Green Beamhouse – A toolbox for cleaner Waste water

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xxx
1. Introduction

2. Green Beamhouse – Lanxess’ roadmap for cleaner waste water
   a. TDS/Salt reduction: The Peltec C process
   b. COD reduction: The Peltec X-Zyme process
   c. Sludge reduction: The Peltec X-Zyme SLR process

3. Details Green Beamhouse - A Life Cycle Assessment (LCA) of the X-Zyme process
Sustainability has become one of the mega-trends – also for leather production

Sustainability = Waste water improvement

“Green Beamhouse Toolbox” by Lanxess

Component | Product
--- | ---
Salt | Blancorol® HP, Peltec® C
COD | Peltec® X-Zyme SN / U
Sludge | Peltec® X-Zyme SLR
Sulfide | Peltec® X-Zyme U
Nitrogen | Peltec® UNF
Ammonia | Peltec® DLP / DL

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Target of lower waste in waste water can be achieved in different ways

**Process-based improvements**

Waste water improvements which require change of tannery processes or different mechanical processes, e.g.

- Fresh hide utilization / Brine curing CLRI
- Green fleshing
- Lime recycling
- Hair saving process
- Lime splitting

**Product-based improvements**

Waste water improvements which require changes of the recipe. Changes can significantly impact all relevant waste-water components, for India e.g.

- TDS
- COD
- Sludge

**Green Beamhouse Toolbox**
Salt Improvement: Avoidance of pickle or utilization of a low-salt pickle

**General idea / theory**

### Origin of salt
- Largest amount of salt derives from preservation (salting) of raw-hides
- Second largest salt-addition is during pickling, ending up in the waste water

### How to avoid salt
- Utilization of fresh hides
- Avoidance of pickle by switching to specific organic tanning agents (e.g. X-Tan®)
- Reduction of pickle-salt addition by utilization of Blancorol® HP

**LXS product solution**

### Peltec® C /DLP
- Deliming with Peltec® C or Peltec® DLP reduces salt application
- Pickling with Peltec® C combined with Blancorol® HP does not require additional salt

### Blancorol® HP
- Blancorol® HP helps to reduce salt requirements to 3.8 Bé (std: 6-8 Bé) ➔ less salt in waste water
- 1.5 to 2% Blancorol® HP (fully) replaces sulfuric acid plus partly formic acid
- Blancorol® HP enables earlier chrome addition and reduces pickling time <1 hour

**Impact of Peltec® C, Blancorol® HP**

- [Graph: Reduction of salt from 80 to 44%]
Low salt Deliming Process
Peltec\textsuperscript{®} C and Blancorol\textsuperscript{®} HP save salt and water

Application Details

- Pelt splitting recommended
- Peltec\textsuperscript{®} C to be used as single deliming agent
- Bating at pH 8.5
- Best results in combination with Blancorol\textsuperscript{®} HP pickle process
- No wash after deliming, only float reduction
- Float Bé of 4° required, can be adjusted with Peltec\textsuperscript{®} C
- Addition of Blancorol\textsuperscript{®} HP as replacement for sulfuric acid
- Application of CTS at penetration of pickle of ca. 50%
  Gain: More time for CTS penetration

Standard vs. Peltec\textsuperscript{®} C process = 70kg/t less salt

<table>
<thead>
<tr>
<th>Product</th>
<th>Standard process</th>
<th>Peltec C process</th>
<th>Δ - TDS</th>
<th>Δ - water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deliming water</td>
<td>50%</td>
<td>50%</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>ammonia sulfate</td>
<td>2.5%</td>
<td>0%</td>
<td>-2.5%</td>
<td></td>
</tr>
<tr>
<td>PELTEC C</td>
<td>0%</td>
<td>1.5%</td>
<td>+1.5%</td>
<td></td>
</tr>
<tr>
<td>Na- bisulite</td>
<td>0.3%</td>
<td>0.3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bating agent</td>
<td>0.4%</td>
<td>0.4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wash water</td>
<td>200%</td>
<td>0%</td>
<td>-200%</td>
<td></td>
</tr>
<tr>
<td>Pickle water</td>
<td>50%</td>
<td>0-20%</td>
<td>-6%</td>
<td>-30%</td>
</tr>
<tr>
<td>NaCl</td>
<td>6%</td>
<td>0%</td>
<td></td>
<td>-6%</td>
</tr>
<tr>
<td>sulfuric acid</td>
<td>1.3%</td>
<td>0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BLANCOROL HP</td>
<td>0%</td>
<td>1.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTS</td>
<td>6%</td>
<td>6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.5%</td>
<td>0.5%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Savings

-7%  -230%
X- Blue Tanning, Pickle Free Tanning system
A Two Step Tanning Process with salt savings

1. X-Tan® Wet White Process
   - Pelt splitting recommended
   - Salt fee deliming with Peltec® DLP
   - Bating at pH 8.5
   - No pickle required ➔ no addition of NaCl required
   - Tanning process starts at pH 8.5 and ends at pH 4.5

2. X-White Chroming Process
   - Shaving of wet white
   - Reduction of products/salt due to 1/3 less hide weight
   - Start retannage with chrome tannage
   - No pickle required ➔ no addition of NaCl required

<table>
<thead>
<tr>
<th></th>
<th>Standard process</th>
<th>X-Blue Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deliming water</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>ammonia sulfate</td>
<td>2.5%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Na- bisulphite</td>
<td>0.3%</td>
<td>0.3%</td>
</tr>
<tr>
<td>bating agent</td>
<td>0.4%</td>
<td>0.4%</td>
</tr>
<tr>
<td>wash water</td>
<td>200%</td>
<td>200%</td>
</tr>
<tr>
<td>Pickle water</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>NaCl</td>
<td>6%</td>
<td>3%</td>
</tr>
<tr>
<td>sulfuric acid</td>
<td>1.3%</td>
<td>1.3%</td>
</tr>
<tr>
<td>CTS</td>
<td>6%</td>
<td>3%</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5%</td>
<td>6%</td>
</tr>
<tr>
<td><strong>Total Salt:</strong></td>
<td><strong>17%</strong></td>
<td><strong>11%</strong></td>
</tr>
</tbody>
</table>

Standard vs. X-Blue process = 35% less salt

Deliming water 50%
Pelitec DLP 2.0%
Na- bisulphite 0.3%
bating agent 0.4%
wash water 200%
Pickle water 50%
X-Tan Tannage water 50%
X-Tan W 3%
Tanigan HS 3%
formic acid 1%
shaving 1/3 weight reduction
Retannage
Chroming formic acid 0.5%
CTS 6%
Neutralisation customer
Retannage customer
**Total Salt:** 11%
COD Improvement: Removal of hide components and reduction of surfactants by enzymatic process

**General idea / theory**

- **Origin of COD**
  - Organic matter of raw hides which is washed out during beamhouse process
  - Organic beamhouse chemicals added to the process and finally end up in waste-water as COD

- **How to avoid COD**
  - Avoidance of unnecessary hydrolysis of the hide / switching to hair saving process
  - Reduction of organic chemical additives by switching to enzymatic process

**LXS product solution**

- **Peltec® X-Zyme SN**
  - Enzyme-based product ensuring the mild washing out of hyaluronic acid during soaking
  - Peltec X-Zyme SN reduces otherwise required surfactants that end up as COD in waste water

- **Peltec® X-Zyme U**
  - Enzyme-based product which cleaves the hair roots forming easily filterable hair
  - Subsequent hair saving process allows significant reduction of COD

**Impact of Peltec® X-Zyme SN / U**

- Peltec X-Zyme SN reduces COD by 39%
- Peltec X-Zyme U reduces COD by 42%
COD Improvement
Peltec® X-Zyme Process

Soaking: Peltec® X-Zyme SN

Background
- Key target is removal of non-collagenous proteins
- Hyaluronic acid (HA) is locked in place by glucose amino glycans (GAGs) of dermatan sulfate proteoglycan (DSP)

Process
- Cleavage of GAGs allows easy removal of HA
- No proteolytic activity of enzyme: No damage of collagen during prolonged soaking or accidental overdosing

COD reduction
- No application of wetting agent
- Strongly reduced amount of emulsifier required
- No degreasing during soaking
- Application of Peltec® BLE-F for grease reduction

Unhairing: Peltec® X-Zyme U

Background
- No pulping of hair improves the waste water
- Reduction of lime: moderate swelling causing less wrinkles

Process
- Peltec® X-Zyme U selectively degrades basal membrane of epidermis and loosening the hair roots
- Hair loosening is achieved after ca. 45-60 min; enzymatic activity is completely stopped by pH-increase
- Addition of lime results in immunization of hair

COD reduction
- Subsequent (semi) hair-saving process with reduced amount of lime removes residual hair with moderate swelling
- Replaces application of organic sulfur compound (mercaptan), which increases the COD
- Application of lipase Peltec® BLE-F does not contribute to COD
Sludge Improvement: Removal of inorganic sludge by replacement of lime during opening up

General idea / theory

Origin of Sludge
- Organic sludge results from unhairing: hair and pulped hair plus epidermis. Furthermore it originates from dirt / dung and scraped of sub cutis
- Inorganic sludge mainly results from hydrated lime

How to avoid Sludge
- Employment of hair saving process incl. hair filtering, green fleshing
- Replacement or reduction of lime by alternative products

LXS product solution

Peltec® X-Zyme SLR
- Replacement for hydrated lime
- Enzyme-based product
- Ensuring good “opening up” of collagen
- Uniform soaking

Peltec® X-Zyme U
- Enzyme based unhairing auxiliary
- Improved hair saving process with hair filtering

Impact of Peltec® X-Zyme SLR

Sludge not pressed

-60%
Sludge reduction
Peltec® X-Zyme SLR process

Lime free opening up results in significant sludge reduction

Background
- Enzymatic lime free opening up of the fiber structure
- Strong selective action on dermatan sulfate proteoglycan → opening up process

Process
- Opening up moved to soaking process → Peltec® Zyme SLR applied in the soaking
- Small amount of lime (0.8%) added for immunization
- Reduced offer of swell regulator required due to lower alkalinity
- Reduced volume of deliming agent required due to less lime added
- Full sustainability results achieved in combination with Peltec® X-Zyme U

Sludge reduction and more advantages
- Significantly less sludge with good biodegradability achieved (ca. 40-70% reduction)
- Improved COD vs. standard X-Zyme process
- Crust with soft round handle
- Good physical properties
- Excellent waterproofing conditions
Summary: Reduction factors of critical waste water components

<table>
<thead>
<tr>
<th>Waste water component</th>
<th>Product</th>
<th>Reduction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td>Blancorol® HP, Peltec® C</td>
<td>-44%</td>
</tr>
<tr>
<td>COD</td>
<td>Peltec® X-Zyme S, U</td>
<td>-42%</td>
</tr>
<tr>
<td>Sludge</td>
<td>Peltec® X-Zyme SLR</td>
<td>-60%</td>
</tr>
<tr>
<td>Sulfide</td>
<td>Peltec® X-Zyme U</td>
<td>-24%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Peltec® UNF</td>
<td>-20%</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Peltec® DLP / DL</td>
<td>-74%</td>
</tr>
</tbody>
</table>

Next step: LCA X-Zyme process

- A Life Cycle Assessment (LCA) describes the impact of a complete BH-process, not of single products. It looks at all relevant compartments:
  - Fossil energy
  - Global warming
  - Eutrophication
  - Toxicity
  - Acidification
  - Photo chemical ozone formation
  - Agricultural land use
  - Fresh water use
  - Solid waste

- In comparative LCA only the differences caused by process shift are analyzed and reviewed
Comparative LCA: Peltec® X-Zyme process offers significant reduction of chemicals

Recipe-comparison between Standard- and X-Zyme process

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Soaking</td>
<td>Surfactant</td>
<td>0,20%</td>
<td>0,10%</td>
<td>-0,10%</td>
</tr>
<tr>
<td></td>
<td>Protease</td>
<td>0,50%</td>
<td></td>
<td>-0,50%</td>
</tr>
<tr>
<td></td>
<td>Peletec X-Zyme S</td>
<td>0,12%</td>
<td>0,12%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Preservative</td>
<td>0,15%</td>
<td>0,15%</td>
<td>0,00%</td>
</tr>
<tr>
<td>Liming</td>
<td>Surfactant</td>
<td>0,10%</td>
<td></td>
<td>-0,10%</td>
</tr>
<tr>
<td></td>
<td>Thioglycolic acid</td>
<td>0,80%</td>
<td></td>
<td>-0,80%</td>
</tr>
<tr>
<td></td>
<td>NaHS</td>
<td>1,00%</td>
<td>1,00%</td>
<td>0,00%</td>
</tr>
<tr>
<td></td>
<td>Ca(OH)₂</td>
<td>3,00%</td>
<td>2,50%</td>
<td>-0,50%</td>
</tr>
<tr>
<td></td>
<td>Na₂S</td>
<td>2,50%</td>
<td>1,00%</td>
<td>-1,50%</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
<td>0,34%</td>
<td>0,34%</td>
<td>0,00%</td>
</tr>
<tr>
<td></td>
<td>Na₂CO₃</td>
<td></td>
<td>0,20%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peletec X-Zyme U</td>
<td>0,08%</td>
<td>0,08%</td>
<td></td>
</tr>
</tbody>
</table>

In this example a semi hair saving (tannery std.) and a X-Zyme hair saving process were compared.

- Recipes are customer specific, but principles apply to virtually all tanneries.
- All values derive from full size production trials.
- Both processes are suitable for upholstery and shoe-upper leather.
- Net-reduction of chemicals are 30kg / ton of pelts.
- Significant improvement of waste water regarding COD, BOD, sulfide.

Published: International Leather Maker Nov/Dec 2017
Comparative LCA: Peltec® X-Zyme process leads to beneficial results in almost all impact categories

Comparison of waste water values

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit</th>
<th>Saved</th>
<th>Induced</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global warming</td>
<td>kg CO₂ equivalents</td>
<td>65</td>
<td>14</td>
<td>50</td>
</tr>
<tr>
<td>Acidification</td>
<td>g SO₂ equivalents</td>
<td>360</td>
<td>58</td>
<td>302</td>
</tr>
<tr>
<td>Nutrient enrichment</td>
<td>g PO₄³⁻ equivalents</td>
<td>107</td>
<td>40</td>
<td>66</td>
</tr>
<tr>
<td>Photochemical ozone formation</td>
<td>g C₂H₄ equivalents</td>
<td>36</td>
<td>3</td>
<td>32</td>
</tr>
<tr>
<td>Energy resources</td>
<td>MJ lower heating value</td>
<td>931</td>
<td>199</td>
<td>731</td>
</tr>
<tr>
<td>Agricultural land use</td>
<td>m²y</td>
<td>4.4</td>
<td>8.5</td>
<td>-4.1</td>
</tr>
</tbody>
</table>

X-Zyme process savings on global warming for 1000hide tannery:
Equivalent to 122 cars / y
How to improve waste water

Process changes (e.g. hair saving) have large effects on waste water.

Green Beamhouse offers further improvements by recipe changes.

Peltec X-Zyme process is the flagship for waste water improvements.
Quality avoids waste
Sulfide Improvement: Replacing sulfide containing reduction agents by enzymatic unhairing system

**General idea / theory**

**Origin of sulfide**
- Sulfides are added for unhairing in the form of Na$_2$S, NaHS or mercaptans

**How to avoid sulfide**
- Reduce required sulfide-volume by switching from hair burning to hair saving process
- Switching to a non-sulfide unhairing system (e.g. oxidative unhairing)
- Reduction of sulfide addition by utilizing enzymatic unhairing additives

**LXS product solution**

**Peltec X-Zyme U**
- Enzyme-based product cleaving the hair roots. Hereby partly substituting sulfide action and leading to less required sulfide
- Improved removal of hair roots leading to cleaner grain
- Pelts are reported to be flatter and smoother

**Impact of Peltec X-Zyme S/U**

<table>
<thead>
<tr>
<th>Sulfide [mg/l]</th>
<th>Hair Burning</th>
<th>Hair Saving</th>
<th>X-Zyme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide</td>
<td>3,500</td>
<td>3,200</td>
<td>2,600</td>
</tr>
<tr>
<td>Impact (%)</td>
<td>-28%</td>
<td>-24%</td>
<td></td>
</tr>
</tbody>
</table>
Nitrogen Improvement: Introduction of lime recycling and utilization of amine-free swell regulators

**General idea / theory**

Origin of nitrogen
- Nitrogen derives from proteins of the raw hides ending up in the waste water
- Swelling regulators in liming are traditionally based on amines

How to avoid nitrogen
- Reduce amines from hides:
  - Liming: Switch to hair saving
  - Pickle: Shorten time and reduce temperature to avoid hydrolysis
- Introduce lime-recycling system which re-utilizes liming float including swell regulators
- Utilization of nitrogen-free swell regulators

**LXS product solution**

Peltec UNF
- Product is based on patent-applied nitrogen-free chemistry:
  - No nitrogen is added to the float
- Product regulates the swelling during liming process and ensures good opening up
- No extensive plumping leads to reduced growth marks and belly draw as well as better removal of hair roods which results in clean pelts
- Cost competitive versus traditional products

**Impact of Peltec X-Zyme S/U**

<table>
<thead>
<tr>
<th>Nitrogen in liming float [mg/l]</th>
<th>Hair burning</th>
<th>Hair saving</th>
<th>Peltec UNF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-38%</td>
<td>-20%</td>
</tr>
</tbody>
</table>
Ammonia Improvement: Deliming with ammonia-free deliming agents

**General idea / theory**

### Origin of ammonia
- Ammonia is added as a standard deliming agent to buffer the pelt after liming

### How to avoid ammonia
- Utilization of ammonia-free deliming agents significantly reduce the nitrogen content in the waste water
- Current solutions (boric acid / dicarboxylic acids) have HSEQ-/performance disadvantages

**LXS product solution**

### Peltec DLA
- Ammonia-reduced deliming agent which can be combined with CO\(_2\) deliming

### Peltec DLP / DL
- Products are completely free of nitrogen salts and ammonia compounds
- Peltec DLP quickly and uniformly penetrates even full substance pelts, time can be adjusted by addition of Peltec DL

**Impact of Peltec X-Zyme S/U**

![Graph showing nitrogen in deliming float (mg/l) with bars for (NH4)2SO4 Peltec DLA, Peltec DLA + CO2, and NH-free / Peltec DLP + DL with -23% and -74% reductions.]
**Comparative LCA: X-Zyme process shows significant reduction of waste water values**

Comparison of waste water values

- Common waste water value measurement performed on soaking and liming floats
- Hides were washed before soaking to exclude variable load of dirt attached to the hides
- Pollution of beamhouse waste water can be reduced by up to 50%

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>Conventional process</th>
<th>X-Zyme process</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD after soaking</td>
<td>kg/m³</td>
<td>14,9</td>
<td>4,7</td>
</tr>
<tr>
<td>BOD after unhairing/liming</td>
<td>kg/m³</td>
<td>23,1</td>
<td>12,9</td>
</tr>
<tr>
<td>COD after soaking</td>
<td>kg/m³</td>
<td>24,2</td>
<td>12,0</td>
</tr>
<tr>
<td>COD after unhairing/liming</td>
<td>kg/m³</td>
<td>54,0</td>
<td>25,5</td>
</tr>
<tr>
<td>Total nitrogen after liming</td>
<td>kg/m³</td>
<td>4,0</td>
<td>2,5</td>
</tr>
<tr>
<td>Sulfide after unhairing/liming</td>
<td>kg/m³</td>
<td>3,4</td>
<td>1,9</td>
</tr>
</tbody>
</table>

* Given per tonne of hides (the functional unit)
Comparative LCA: X-Zyme process savings on global warming equivalent to 122 cars / y

- Global warming: 50kg CO₂ eq. per ton of salted hides
  => Impact mid-size tannery (1.000 hides/day) is equivalent to 122 cars/y*

- Fossil energy: 730 MJ LHV (lower heating value)
- Land use: - 4.1m²y
  => 180 MJ/m2y is the gain of the additional land use.
  => This, compared to the yield achieved for bio-ethanol, outperforms the savings by 16 times**

* 142g/PKm CO₂ eq., Umwelt Bundesamt, 1.5P/Car, 20.000Km/y
** FOA of United Nations 2008: 11MJm²y for bioethanol