Sustainable Leather Manufacture – Realistic Objective or Wishful Thinking?

Heinz-Peter Germann
Lederinstitut Gerberschule Reutlingen (LGR) - GERMANY

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Definition of “Sustainable development”

…according to the World Commission on Environment and Development:

= development that “meets the needs of the present without compromising the ability of future generations to meet their own needs”
Scheme of sustainable development – at the confluence of three constituent parts

Sustainable

Social

Environment

Economic

Bearable

Equitable

Viable
Historical development
– past progress made by chance

• some hundred thousand years ago:
  – discovery of a stabilized animal skin by chewing (principle of chamois tannage)
  – smoke tannage following to the discovery of fire

• more recent evidence dating back to the 4th Millenium BC (Copper age):
  – the “Iceman” (found in the Alps on the icy heights of the Schnalstal Glacier frontier area between Italy and Austria) wearing fur clothes “tanned” by a special fatliquor procedure
Historical development
– past progress made by chance

• (main) interest: stabilisation of hides and skins – available from animals hunted for the need of nourishment – for the use of personal protection

• implying also the first attempt for “pollution prevention and control” by avoiding uncontrolled rotting of hunting/slaughtering waste in the environment!? 
Leather manufacturing

- … is in itself *recycling*

- … is a *sustainable* environmental solution to the disposal problem of hides and skins that originate from the meat industry
Principle of the unhairing
by lime-sulphide systems

1. Step: attack of disulphide crosslinks in keratin

\[
\begin{align*}
-\text{CH}_2\text{-S-S-CH}_2^- & \quad \rightarrow \quad -\text{CH}_2\text{-SH} \quad + \quad \text{HS-CH}_2^- \\
+ \ 2 \ \text{NaSH} & \quad + \quad \text{Na}_2\text{S}_2
\end{align*}
\]

2. Step: splitting of peptide bonds

\[
\begin{align*}
\text{CO} \quad + \quad \text{OH}^- & \quad \rightarrow \quad \text{CO-O}^- \\
\text{NH} \quad + \quad \text{RCH} & \quad \text{pH} > 10.5 \quad + \quad \text{RCH-NH}_2
\end{align*}
\]
Principle of hair immunization

\[
\text{cysteine} + \text{dehydroalanine} \rightarrow \text{lanthionine}
\]
Figure: High-Speed Penetrator
LGR’s investigations on high-pressure injection of process chemicals

... with the following objectives:

– set-up a throughfeed process

– rapid penetration and uniform distribution of the process chemicals

– avoidance of any residual process liquors

– conducting e.g. chrome tannage without pickling
Limitations observed in semi-technical scale trials which impeded an industrial application

• partially incomplete penetration of process chemicals in the case of heavier bovine hides
• enzyme unhaired skins need an additional reliming step for opening up the fibre structure and to guarantee complete removal of short hair
• wet-blues require a subsequent storage (up to 2 h) for a good chrome fixation
• especially, in the case of woolled sheepskins clogging of the filtering units by e.g. sand and fibres turned out to be a problem
Tanning techniques employed in the pre-industrial period

- Vegetable tannage
  
or
  
- Aluminium tannage (tawing)

depending on the intended use of the resulting leather – based on the leather characteristics (e.g. heavy & stiff ./ light & soft)
Dating from the end of the 19th Century: Chrome tannage

- discovery of the tanning effect of chromium salts is attributed to Friedrich Knapp ("On the nature and essential character of the tanning process and of leather", 1858)
- two-bath tanning process of August Schultz in 1884
- practical one-bath chrome tannage was patented by Martin Dennis in 1893
Dating from the end of the 19th Century: Chrome tannage

- at the beginning, no environmental concerns
- main interest: rationalisation of the tanning process
  - benefits in cost and speed of the reaction
  - significant cut of throughput time
  - highly versatile basis for leather manufacture
- major step towards industrialisation

Ref.: www.vallero-international.com
Within the last 50 years:
Different approaches for an improved chrome management

- chrome recycling techniques
- better understanding on the influence of process parameters:
  - mechanical action  - temperature  - pH
  - concentration  - processing time  - Cr offer
- development of high exhausting chrome tanning systems … based on the general principles of: low chrome offer, optimised process parameters and application of special auxiliaries
Alternatives to chrome tanning?

→ Amount of tanning agent required for a bovine hide (40 kg pelt weight)

**Chrome:**
8% tan.ag. = 2% Cr-oxide

**Vegetable (Mimosa):**
25% tannins (70% tan.cont.)

**Chamois (Oil):**
25% offer

**White-tan. (Syntan):**
20% tan.ag. (95% tan.cont.)
Importance of tanning methods, today

- **Chromium Tannage:**
  ca. 80 – 85 %

- **Chrome-free Tannages:**
  ca. 15 – 20 %
  
  - Percentage of chrome-free Automotive Leather (FOC)
    ca. 25 – 30 %
Worldwide leather production
– in % of industrial application field –

Source: Estimation on basis of FAO- & other statistical data
Chrome-free leathers ("FOC-leathers") – mainly in the automotive sector –

**Principle:**

- Wet-white pre-tannage by glutaraldehyde-tanning agents (partially modified) or THPS
- Retanning by polyphenols (vegetable and syntan tanning agents) and other organic-synthetic retanning agents
Chrome-free leathers ("FOC-leathers")

**Advantages** + **Disadvantages** in comparison to chrome leathers

**Advantages:**
- no “heavy metal”
- less problems in solid waste disposal (including sludge)
- improved dry-shrinking behaviour
Chrome-free leathers ("FOC-leathers")

Advantages + Disadvantages in comparison to chrome leathers

Disadvantages:

- higher COD in the effluent
- reduced fixation of dyestuffs and fatliquoring agents
- extremely difficult hydrophobing
- more difficult “handling” in production and processing
- lower stability and mould resistance of semi-finished products (wet-white)
The course of tanning in modern processing

**Pre-tanning/Main Tanning**
- stabilisation for mechanical treatment (sammying, shaving)
- production of a storable and transportable semi-finished leather product (wet-white, wet-blue)

**Retanning/Filling**
- adjustment of the required leather characteristics (e.g. fullness, shape-retention ability, grain firmness, embossability, buffability)
• Application of
  – vegetable tannins
  – resins
  – mineral tanning agents
  – syntans
  – polymers
  – aldehydes

Retanning/Filling
Recent research & developments

… concerning

“Pre-tanning”

- search for new, ecologically beneficial methods of pre-tanning / resp. stabilising of the skin (collagen matrix)

  e.g.:
  - wasserglass stabilisation
  - enzymatic crosslinking
  - application of natural plant crosslinkers (from olive waste)
Main objectives

➢ To establish an innovative, sustainable and environmentally friendly tanning system – *as an appropriate complement to the existing tanning methods*

➢ The stabilisation/pre-tanning of the skin material – under the avoidance of conventional chemical tanning agents – so that a satisfactory mechanical processability (shaveability) can be achieved

➢ To obtain by-products/waste (shavings), enabling practically unlimited usage
Wasserglass stabilisation

😊 Skin stabilisation by *Wasserglass* results in a white, stable and shaveable material.

😊 Stabilised pelts are storable for months

🚫 However, there is no (significant) increase in the shrinkage temperature

→ hesitations / reluctance for technical application
Basis of the biotechnological tanning system

• application of an enzyme from the group of *Transglutaminases*

• technical applications already exist in the field of food-technology

• the effect of crosslinking results in the formation of high-molecular protein aggregates with modified characteristics (e.g. increased thermal stability)

• irreversible crosslinking by covalent isopeptide bonds between Glutamine- and Lysine-side chains.
Enzymatic crosslinking

Glutamine + Lysine

Transglutaminase + H⁺

− NH₄⁺
Enzymatic crosslinking

\[
\text{Glutamine} \quad \text{Lysine}
\]
Status and limitations

❌ By the application of Transglutaminase, sufficient stabilisation (significant increase in the shrinkage temperature) – as required for leather manufacturing – could not be achieved.

😊 Transglutaminase (TG) produces, however, irreversible crosslinking with denaturated collagen (gelatine).

❓ Why collagen-crosslinking without denaturation is not adequate?
- TG is too large?
- No diffusion into the „right position“?
- sterical conditions / crosslinking distance of liable groups are inappropriate?
Natural plant crosslinkers

😊 Application of an activated extract from olive solid waste produced technically promising results:

- a stable leather intermediate ("wet-green®")
- with good shaveability
- and $T_S > 70^\circ C$
- forming an excellent basis for crust leather production

Olea europea
Economical feasibility – raw material availability

- Olive solid waste material: leaves, pomace/residue, effluent from olive oil- and table olive production
- In Europe (> 95% of world cultivation area for olive trees) approximately 30 mio. tons of olive-solid waste materials are produced
- Future research work with our partners will focus on practical application and improvements in the economics of the new („wet-green-tanning“) process
The issue of mould growth in a (semi-processed) leather

- A delay of further processing in the wet-blue or wet-white stage can lead to mould growth and hence a potential loss in quality and value

- Avoiding such losses includes the use of effective preservatives (fungicides) in the (pre-)tanning system
Future investigations

“Pre-tanning”

NEW additional objective:

- an universal intermediate stage requiring no preservation

i.e. an intermediate stage of leather which can be

- subjected to drying and
- subsequently wetted-back

without any problems
Future investigations

Aims:
- avoiding losses from mould attack
- avoiding the application of undesirable chemical agents

Tasks:
- appropriate stabilisation / crosslinking and sufficient increase in the shrinkage temperature to enable sammying and shaving
- appropriate “fibre separation” (e.g. by the filling effect of certain tanning agents or fatliquors) to enable drying without sticking within the fibrous collagen structure
Sustainable leather manufacture – future challenges

- In principle, leather manufacturing is in itself ‘recycling’ – i.e. it is a sustainable solution to the disposal problem of a by-product that originates from the meat industry.

- The concept of ‘globalization’ in leather production has to be updated / adjusted by taking more into account additional factors like e.g. raw material sourcing that is also relevant to the subject of sustainability.

- Sustainability of leather manufacture can be further increased by using resources (i.e. water, fossil fuels and other natural resources) sparingly, and giving priority to the use of renewable resources.
Thank you very much for listening