



The potential of silicates in leather production Part 4 of 4

Research into leather related silicon chemistry

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Major benefits from the use of sodium silicate in leather manufacture have been researched and developed. The project - with the acronym "SILIC-SALT"—was funded under the EC programme INCO-DEV⁹. Four important sets of findings were gained from this project:

1. *Silicates can be successfully used for the long-term preservation of hides and skins, and the subsequent manufacture of commercially acceptable leathers.*
2. *Within leather processing:*
 - *Lime can be replaced by silicates within the liming and unhairing process.*
 - *An additional silicate penetration/neutralisation of pelts led to improved uptake of tanning and retannage agents, dyestuffs and fatliquoring—hence rationalised and cleaner processing.*
 - *The development of new trading commodities.*
3. *Silicates in tannery wastewaters are not detrimental to plant health. In contrast, common salt at levels normally found in tannery effluents is highly detrimental.*
4. *Information regarding silicate related chemistry, and interactions within leather manufacture at fundamental level.*

Parts 1, 2 and 3 were published in World Leather February/March, April and May 2006; Each part presents the findings from that component of the investigation.

The fundamental effects of alkali silicates within the collagen structure

The opening-up of the collagen structure and unhairing process is one of the most essential process steps in leather production. The impact of lime substitution by Wasserglass was therefore scrutinised by means of Attenuated Total Reflectance (ATR)—Fourier Transform Infrared (FTIR) spectroscopy. The spectrographs following lime/unhair and silicate/unhair are shown in *Panels 1 and 2* respectively.

Both ATR-FTIR spectra display the typical polypeptide nature of collagen. The exact position of amide-I-band is related to the backbone conformation of collagen, and is similar for lime/unhair and silicate/unhair. This is especially important as it confirms that Wasserglass (*silicate*) has no negative impact on pelt properties when compared with the use of lime.

The performance of silicates from different commercial sources

Although the specification of Wasserglass used within the project

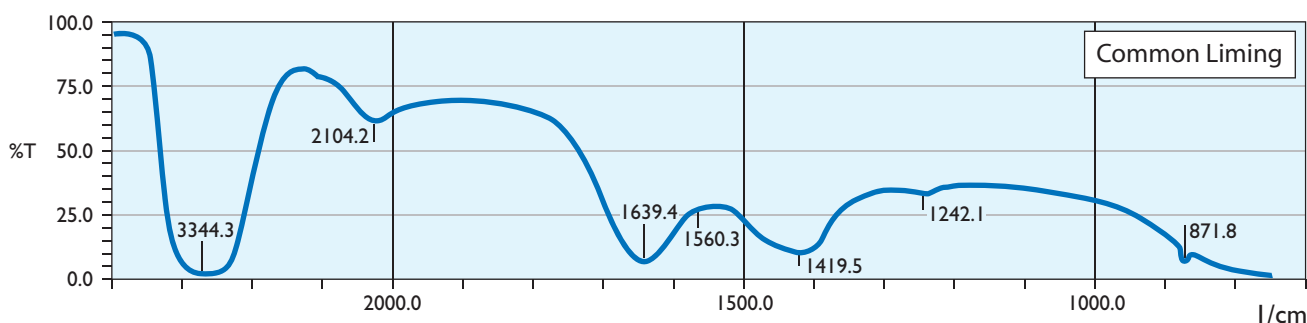
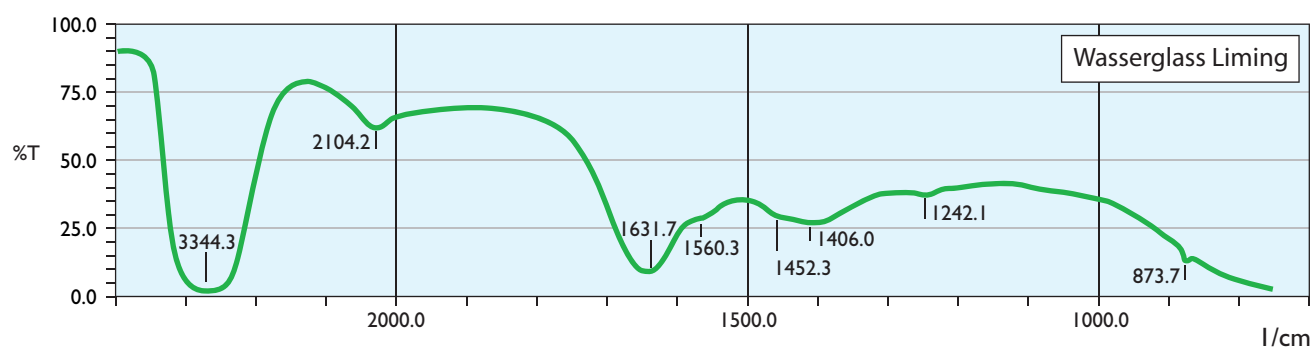
was clearly defined when the project commenced (*SiO₂ content, ratio SiO₂: Na₂O*), the technological results were not fully comparable.

The institutes using an international brand of Wasserglass, found higher silicate concentrations in the outer layers of pelts and crusts. However, the Indian institute, using a local brand, detected higher silicate concentrations in central layers of the cross section. These phenomena were scrutinised by means of Nuclear Magnetic Resonance Spectroscopy (NMR), and it was found that there were differences in the predominance of various species of silicates within the two products.

This indicated higher cross-linking in the international brand, while the lower cross-linking of the local brand lead to the conclusion of smaller particle size.

The influence of silicates in the improved uptake of auxiliaries

From leather and effluent analyses, it was concluded that the presence of silicates would positively influence the uptake of auxiliaries—especially tannins, fatliquors and dyestuffs. In order

**Panel 1: Pelt spectrograms after lime/unhair****Panel 2: Pelt spectrograms after silicate/unhair**

to find an explanation for these phenomena, comparative trials have been carried out. This employed penetration/neutralisation with Wasserglass after deliming and bating (*Refer Part 2*) and before tanning.

The resulting crusts were then analysed using applying Nuclear Magnetic Resonance Spectroscopy, Scanning Electron Microscopy/Electron Dispersive X-Ray Spectroscopy techniques. An example of a typical SEM/ EDX—spectrogram on element distribution (*line scan*) in the cross section of a crust are shown in the following SEM image and graph as *Panel 4*.

It was found that silicates influence the uptake of auxiliaries as follows:

- Wasserglass used for curing and liming does not seem to be carried into the wet blue. However, significant amounts of silicates when used for pre-treatment in conjunction with syntans and fatliquors, are bound within the structure. This influences the subsequent binding of auxiliaries in tanning, retanning and dyeing processes.
- Silicate pre-treatment leads to a significant build up of silicates on the surface when the international brand Wasserglass is applied. With locally produced Wasserglass, a significant build up of silicates in the inner layers occurs.
- NMR techniques have been employed to track the binding of fatliquors in silicate (*pre*)treated leathers. Fat liquors derived from phosphates have been employed and ^{32}P signals have been monitored. According to these signals, ^{32}P in silicate pre-treated leathers is considerably larger than those in control leathers.
- Similar observations, mainly based on SEM/EDX—investigations, have been made detecting chrome and copper (*core atom of metal complex dyes*).

- The uptake and binding of auxiliaries was improved when applying either internationally or locally produced Wasserglass. Accordingly, it can be assumed that the presence of silicate is responsible for the higher exhaustion of auxiliaries.

Findings from the research component of the investigation

- Investigations using ATR - FTIR show that silicate treatment in beamhouse procedures does not influence the backbone structure of collagen. This is proved, as the substitution of lime by alkali silicates does not have any negative impact on physical leather properties.
- NMR techniques have been employed to study the composition of the various types of applied Wasserglass. It could be shown that locally produced alkali silicate solution contains less Q3- and Q4-species than internationally supplied Wasserglass.
- Both ^{29}Si -CP-MAS-NMR based investigations and SEM-EDX studies mutually confirm both the amounts of silicates bound, and their layer-wise distribution.
- For curing and liming operations, more diffusive salts of soluble silicates (*higher content of Q2-species*) may be preferred in view of their ability to distribute uniformly.
- The use of silicates for curing will not influence the uptake of auxiliaries (*tannins, retanning agents, fat liquors, and dyestuffs*).

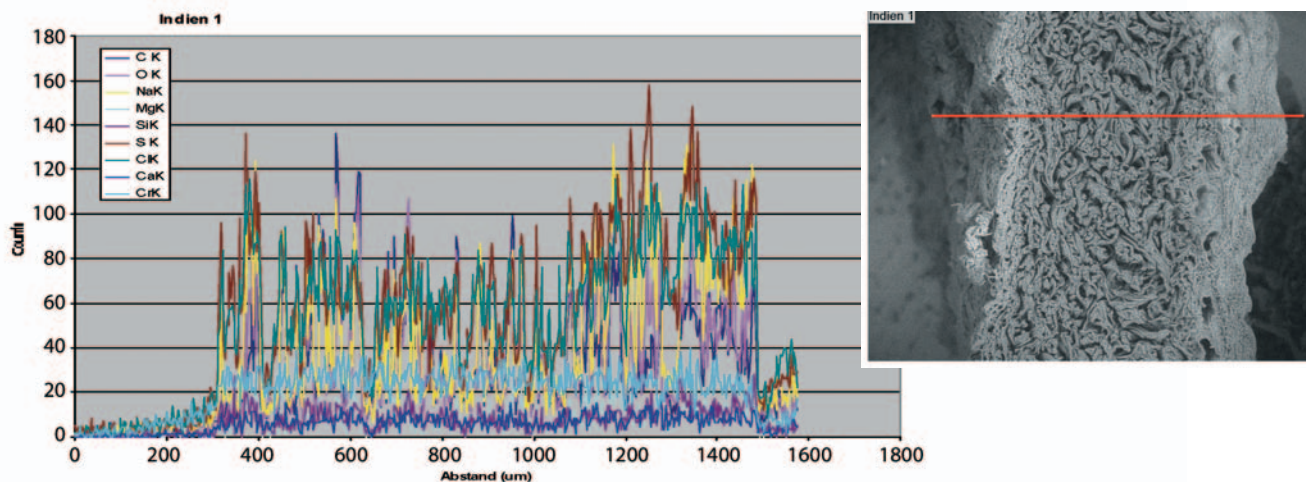
Improved auxiliary exhaustion is obtained when pelts are pre-treated by Wasserglass penetration before tanning.

For improved auxiliary exhaustion the sole presence of silicates seems to be more important than the real silicate concentration. ➤



THE POTENTIAL OF SILICATES IN LEATHER PRODUCTION

Panel 4: SEM/EDX – spectrogram on element distribution



Legend:

1. Advanced Federal Teaching and Testing Institute for Chemical Industry
2. Lederinstitut Gerberschule Reutlingen
3. Central Leather Research Institute
4. Greentech + Associates
5. Lederfabrik Vogl GmbH & Co Kg
6. Bangladesh College of Leather Technology
7. Leather Research Institute of Bangladesh Council for Scientific and

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