

Wasserglass in leather production

K.H. Munz (Versuchsanstalt fuer Lederindustrie, Austria)

S. Banaszak (Lederinstitut Gerberschule Reutlingen, Germany)

G. Manzo, G. Grasso (Stazione Sperimentale per l'Industria delle Pelli, Italy)

Wasserglass is a simple non-toxic product, and has been widely used by industry for many years. Investigations have shown that it has potential for the stabilisation of collagen before tannage and utilisation of shaving wastes. This has been previously reported in detail in World Leather August/September 2001⁽¹⁾.

Investigations have continued, and it is clear that opportunities have been provided within the leather sector in five major areas:

- *The stabilisation of hides and skins before tannage for long periods of time, and the possibilities of a new trading commodity*
- *The ability to split and shave before commitment to tannage*
- *Shavings that are close to collagen, hence available for a wide number of outlets*
- *Improved chrome fixation within chrome tannage*
- *Substitution for lime within 'liming' and unhairing processes*

The main objective of this project—funded by the CRAFT programme of the EC⁽²⁾—was to develop findings from a previous investigation on the application of Wasserglass.

In the study, procedures for pelt treatment with Wasserglass⁽³⁾ to enable shaving in the stabilised state were developed further, together with the utilisation of the resultant shavings. The new EU directive on waste disposal (effective with spring 2004) limits the organic content of wastes to 5%. If this limit is exceeded, a thermal treatment has to be carried out prior to disposal. Alternative uses for wet white and wet blue shavings are limited, however the (nearly) native shavings from Wasserglass applications should help to overcome disposal problems by presenting new opportunities for utilisation.

Further investigations have also led to the substitution of lime $\text{Ca}(\text{OH})_2$ within the 'liming' and unhairing process.

1. Lime substitution in unhairing processes

Wasserglass substituted common lime $\text{Ca}(\text{OH})_2$, with pH adjustment using sodium hydroxide. Many variations were applied but, dependent upon raw materials, the outline procedures were as follows:

STANDARD DRUM UNHAIRING/LIMING WITH SUBSTITUTION:

- 4 - 6% Wasserglass
- 2 - 4% Sodium sulfide
- 2% Sodium hydroxide
- @ 50 - 100% water

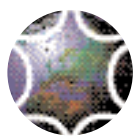
DRUM PAINT UNHAIRING + LIMING WITH SUBSTITUTION:

- 4 - 6% Sodium sulfide @ 20% water
- 4 - 6% Wasserglass @ 30-60% water

As a result of these trials the following statements can be made:

- Lime can be completely replaced. To support the opening-up of the hide structure and to improve fibre swelling the addition of extra alkali, preferably 1-2% sodium hydroxide, is required.
- unhaired pelts show improved grain cleanness and a brighter colour than those from conventional unhairing. This will be an advantage for the production of bright dyed leathers.
- Pelts show fewer wrinkles and can be split with higher accuracy (*see Panel 1*). Accordingly less levelling is needed in shaving, thus reducing wastage and shaving volume
- Effluent waste streams show higher organic load in terms of Chemical Oxygen Demand (COD) and Suspended Solids (SS). This, and the reduced fat content of limed pelts, indicates a better dispersing and saponifying effect of alkali silicates in combination with NaOH.
- The quality of resulting leather does not change.

In the previous project, where pre-tannage fibre stabilisation was developed, an improved exhaustion of auxiliaries was found. However, Wasserglass-unhairing only improves exhaustion marginally. To gain significant exhaustion, an additional ➤



Panel I:

Splitting properties Adjusted Thickness: 3 mm

Splitting machine: Mosconi Zenit; Working width: 3 m; Speed: 15 m/min

Process	Trial 1 Standard drum procedure with lime	Trial 2 Standard drum procedure with Wasserglass (6 %)	Trial 3 Drum-painting with Wasserglass	Trial 4 Standard drum procedure with Wasserglass (10 %)
Pelt-splitting thickness	2.6 - 3.2 mm	3.1 - 3.3 mm	2.7 - 3.3 mm	2.9 - 3.1 mm
After samming before shaving thickness	2.1 - 2.6 mm	2.1 - 2.6 mm	2.4 - 2.8 mm	2.2 - 2.4 mm
After shaving thickness	1.4 mm	1.4 mm	1.4 mm	1.4 mm
After drying crust thickness	1.4 - 1.5 mm	1.6 - 1.7	1.9 - 2.0	1.7 - 1.8

Appearance & Remarks

Process	Trial 1	Trial 2	Trial 3	Trial 4
Liming Swelling	Normal	Normal (after adjusting with NaOH)	Normal (after adjusting with NaOH)	Normal (after adjusting with NaOH)
Hair removing	Hair residues	Clean	Clean	Clean
Liming folds	Strong	Less - strong	Less - strong	Less - strong
Acid swelling. Pickling without salt before chrome tanning after fixation of wasserglass	Standard with Salt ! no swelling	Slight swelling	Slight swelling	Slight swelling
Observations:	-	Small particles in float	Small particles in float	Small particles in float
Colour of wet-blue	Grey-blue	Dark blue	Dark blue	Dark blue
Smell of wet-blue	Slightly acid smell	Slightly acid smell	Slightly acid smell	Slightly acid smell

treatment is needed followed by neutralisation/stabilisation. This is discussed in the following section.

2. Fibre stabilisation with Wasserglass

Delimed and bated pelts from conventional and Wasserglass unhairing were penetrated with Wasserglass as follows:

50 - 100% float
4% Salt
4 - 6% Wasserglass Run 120-300 minutes.
(Time dependent on thickness of hides and skins)

After draining and re-floating, the pelts were neutralised, preferably with formic acid to pH = 3.5. After draining, the stabilised pelts were sammied, horsed, and then shaved.

This treatment leads to a physical stabilisation of the pelt. No tanning effects or increases in shrinking temperatures were observed either after penetration or after neutralisation/stabilisation. However, the fibres were stabilised and the following statements can be made:

- The penetration of delimed and bated pelts with Wasserglass, followed by neutralisation/stabilisation to pH 3.5, leads to shaveable pelts.
- For stabilisation, either formic acid or a mixture of formic

acid and stabilising agent⁽⁴⁾ is required. The addition of the stabilising agent should be carried out very slowly over a long period of time or in a number of steps (at least 6).

- Stabilised pelts, both before and after shaving are storable for more than one year without addition of any preservative.
- These pelts feel like leather as opposed to untanned skin. After storage, even if they have been allowed to become dry, they can be re-soaked without problem.
- After stabilisation, the pelts should be horsed for three to four days. The findings from trials indicate better shaveability after storing.
- Shaving can be carried out under usual conditions. All comparative trials have indicated that—independent of the type of tannage ultimately used—the leather quality is at the same level as from conventional procedures.
- After Wasserglass treatment, all types of tannages are possible. For wet white processes, especially when heavy shaving is needed, additional tests are necessary. Although excellent results have been obtained, in semi-technical trials there has been some variation leading to leathers of only fair leather quality.

This indicates the development of a new commodity. In addition, it seems to be likely that Wasserglass can substitute commercial preservatives. Trial in this respect will be carried out in near future. ➤

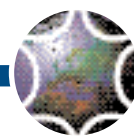


Figure 1: COD in final unhairing floats

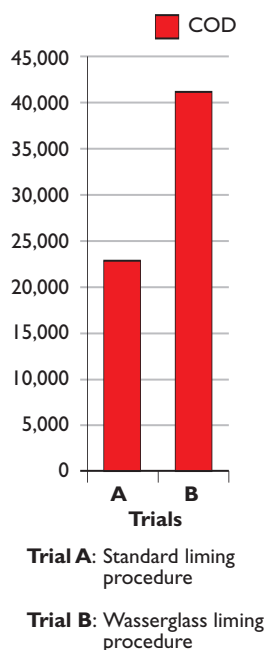


Figure 2: Chrome in final tanning float

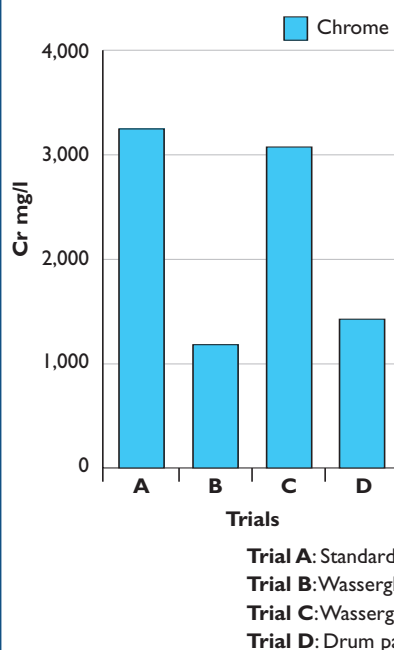
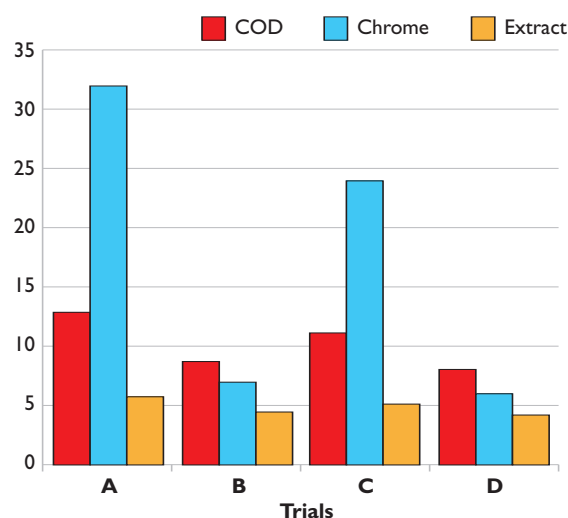


Figure 3: Exhaust retan and fatliquor bath: Residual chrome, fat and COD



The impact on auxiliary exhaustion and effluent composition

The use of Wasserglass has led to a significant improvement in the exhaustion of many auxiliaries, especially chrome tanning agents and fatliquors. This was not expected, and is associated with pelt stabilisation and not unhairing applications.

EFFECTS OF WASSERGLASS ON END FLOATS

Unhairing floats: Final floats from Wasserglass unhairing show higher organic load as COD and in SS. This indicates a better dispersing and saponifying effect of alkali silicates in combination with NaOH as shown in Figure 1.

Deliming and bating floats: No significant differences to conventional processing were observed.

Chrome tannage floats: The use of Wasserglass in unhairing compared with conventional processing has little impact on chrome uptake. However an additional treatment after deliming and bating will improve the chrome exhaustion significantly as shown in Figure 2.

Retannage and fatliquoring floats: The effects of treatment after deliming and bating is also found in retanning systems where the levels of leachable chrome content are considerably lower. The COD also decreases due to improved exhaustion of fat liquors as shown in Figure 3.

Influence on dyeing: Although analytical data for dye exhaustion are not available, it can be stated that Wasserglass application not only leads to brighter surface dyeing, but also to more uniform colour tones in cross-section.

THE INFLUENCE OF WASSERGLASS ON EFFLUENT

Experience is based on semi-technical trials, so it has not ➤

Figure 4:

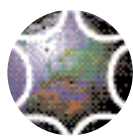
Effluent part stream comparison

Mean values			
	Common procedure	Wasserglass procedure	Difference (%)
Unhairing, deliming & bating			
SS (mg/l)	170	271	
TDS (mg/l)	33703	32613	
COD (mg O ₂ /l)	22937	26703	
Wet-end processes			
SS (mg/l)	1027	888	
TDS (mg/l)	9927	5150	
COD (mg O ₂ /l)	3513	2978	
Chrome (mg Cr/l)	214	48	
Total			
SS (mg/l)	1197	1159	- 3.2 %
TDS (mg/l)	43630	37763	- 13.5 %
COD (mg O ₂ /l)	26450	26601	+ 0.6 %
Chrome (mg Cr/l)	214	48	- 77.5 %

Figure 5:

Final float from chrome tannage and 1st wash

Mean values	Common procedure	Wasserglass procedure	Difference (%)
SS (mg/l)	373	313	- 16.1 %
TDS (mg/l)	18150	9000	- 50.4 %
COD (mg O ₂ /l)	4327	4303	- 0.6 %
Chrome (mg Cr/l)	887	203	- 77.1 %



been possible to study effects on combined effluents. However, an evaluation has been made based on analysis of final floats from bovine processing with Wasserglass compared with conventional procedures as shown in *Figure 4*.

If the effluent composition is calculated according to the volume and composition from each stage, parameters as SS, TDS, and COD show little differences compared to conventional processing. However, the levels of chrome in mixed effluent will be significantly lower as shown in *Figure 5*.

Utilisation of shavings

Pelts fully penetrated with Wasserglass, and then stabilised/neutralised by adjustment to pH 3.5 can be shaved. These shavings are uncontaminated by tanning or pre-tanning agents, and

are therefore almost in a 'native' state. Analytical comparisons of shavings from various processes are shown in *Figure 6*.

POTENTIAL IN HYDROLYSATES

Alkaline solubilisation of these shavings can be performed at 60°C in only 2 hours without changing the fragment pattern. Electrophoretic analysis from large scale trials showed that subsequent enzymatic treatment gives digestion-fragments which range from 25 to 38kD in the case of a BLAP-S260 digest, or from 30 to 75kD if Neutrase is used.

These peptides are rather uniform peptides. In application trials as a leather auxiliary, better results than with current commercial products⁽⁵⁾ were achieved. These are not expected to be smaller than 3-5 kD, but other enzymes may be used to obtain smaller fragments. ➤

Figure 6: Composition of shavings

	Conv. Cr ^a	Conv. Veg ^b	Wasserglass ^c	Wasserglass ^d	Raw Hide ^e
Moisture (%)	56.9 - 59.0	58.8 - 60.1	54.4	53.0 - 55.4	11.9 - 13.7
ALL RESULTS RELATED TO 0 % MOISTURE					
Ash content (%)	10.8 - 12.6	3.1 - 5.4	14.5 - 18.6	7.0 - 11.5	1.4 - 2.8
Organic Substance (%)	83.4 - 85.4	94.6 - 96.6	82.4 - 85.5	84.4 - 87.2	97.2 - 98.0
Total (Kjeldahl) N (%)	12.7 - 13.1	13.3 - 14.7	10.9 - 12.5	12.8 - 14.1	15.0 - 15.7
Hide substance (Nx6.25) (%)	79.4 - 81.9	83.1 - 91.9	68.1 - 78.1	80.0 - 88.1	93.8 - 98.1
Fat content (%)	1.2 - 3.4	1.2 - 1.9	2.6 - 4.8	3.1 - 4.7	0.8 - 1.3
Digestibility (%)	51.9 - 56.0	67.2 - 73.1	82.3 - 90.7	89.9 - 91.6	92.0 - 94.3
pH of aqueous extract	3.2 - 3.5	3.2 - 3.7	3.7 - 4.2	3.2 - 3.7	7.8 - 8.0
Cr (g/kg)	51.8 - 59.3	absent	absent	absent	absent
Si (g/kg)	-----	-----	1.8	5.8 - 8.9	-----

^a Chrome – shavings from calf skins
^b Vegetable shavings from goat skins
^c Shavings from Wasserglass – procedure from calf skins
^d Shavings from Wasserglass – procedure from bovine hides
^e Starting material for dog chewing articles (limed and delimed, dried pelts) trade product

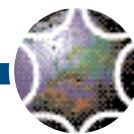
Figure 7: Plant yield in relation to applied fertilisers

Treatment	1st cut, g/pot (standard deviation)		2nd cut, g/pot (standard deviation)		Total weight, g/pot (standard deviation)	
	wet	LSD	wet	LSD	wet	LSD
T	83.25 (5.01)	A	54.87 (2.45)	A	138.09 (2.90)	A
U	139.64 (12.63)	B	118.72 (10.98)	B	258.35 (22.75)	B
W	145.05 (20.78)	B	101.22 (19.20)	B	246.27 (18.97)	B
WU	137.08 (18.81)	B	105.12 (29.92)	B	242.19 (34.33)	B

Treatment	1st cut, g/pot (standard deviation)		2nd cut, g/pot (standard deviation)		Total weight, g/pot (standard deviation)	
	wet	LSD	wet	LSD	wet	LSD
T	5.48 (0.57)	a	4.13 (0.16)	a	9.61 (0.41)	A
U	7.55 (0.90)	b	8.40 (1.84)	c	15.94 (2.70)	B
W	7.41 (1.10)	b	6.31 (0.55)	b	13.71 (1.16)	B
WU	7.03 (1.10)	b	6.90 (1.60)	b, c	13.93 (2.23)	B

T - Soil only **U** - Urea base **W** - Wasserglass shavings **WU** - Wasserglass shavings and urea

Comparison between chicory weights of the 1st and 2nd cut. Lowest significant differences test (LSD); capital and small letters indicate probability that the means of the groups will be significantly equal at respectively probability levels of $P < 0.01$ and $P < 0.05$. Sequence A, B, C indicates the order of significance level.



POTENTIAL AS A FERTILISER

Direct application of shavings as a long-term source of nitrogen was investigated in comparative trials. The findings are given in *Figure 7* where:

- T = soil alone as the Test control.
- U = soil plus commercial Urea based fertiliser supplying a nitrogen content of 120 kg/ha.
- WU = soil plus 1:1 Wasserglass shaving-Urea mixture at the same nitrogen content as the treatment U.
- W = soil plus Wasserglass shavings only at the same nitrogen content as treatments U and WU.

In these trials, it appears that the yield of chicory plants was similar irrespective of the fertiliser used. When no fertiliser was applied significantly lower yield was observed. As part of these investigations the nitrate content of the soils were determined over a period of time. This was to evaluate the impact on ground waters, and the findings are given in *Figure 8*.

Figure 8: Nitrate content of soils according to fertiliser application. Analysis over a 4-month period

Trial #	% Nitrate content of soil Monthly Analysis			
	1	2	3	4
T - soil only	2.28	2.29	3.42	3.21
U - urea base	5.75	8.72	6.95	7.01
WU - urea base + Wasserglass shavings	7.01	5.99	6.81	7.96
W - Wasserglass shavings	8.33	5.98	5.19	3.22

While commercial fertilisers (U, WU) led to increased nitrate content even after 4 months, the sole application of shavings (W) minimised the nitrate content, hence loss as a leachable extract.

Advantages stemming from Wasserglass applications

Wasserglass is non-toxic and has long been used by industry. It is contained in products found in everyday domestic use, cosmetics, and the food and catering sector. It is readily available,

low in cost, and can be viewed as a very environmentally friendly product. In leather processing it offers high potential, and, as discussed can provide the following advantages:

- Complete substitution of common lime in unhairing processes.
- Pelts show improved grain cleanness and can be split with improved accuracy.
- After delimed and bating, fully penetrated pelts when adjusted to pH 3.5 provide sufficient stability to perform shaving.
- Pelts from this treatment can be stored for very long periods and offer new commercial potential.
- Treatment leads to improved exhaustion of many auxiliaries used in leather manufacture
- There is a considerable improvement in the uptake of chrome within tannage, with potential for savings in chrome application and a reduction within wastewater discharges.
- Shavings are free of chemicals normally used for tanning or pre-tannage, and are almost native.
- These shavings can easily be hydrolysed. Resulting protein fractions are suitable as a starting material for the production of various auxiliaries.
- Shavings can be directly applied as fertiliser. Growth is improved, and the long term slow release as nitrate content in soils in comparison with commercial products can be considered as an environmental advantage. 🌱

Legend

1. *World Leather August/September 2000, p40: "Fibre stabilisation with Wasserglass: the effects on leather making and its potential for better utilisation of shavings"*
2. *CRAFT-RE&D projects are supported by the EU, especially designed for small and medium enterprises (SMEs)*
3. *Wasserglass, also known as Waterglass, are aqueous solutions of alkali silicates*
4. *Tannit (R) by Boehme*
5. *Hair protective agent for fur production*

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