drum 10 min
Drain

**Dyeing and Fatliquoring**
100 % water at 45°C
Drum 5 min
7 % sulphated triolein
1 % sulphonyl chloride paraffin
1 % phosphoric ester  (Emulsified 1:10 with water at 45°C)
Drum 40 min
2.5-3 % dye diluted 1:20.
Drum until penetration
1.5 % formic acid diluted 1:3
Drum 30 min  pH around 3.5
Drain
250 % water at 20°C
Drum 5 min
Drain.
Keep 24 h on a horse.
Setting-out
Air drying
Dry milling for 4 hours

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Table II. Recipe for clothing nappa (offers on wet-blue weight)
Wetting
250 % water at 35ºC
0.1 % acetic acid
0.1 % wetting agent
Drum 10 min
Drain

Retanning
100 % water at 40ºC
10 % naphtalen sulphonic acid (45 % solids)
Drum 2 hours  pH around 4.
Drain
250 % water at 30 ºC
Drum 10 min
Drain

Neutralisation
100 % water at 25ºC
1 % sodium formate. Drum 15 min
0.8 % sodium bicarbonate diluted 1:12 with water
Drum approx. 80 min. pH: 5.4 – 5.8
Penetration control with bromocresol green
Drain
200 % water at 40ºC
Drum 10 min
Drain

Dyeing
30 % water at 20ºC
Drum 2 min
1 % dispersant (naphthalene sulphonic neutral)
2.5-3 % dye (powder)
2 % mimosa
Drum 2 hours (until penetration)

Fatliquoring
200 % water at 50ºC
Drum 5 min
5 % sulphated triolein
1 % sulphonyl chloride paraffin
1 % phosphoric ester  (Emulsified 1:10 with water at 45ºC)
Drum 45 min
1.0 % formic acid diluted 1:4
Drum 25 min  pH around 3.5
Drain
250 % water at 20ºC
Drum 3 min
Drain.
Keep 24 h on a horse.
Setting-out
Air drying

Table III. Recipe for footwear nappa (offers on wet-blue weight)
Results

Chromium content and shrinkage temperature after tannage

The shrinkage temperature was measured after 3 days of resting. The chromium content was determined in samples dried in a standard atmosphere of 23 ºC and 50 % relative humidity.

The shrinkage temperature of the two alternative wet-blue skins was only slightly lower than the value obtained for the conventional wet-blue skins: 109 ºC (p-hydroxydiphenil sulphonic acid) and 111 ºC (naphtol 3-6 disulphonic acid) compared to 114 ºC. The amount of Cr₂O₃ fixed by the skins was also very similar: 3.6 % Cr₂O₃, 3.8% Cr₂O₃, and 3.5% Cr₂O₃, respectively. These small differences can be attributed to the inexactness in taking the initial weight of each group of sides.

Organolectic properties

It is of paramount importance that the new processes do not impede the appearance and the organoleptic properties of the obtained leather.

Before sampling for the physical and chemical testing, the following parameters of the obtained skins were evaluated by an expert panel: handle, colour uniformity, colour depth, appearance of the grain, and grain firmness. The left halves (conventional pickling process), for both clothing nappa and footwear nappa, were compared to the right halves (alternative pickling processes). Each parameter was marked from 1 (bad result) to 5 (good result).

The average values of the results obtained did not show any significant difference except for the handle of footwear nappa, which reached a higher value (5) for the conventional halves than that of the “NA” and “p-H” groups (4 and 4.5 respectively).

Physical Resistances

Samples for physical testing were taken from every left and right side of the nappa skins obtained. Conditioning was carried out in accordance with the IUP 3 Standard.

Tensile Strength, Elongation at break, Tearing Load, and Grain Resistance were systematically measured in accordance with the IUP 6, IUP 8, and IUP 9 methods respectively. From each half-skin from conventional pickling process, three samples were cut, giving a total number of 48 samples for IUP 6, 48 for IUP 8, and 48 for IUP 9 Tests. From each half-skin from naphtol 3-6 disulphonic acid pickling process, four samples were cut, resulting in a total number of 32 pieces for every test. The same sampling was done for the half skins treated with p-hydroxydiphenil sulphonic acid.

The results obtained are shown in tables III and IV.

Slight differences between the three groups for clothing nappa skins (table III) were observed. The comparison between average values of conventional and alternative pickling processes was not statistically significant by applying the Student-t Test at 95 % confidence level.

On the other hand, the physical resistances of footwear nappa skins (table IV) treated with the p-hydroxydiphenil sulphonic acid were somewhat lower. For grain resistance, the difference with the conventionally pickled group was statistically significant.
Conventional naphtol 3-6 disulphonic acid
p-hydroxydiphenil sulphonic acid

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>naphtol 3-6 disulphonic acid</th>
<th>p-hydroxydiphenil sulphonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (N/mm²)</td>
<td>18.8 (± 2.6)</td>
<td>18.1 (± 3.0)</td>
<td>17.5 (± 2.4)</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>80.8 (± 8.7)</td>
<td>75.5 (± 7.6)</td>
<td>82.7 (± 7.5)</td>
</tr>
<tr>
<td>Tearing Load (N/mm)</td>
<td>67.6 (± 6.1)</td>
<td>75.2 (± 9.0)</td>
<td>72.8 (± 4.4)</td>
</tr>
<tr>
<td>Grain Distension (mm)</td>
<td>12.7 (± 1.1)</td>
<td>12.8 (± 0.40)</td>
<td>12.4 (± 0.71)</td>
</tr>
</tbody>
</table>

Table III. Mean values of physical testing for clothing nappa. Standard deviation in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>naphtol 3-6 disulphonic acid</th>
<th>p-hydroxydiphenil sulphonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (N/mm²)</td>
<td>16.0 (± 1.9)</td>
<td>15.6 (± 1.5)</td>
<td>15.4 (± 1.7)</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>53.0 (± 4.0)</td>
<td>48.3 (± 4.7)</td>
<td>49.4 (± 3.5)</td>
</tr>
<tr>
<td>Tearing Load (N/mm)</td>
<td>41.5 (± 6.3)</td>
<td>39.0 (± 6.9)</td>
<td>37.9 (± 2.6)</td>
</tr>
<tr>
<td>Grain Distension (mm)</td>
<td>10.0 (± 0.68)</td>
<td>9.9 (± 0.24)</td>
<td>9.0 (± 0.57)</td>
</tr>
</tbody>
</table>

Table IV. Mean values of physical testing for footwear nappa. Standard deviation in brackets.

However, the physical resistances of the skins obtained in this work clearly exceeded the minimum values provided by the German Quality Guidelines\(^5\) and by GERIC\(^6\) for footwear and clothing leathers. For instance, the lowest value for grain distension for footwear obtained in this study (9.0 mm) was markedly higher than the minimum value recommended (7mm).

**Water absorption**

Water absorption of each skin was measured in static conditions after 12 hours. Although the differences between the conventionally and non-conventionally pickled skins were not very high, the results (table V) showed a tendency to lower water absorption values for skins pickled under low salinity conditions.

However, only the difference between the conventionally pickled group and the naphtol 3-6 disulphonic acid treated skins for clothing was statistically significant at a confidence level of 95%.

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>naphtol 3-6 disulphonic acid</th>
<th>p-hydroxydiphenil sulphonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nappa for clothing (%)</td>
<td>129 (± 13)</td>
<td>109 (± 2.5)</td>
<td>112 (± 6.7)</td>
</tr>
<tr>
<td>Nappa for footwear (%)</td>
<td>127 (± 15)</td>
<td>112 (± 2.0)</td>
<td>114 (± 13)</td>
</tr>
</tbody>
</table>

Table V. Mean values of water absorption after 12 hours. Standard deviation in brackets.
Light fastness

Light fastness was evaluated on skins without finishing. Thirty-two determinations were carried out.

Footwear nappa: Grades 1-2 on the Grey Scale were achieved for the three nappa types.

Clothing nappa: Grades 2-3 on the Grey Scale were obtained for conventional and p-hydroxydiphenil sulphonic acid skins whereas skins treated with naphtol 3-6 disulphonic acid showed a Grade of 2.

A negative influence of the retanning operation with both vegetable extracts and naphthalene sulphonic agents was noticed in the nappa for footwear produced. No very marked difference between naphtol 3-6 disulphonic acid and p-hydroxydiphenil sulphonic acid for clothing nappa was observed. However, these results should be confirmed in later studies.

Concentration of chlorides and other water-soluble substances

A lower chloride concentration in the nappa skins obtained under low salinity conditions than in the conventionally pickled nappa could be expected.

This reduced concentration of inorganic soluble components would possibly result in some advantages: a decreased tendency to migrations and a lower risk of corrosion of metallic components annexed to leather.

However, the results of organic and inorganic soluble matter, determined in accordance with the IUC 6 and IUC 7 Standards (tables VI and VII), did not show any relevant differences. To verify these results, the aqueous extracts of the six types of nappa skins were analyzed by Capillary Electrophoresis in order to determine the concentration of chlorides.

Capillary Electrophoresis (CE) is a powerful separation technique. Its selectivity is based on the ionic equivalent conductances of the analytes and its separation efficiency typically exceeds 100,000 theoretical plates. Capillary Electrophoresis has been previously applied in the determination of different anionic substances in samples from the leather industry.

Figure 1 and tables VI and VII show the results obtained. They revealed that the differences in chloride concentration between the conventionally and non-conventionally pickled skins were lower than a 10% factor, a small value of no practical consequence.

In all the cases, the type of retanning process appeared to be a more important factor. For instance, the content of soluble sulphates in the skins for footwear was almost twice that of the skins for clothing.

Therefore, it has to be concluded that the washings carried out during the whole process have nearly eliminated the excess of sodium chloride of the conventional pickling method.
### Table VI. Concentration of water-soluble substances in clothing nappa

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>naphtol 3-6 disulphonic acid</th>
<th>p-hydroxydiphenil sulphonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble chlorides</td>
<td>0.24 % Cl⁻</td>
<td>0.23 % Cl⁻</td>
<td>0.22 % Cl⁻</td>
</tr>
<tr>
<td>Soluble sulfates</td>
<td>0.36 % SO₄²⁻</td>
<td>0.44 % SO₄²⁻</td>
<td>0.39 % SO₄²⁻</td>
</tr>
<tr>
<td>Total soluble matters</td>
<td>1.6 %</td>
<td>1.6 %</td>
<td>1.4 %</td>
</tr>
<tr>
<td>Inorganic soluble matters</td>
<td>1.1 %</td>
<td>1.2 %</td>
<td>1.1 %</td>
</tr>
<tr>
<td>Organic soluble matters</td>
<td>0.5 %</td>
<td>0.4 %</td>
<td>0.3 %</td>
</tr>
</tbody>
</table>

### Table VII. Concentration of water-soluble substances in footwear nappa

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>naphtol 3-6 disulphonic acid</th>
<th>p-hydroxydiphenil sulphonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble chlorides</td>
<td>0.23 % Cl⁻</td>
<td>0.21 % Cl⁻</td>
<td>0.21 % Cl⁻</td>
</tr>
<tr>
<td>Soluble sulfates</td>
<td>0.68 % SO₄²⁻</td>
<td>0.75 % SO₄²⁻</td>
<td>0.79 % SO₄²⁻</td>
</tr>
<tr>
<td>Total soluble matters</td>
<td>2.7 %</td>
<td>3.0 %</td>
<td>2.9 %</td>
</tr>
<tr>
<td>Inorganic soluble matters</td>
<td>1.6 %</td>
<td>1.7 %</td>
<td>1.8 %</td>
</tr>
<tr>
<td>Organic soluble matters</td>
<td>1.1 %</td>
<td>1.3 %</td>
<td>1.1 %</td>
</tr>
</tbody>
</table>

### Conclusions

The tanning process of the skins pickled under low salinity conditions was carried out without problems. The amount of chromium fixed by these skins was very similar to that of skins conventionally pickled. Consequently, satisfactory shrinkage temperatures were obtained. As far as organoleptic properties are concerned, handle and appearance were similar in all the nappa skins obtained, independently of the pickling process applied.

Tests of physical resistances such as Tensile Strength, Tearing Load, and Grain Resistance gave rise to good results for all the skins subjected to the different pickling processes. Specially, no marked difference was observed between conventional skins and those treated with naphtol 3-6 disulphonic acid. Resistances were somewhat lower for footwear skins pickled with p-hydroxydiphenil sulphonic acid. In any case, all the skins obtained in this work fulfilled the existing Quality Guidelines. Most of the differences between results obtained as a function of the pickling process applied were not statistically significant. However, in some cases, a tendency could be observed.

Skins pickled under low salinity conditions showed a tendency to reduced water absorption values.

As expected, a lower chloride concentration in the non-conventionally pickled nappa skins was found. However, the differences were negligible, and the percentage of inorganic soluble matters was very similar in the conventionally and non-conventionally pickled skins.
In conclusion, the use of products with non-swelling capacity appears to be an excellent alternative to conventional pickling/tanning operations in the production of nappa sheepskins. It allows a significant diminution of salinity (a reduction of sodium chloride consumption of around 75 %) while the functional and sensorial properties of the nappa are maintained when compared to skins produced conventionally.

Acknowledgements

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References

**Chemicals utilized in this work**

Retanal HD:  p-hydroxydiphenyl sulphonic acid
Retanal A-4:  naphtol 3-6 disulphonic acid:
Plenatol HBE: basifying agent in table 1.

![Electropherogram](image)

**Figure 1.** Comparison between the electropherogram of the water soluble substances extracted from the conventionally pickled nappa skins for footwear (in green) with those of skins treated with the low salinity processes (in red and blue). 10 mL of the samples, which were obtained in accordance with the IUC 6 Standard, were diluted to 150 mL, and molybdate ion was added as internal standard. Peaks: 1 = chloride; 2 = sulphate; 3 = molybdate; 4 = formate. Concentration of internal standard in each diluted sample was 20 mg/L of $\text{Mo}_7\text{O}_{24}^{6-}$. Concentration of chlorides ranged from 2.8 to 3.1 mg/L, sulphates were between 9.1 and 10.5 mg/L, and formate ion was not quantified. Instrument: Waters CIA System. Capillary: Fused-silica 60 cm x 75 μm. Electrolyte: Potassium chromate with electro-osmotic flow modifier in the hydroxide form. Indirect UV detection performed with a Hg lamp at 254 nm.