ECOLEATHER

SUSTAINABLE DEVELOPMENT OF PRODUCTION TECHNOLOGIES IN LEATHER INDUSTRY
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Partners and financiers

- Technology Centre KETEK Ltd.
- Ahlskog Leather,
  - Main product: Reindeer leather
- Kokkolan Nahka
  - Main product: Moose leather
- Centre for Economic Development, Transport and the Environment (financier)
- KOSEK (financier)
- European Regional Development Fund (financier)
What is EcoLeather?

- Reason we are here at LeatherKokkola
  - Idea
  - Funding
What is EcoLeather?

• Project started at summer 2013
• Preliminary literature study before that at spring 2013
  • Different tanning processes and chemicals
  • Waste information
  • Different Ecolabels
• Ends at december 2014
• Follow-up to Nahkajäte-project
What is EcoLeather?

• Project was started to help local tanneries to make their products more eco-friendly and business more profitable.
  • Only two tanneries left in local area.
• Local tanneries can compete only with quality not quantity
  • Lots of leather comes from Asia
• New restriction in waste amounts in Finland
  • Chromium, sulphates, chlorides
  • Banning of chromium salts in leather tanning in EU?
What is EcoLeather?

Goal is to...

- develop chromium-free tanning process or at least decrease chromium(III)salt amounts in our local tanneries if possible
  - More eco-friendly process, waste problems
  - Brighter colours
- Chloride and sulphate amounts has to be decreased
  - Waste problems
  - Decreasing of chloride amounts is difficult
- Get information about different Eco labels
  - Added value to product?
- Nanotechnology in leather products?
  - Tanning
  - Finishing
What is EcoLeather?

How everything is done?

• Find information about new tanning chemicals
  • Chromium-free
  • Sulphate-free
  • Produces white and bright leather
  • Nanotechnology?
    • Six most promising chemicals selected
• Lab scale testing
  • Comparison with colour and feel, shrinkage temperature and mechanical tests
  • Reindeer and moose hides
• Pilot testing for the most suitable modern tanning chemicals
• Analyzation of wastes produced in tanneries after pilot testing
Ecolabels

- Nordic
  - Supervised in Finland by Motiva
  - Mostly know in nordic area
  - New criteria for leather and textile products in Dec 2012
    - Possibility to get ecolabel for reindeer and moose products
    - Before only for farm animal hides
  - Very tight criteria and limits for example in waste amounts
  - No nanos!!
  - Some unaccurate criteria
    - E.g. mechanical test limits
  - No added value to our local tanneries

Ecolabels

- EU Ecolabel
  - Not clear criteria for leather products
    - Some criteria for leather shoes
    - Motiva says, that criteria for Nordic ecolabel can be used when applying
    - Might bring added value to finished products in the future
      - Big clients in southern Europe
Preliminary tests

Materials:
• Leather
  • Mostly pickled reindeer and moose hides
    • Provided by AhlSkog Leather and Kokkolan Nahka
  • As even thickness as possible
  • One tanning chemical required unpickled hides
• Tanning chemicals
  • Mostly commercial tanning chemicals
    • Provided by manufacturers as free test samples
  • D-Lysine + glutaraldehyde
    • D-Lysine made from L-lysine monohydrochloride with racemization
  • Nano-SiO2
  • Sigma-aldrich

Preliminary tests

- Overhead shaker
- Four 500 ml glass bottles with wide neck
Preliminary tests

- Shrinkage temperature
  - DSC
  - ISO 3380
- Tear load, tensile strength, Elongation at break
  - tests were made in textile lab of Centria University of Applied Sciences, Kokkola
  - Tensile tester with 5 kN load cell
  - ISO 3377-1, 3380, 3376
  - At least two test pieces parallel and perpendicular to backbone
- The feel and appearance of the leather
Preliminary tests

• With CrSO4
• To check how good leather our system produces
• Comparison to leathers of tanneries
  • Shrinkage temperature, Tear load, the feel and appearance

<table>
<thead>
<tr>
<th></th>
<th>Shrinkage temperature</th>
<th>Tear strength, parallel to backbone (N)</th>
<th>Tear strength, perpendicular to backbone (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>reindeer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrSO4 (ahlskog)</td>
<td>&gt;100</td>
<td>27.1</td>
<td>17.0</td>
</tr>
<tr>
<td>CrSO4 (KETEK)</td>
<td>&gt;100</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>moose</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrSO4 (Kokkolan nahka)</td>
<td>~115 (DSC method)</td>
<td>150.9</td>
<td>148.9</td>
</tr>
<tr>
<td>CrSO4 (KETEK)</td>
<td>93</td>
<td>76.6</td>
<td>77.9</td>
</tr>
</tbody>
</table>
Preliminary tests

- Shrinkage temperature and mechanical tests are made also for finished leathers of tanneries with different thicknesses
  - Information of properties of current products
  - When thickness increases, tear load and breaking force increases exponentially

*Graph showing force (N) vs. thickness of leather (mm) for Kokkolan nahka 1; 1,5 and 2,0 mm*
Problems:

- Wasn’t possible to take samples according standard ISO 2418
  - Small test pieces from different areas of hides
- Different properties in different areas of leather
- Thickness of moose leather
  - Sometimes over 4 mm

ISO 2418:2002, Leather – Chemical, physical and mechanical and fastness tests – Sampling location
Preliminary tests

Shrinkage temperature, DSC method

- Differential Scanning Calorimetry
  - Detects endothermic or exothermic reactions of sample such as leather shrinkage
- Possibility to determine shrinkage temperatures of $>100 \, ^\circ C$
  - ISO 3380 only for $\leq 100 \, ^\circ C$
- 5 K/min heating to $170 \, ^\circ C$, high-pressure pans
- Onset or peak temperature?
- Peak broadening was a problem with some samples

\[\text{2 Loke W.K., Khor E. Biomaterials, 1995, 16, 251-258}\]
# Shrinkage temperature, DSC method

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>DSC/(mW/mg)</th>
<th>Peak: 132.5 °C</th>
<th>Peak: 119.0 °C</th>
<th>Onset: 70.1 °C</th>
<th>Onset: 128.2 °C</th>
<th>Onset: 127.5 °C</th>
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<td>0.60</td>
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</tbody>
</table>

**File**
- PS13-38-1-01_chul_va...
- PS13-38-1-02_chul_va...
- PS13-38-1-03_chul_va...

**Identity**
- Chul. valk. kromi
- Chul. valk. kromi
- Chul. valk. kromi

**Date**
- 27.5.2013 12:45:18
- 27.5.2013 14:09:47
- 27.5.2013 15:38:48

**Mass**
- 6.300 mg
- 6.800 mg
- 6.800 mg

**Segment**
- Y/1
- Y/1
- Y/1

**Range**
- 25 °C/5.0(K/min)/170 °C
- 25 °C/5.0(K/min)/170 °C
- 25 °C/5.0(K/min)/170 °C

**Atmosphere**
- --- / N2/20
- --- / N2/20
- --- / N2/20

**Correction**
- 000
- 000
- 000

---

**Note:**
- The table above shows the shrinkage temperature data obtained using the DSC method. The peak temperatures are indicated for each sample, along with the onset temperatures. The data includes information on the instrument used (NETZSCH DSC 204) and the file names, identities, dates, masses, segments, ranges, atmospheres, and corrections for each sample.
Lab scale tanning

- Six different tanning methods were selected for testing
  - Tanfor T (Taminco)
  - Granofin Easy F-90 (stahl)
  - X-Tan (Lanxess)
  - Zoldine ZE / Zoldine ZA-78 (Oxazolidine based, ANGUS)
  - D-lysine + glutaraldehyde (not commercial, ordered from sigma-aldrich)
  - Nano-SiO2 tanning (not commercial, ordered from sigma-aldrich)
Lab scale tanning

First results:

- Oxazolidines (Zoldine ZE and Zoldine ZA-78)
  - White and bright leather
  - Mechanical properties almost as good as with chromium tanned leather
  - Shrinkage temperature ca. 72 °C (chromium: almost 100 °C)
- Really bad odor
- Leather felt “empty”
- EU-project at 2012 (OXATAN)
- TOXIC!!
  → Not selected for further testing
Lab scale tanning

First results:

- D-lysine + glutaraldehyde tannage
  - D-lysine manufactured from L-lysinehydrochloride by racemization
    - Racemization ratio not determined
      - Krishnamoorthy et al: The yield of D-lysine is 90%
  - Strong yellowish colour
  - Shrinkage temperature over 70 °C
  - Good elongation
  - Not commercial
  - Small amount of glutaraldehyde is used
    - TOXIC!
  - Not selected for further testing

Lab scale tanning

First results:

- Tanfor T
  - the best appearance and feel
  - brightest and whitest colour
    - Simplifies dyeing and finishing
    - Bright colours
  - Similar tanning process with Chromium tanning
  - Cheap
  - Shrinkage temperature over 80 °C
  - Not as good mechanical properties

→ Selected for further testing
Lab scale tanning

First results:

- Granofin Easy F-90
  - white colour
  - Not as bright as Tanfor T
  - “empty” feel
  - No pickle needed!!
    - Simplifies process, less acids and chlorides to wastes
  - Good Mechanical properties
  - Shrinkage temperature under 70 °C

→ Selected for further testing
Lab scale tanning

Retanning of Granofin and Tanfor T tanned leathers

- With 3 w-% of CrSO4
  - Huge effect on shrinkage temperature and mechanical properties
    - On the same level with chromium tanning
  - Only small changes to tanning process
  - Brings back bluish colour to leather
  - Less chromium and sulphates to wastes
  - 3 w-% too much?
# Lab scale tanning

<table>
<thead>
<tr>
<th></th>
<th>Shrinkage temperature</th>
<th>Tear strength, parallel to backbone (N)</th>
<th>Tear strength, perpendicular to backbone (N)</th>
<th>Tensile strength, parallel to backbone (MPa)</th>
<th>Tensile strength, perpendicular to backbone (MPa)</th>
<th>Elongation on break, parallel to backbone (%)</th>
<th>Elongation on break, perpendicular to backbone (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Moose</strong></td>
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<tr>
<td>CrSO4 (KETEK)</td>
<td>93</td>
<td>76.6</td>
<td>77.9</td>
<td>8.9</td>
<td>16.1</td>
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<td>80</td>
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<td>Tanfor</td>
<td>79</td>
<td>33.8</td>
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<td>Tanfor + CrSO4</td>
<td>99</td>
<td>48.7</td>
<td>61.1</td>
<td>11.8</td>
<td>12.3</td>
<td>72</td>
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<tr>
<td>granofin</td>
<td>61</td>
<td>77.9</td>
<td>63.8</td>
<td>12.0</td>
<td>12.1</td>
<td>78</td>
<td>96</td>
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<td>granofin + CrSO4</td>
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<td>98.1</td>
<td>90.0</td>
<td>14.4</td>
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<td>115</td>
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<td><strong>reindeer</strong></td>
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<tr>
<td>CrSO4 (KETEK)</td>
<td>&gt;100</td>
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<td>15.0</td>
<td>9.0</td>
<td>9.7</td>
<td>84</td>
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<td>Tanfor</td>
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<td>5.7</td>
<td>60</td>
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<td>Tanfor + CrSO4</td>
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<td>granofin + CrSO4</td>
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<td>7.9</td>
<td>7.6</td>
<td>122</td>
<td>107</td>
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</table>
Lab scale tanning

Next?

- Retanning optimization
  - Amount of CrSO4
- Tighter comparison between granofin and Tanfor T
  - More mechanical tests
  - Plusses and minuses
- Combination tanning with granofin and Tanfor T?
  - Granofin seems to have better mechanical properties
  - Tanfor T better appearance, feel and colour
- Nano-SiO2 tanning
  - Chinese study \(\rightarrow\) required information in Chinese
Pilot testing

- Tanfor + CrSO4, Granofin Easy F-90 + CrSO4
- Samples for testing after several process phases
- Sampling according ISO 2418 if possible
- Comprehensive testing
  - Mechanical test
    - Tear load, tensile strength, elongation on break
  - Shrinkage temperature
    - According ISO 3380
    - DSC-method if needed
  - Feel, appearance, colour
- Waste analyzation
  - Nahkajäte