



The potential of silicates in leather production Part 2 of 4

Benefits within new chemical procedures, and the development of a new commodity

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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 retanning 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.*

Part 1 was published in World Leather February/March 2006. Findings listed as 3 and 4 are presented respectively as Parts 3 and 4: these will be published in World Leather in May and June/July 2006. Each part presents the findings from that component of the investigation.

The substitution of lime within the liming and unhairing process

The substitution of common lime ($\text{Ca}(\text{OH})_2$) by Wasserglass within the liming/unhairing process has been developed. In some cases of full substitution, sodium hydroxide (NaOH) was added to increase the alkalinity of the unhairing float.

In all trials, full hair removal and satisfactory opening-up of the hide tissue was obtained compared to a control process that employed lime as the main source of alkali. In all cases the resulting pelt showed excellent grain cleanness. When heavy bovine hides were "lime-split", the accuracy was improved compared with the control procedure.

Processes with reduced chemical offer and better uptake

Pelt stabilisation using Wasserglass has also been achieved. For this purpose pelts—either from Wasserglass/unhair or conventional lime/unhair—were penetrated with Wasserglass then neutralised to pH 4.0-5.0. In the case of the conventional liming/unhairing, before penetration with the Wasserglass (*alkali silicate*), a complete deliming was needed to remove all calcium ions. These pelts were then tanned, re-tanned, dyed and fatliquored, then processed to the crust state. The outline procedures used are given in *Panel 1*.

The Wasserglass/unhair process (*Panel 1: Process B*) produced a cleaner grain, but otherwise no differences could be observed ►



THE POTENTIAL OF SILICATES IN LEATHER PRODUCTION

Panel 1: Outline procedures

Control Procedure (A)	Wasserglass-Liming (B)	Wasserglass-Liming & Penetration (C)
Pre-Soak	Pre-Soak	Pre-Soak
Main-Soak	Main-Soak	Main-Soak
Liming (4% Lime, 4% Na ₂ S)	Wasserglass - Liming (5% Wglass, 4% Na ₂ S)	Wasserglass - Liming (5% Wglass, 4% Na ₂ S)
Washing	Washing	Washing
Deliming	Neutralisation (HCOOH)	Wasserglass - Penetration (4% Wglass, 100% float, 4 hr)
Bating	Bating	
Washing	Washing	Neutralisation (HCOOH)
Pickling	Pickling	
Cr-Tanning	Cr-Tanning	Bating
Re-Chroming	Re-Chroming	Washing
Neutralisation	Neutralisation	Pickling
Washing	Washing	Cr-Tanning
Retanning	Retanning	Re-Chroming
Dyeing	Dyeing	Neutralisation
Fatliquoring	Fatliquoring	Washing
		Retanning
		Dyeing
		Fatliquoring

Panel 2: Analytical comparison: calf leathers

(Process D: Chrome and retanning agents reduced by 20%)

	Control	Process B	Process C	Process D
Technology	Lime/unhair	Wasserglass/unhair	Process B + Wasserglass penetration	Process C + Cr/Retannage reduction*
Ash (%)	5.9	7.0	7.8	7.6
Cr ₂ O ₃ (%)	3.9	4.1	4.9	4.6
Si (%)	-	0.9	1.6	1.5
Fat (%)	6.0	6.1	6.6	6.5
Thickness	1.2 mm	1.2 mm	1.2 mm	1.2 mm
Tear Strength	215 N/mm ²	220 N/mm ²	210 N/mm ²	212 N/mm ²
Elongation	54 %	54 %	52 %	50 %
Stitch Tear	45 N/mm	48 N/mm	47 N/mm	46 N/mm
Shrink.Temp.	> 100°C	> 100°C	> 100°C	> 100°C

when compared with the lime/unhair control (*Panel 1: Process A*).

However, when the Wasserglass/unhair process was followed by second Wasserglass addition, with full penetration and then neutralisation (*Panel 1: Process C*), it was found that all auxiliaries that were subsequently applied—especially tannins and dyestuffs—were better exhausted. This improved auxiliary uptake resulted in processes with reduced offers of:

- chrome powder - 20%
- Retannage - 30%
- Fat liquors - 10%
- Dyestuffs - 30%

Panel 3: Analytical comparison: control to optimised post tanning (Goat upper and soft cow upper leathers)

	Control	Optimised post tannage
Goat Upper Leather		
Tensile strength (kg/cm ²)	192	218
Elongation at Break (%)	55	47
Tear strength (kg/cm)	36	42
Softy Cow Upper Leather		
Tensile strength (kg/cm ²)	240	245
Elongation at Break (%)	60	52
Tear strength (kg/cm)	46	46.4
Load at grain Crack (kg)	42	40
Distension at Grain Crack (mm)	8.5	8.0

Leather from this process showed no significant differences of loss of quality compared to standard procedures. The physical performance of these leathers was similar, and this is shown together with the chemical analysis in *Panel 2*.

Similar results are evident from other trials, and are shown in *Panel 3*.

The impact on effluent composition

This reduced chemical offer and improved uptake led to a significant reduction in the effluent loading. When these reductions are taken into account with the diminished loadings achieved by using silicates for curing, the effects are considerable. Some examples from effluent analyses are shown in *Panel 4*.

These reductions in load as COD and Chloride are substantial, and the outcome as Kg Chloride load from processing 1000 kg of raw material are shown as *Panel 5*.

The development of a new commodity

In the curing trials (*Part 1*), it was demonstrated that silicate-cured hides and skins could be shipped from one country to another one without negative impact on the quality of the resulting leathers. However, many (*European*) tanneries are neither equipped nor allowed (*due to environmental restrictions*) to perform beamhouse processes, so they

often start with wet blues or wet whites. Accordingly, trading customs require the development of new types of commodities that can substitute common wet white or wet blues.

These have been developed. Pelts processed as given in *Panel 1: Control Procedure A* - (*Salt preserved + limelunhair*), and silicate-cured pelts processed as given in *Panel 1: Control Procedure B* - (*silicate-cure + silicate/unhair*) were stabilised by a silicate penetration/neutralisation to pH 4.5. These were produced by VAL. When wrapped in plastic covers, these can be stored for six months without any bacterial growth. An example is shown in *Panel 6*.



Panel 4: Environmental profile: TDS and COD as Kg/ton
Conventional vs. Optimised curing and process

Process	Salt cured skins + Control		Silicate cured skins + Process D	
	TDS Kg/ton	COD Kg/ton	TDS Kg/ton	COD Kg/ton
Soaking	280	25.2	95	23.2
Liming	145	91.5	139.3	88.8
Deliming & Bating	17.9	2.04	9.2	1.7
Silicate pre-treatment	-	-	36.7	5.0
Pickling & chrome tannage	64.4	27.9	40.2	16.8
Retanning and fatliquoring	19.1	11.3	13.0	5.92
Combined liquors	580	161.9	375	125.1
% Reduction in combined liquors			- 33%	- 19.8%

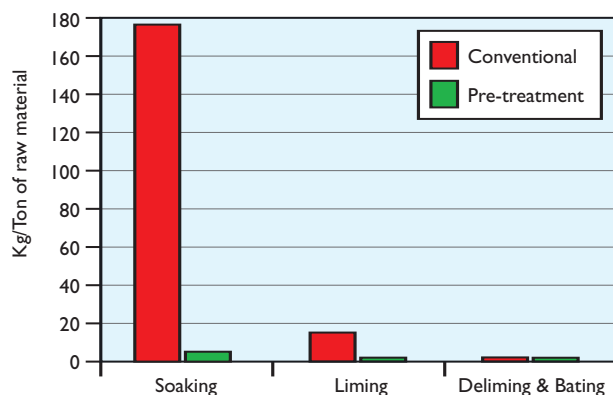
also improve lightfastness.

Moreover, common wet whites need preservatives for storage, but the silicate-containing products can be stored for more than one year without any preserving auxiliary. Besides cost savings (*the silicate procedure is low cost while preserving auxiliaries are rather expensive*), the resultant tannery effluents will not be contaminated with preservatives. This can be crucial in biological effluent treatment.

Meanwhile, these two different procedures have been repeated. In this situation the preparatory work was carried out in a Mexican tannery, and the stabilised pelts shipped to a European upholstery tannery. On

conversion to the crust state the leathers were again rated as “excellent”.

Panel 5: Comparison of Chloride: Kg/ton
Conventional vs. Optimised curing and process



Findings from the new chemical procedures component of the investigation

- It was demonstrated that alkali silicates could substitute lime in a silicate/unhair process. Since silicates are common, there should be no increase in process costs. If more alkalinity is required, this can be provided by sodium hydroxide.
- The silicate/unhair process produces cleaner pelts than the conventional lime/unhair process. In the case of bovine hides, greater splitting accuracy was achieved than with the lime/unhair control.
- If silicates are applied after unhairing and before tannage, the exhaustion of auxiliaries subsequently used is improved. The COD and TDS load of the mixed effluent is reduced up to 20 and 30% respectively due to this improved uptake.
- As a result of this improved chemical uptake, procedures have been adapted, and crust leathers have been produced at several different locations. These leathers have been satisfactory in terms of handle, aesthetic and physical properties.
- By applying silicates in leather manufacture, it is possible to make substantial reductions in chemical offer without any impact on leather quality. 🌱

Panel 6: Shows a hide that has been silicate preveved, processed, then silicate stabilised



Pelts from these two procedures were converted into crust state as upholstery leather using a proven commercial procedure. On examination, the leather was rated as “excellent”. According to the upholstery tannery, the stabilised pelts are similar to wet whites, but provide the advantage of being aldehyde free. This is considered an advantage for the automotive industry, and will

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 Industrial Research
8. Dr. Th. Boehme KG Chem. Fabrik GmbH
9. Industrial Co-operation with Developing Countries

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