

A practical alternative to salt for the preservation of hides and skins⁽¹⁾

Salt as a preservative for hides and skins is simple in application, low in cost and effective. Accordingly it is the most common form of preservation, but in practical term salt cannot be removed within effluent treatment. It enters the environment where the true costs are experienced in reality. Unless discharge is direct into the oceans, this salt represents long term endangering of potable water supplies via contamination of the aquifer. It also prevents the reuse of treated tannery effluents for irrigation purposes where quality waters are at a premium. A new alternative technology has, however, been the subject of investigation. This is low cost, simple, effective, and side-steps these issues.

Silicates, namely alkaline solutions of alkali silicates ("Water glass or Wasserglass") are very common and inexpensive auxiliaries. Other than their high pH when in the concentrated form, they are neither health detrimental, nor will they harm the environment since upon pH reduction they will form SiO₂ or common sand.

Silicates are used in food preservation, household detergents and for cosmetic purposes. Within leather production, they are applied to a certain extent for combined tannages or as filler in wet-end processes. In various R&D-projects, funded by the European Community, new application methods have been developed.

Silicates for fibre stabilisation⁽²⁾

A method for fibre stabilisation with alkali silicates has been developed and previously reported⁽³⁾. As an overview, delimed and bated pelts are first penetrated with aqueous Wasserglass solutions at 4.0% offer in 100% float. This is followed by neutralisation (*preferably formic or citric acid*) to pH 4.0. After horsing for several days, these stabilised pelts can be sammyed and shaved.

These pelts⁽⁴⁾ then can be tanned using the preferred tanning method. Moreover, the remaining silicates improve the uptake of all subsequently applied tanning agents and auxiliaries up to 20%⁽⁵⁾. This is especially useful when chrome tanning.

There are also considerable advantages within solid waste management, as there are no problematic chrome shavings, splitting waste or trimmings for specialised disposal. The

stabilised waste is still native with potential as new raw materials, and so can be utilised in various ways.

Silicates as curing agent⁽⁶⁾

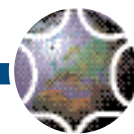
Based on successes for fibre stabilisation, the use of silicates has been extended to the preservation of raw hides and skins.

Today, many skins and most bovine hides are cured using common salt (NaCl). Although this method has been state of the art for centuries, there are associated problems especially in areas with scarce water resources. This is because the main quantity of the curing salt is dissolved from the hides during the beamhouse processes. It is not feasible to remove this salt in effluent treatment, so, because of the high salinity the treated effluent cannot be utilised for irrigation. Furthermore, on end-of-pipe discharge, there is the danger of the salt entering the aquifer, resulting in long term build-up of salinity in potable water.

The aim of this project was to substitute common salt in curing by silicates. This was either via application as a pre-neutralised powder, or by penetration as solution followed by neutralisation to pH 5.0.

Both methods lead by dewatering to raw materials that can be stored over long periods of time. These can be re-soaked without problems, and could serve as a new type of commodity.

The preparation of neutral powdered alkali silicates requires a drying stage, so this technique can be used in hot climate regions with sufficient solar energy for low cost drying. Drum penetration and neutralisation is easy to carry out and requires only very basic equipment. Both methods are low cost and

**Panel I****Silicates as a lime substitute⁽⁷⁾**

Another objective of the project was to develop the substitution of lime by alkali silicates. This has been investigated and reliable procedures have been developed.

The application of lime $\text{Ca}(\text{OH})_2$ in unhairing procedures leads to high sludge volumes in effluent treatment. Because of alkaline action, Wasserglass can substitute lime completely. The resulting pelts show excellent grain cleanliness and can be split with high accuracy.

In addition, Wasserglass seems to have better saponifying and dispersing actions to non-collagenous interfibrillary substances. This leads to a better opening-up of hide-fibres. It was found that the application of silicates for curing and unhairing does not significantly influence the exhaustion of products and auxiliaries used subsequently. Only when the pelts are stabilised after deliming and bating is the exhaustion of auxiliaries improved⁽⁵⁾.

simple, and lead to a significant reduction of salt loading in soaking effluents—approximately 5% of the values stemming from salted hides. This represents a major step in addressing the problems of salinity arising from leather manufacture. 

Legend

- 1) Project partners include: Versuchsanstalt für Lederindustrie (VAL)/Austria, Lederinstitut Gerberschule Reutlingen (LGR)/Germany, Central Leather Research Institute (CLRI)/India, Bangladeshi Leather Research Institute (BLRI), Bangladesh College for Leather Technology (BLCT), Lederfabrik Vogl Gmbh/Austria, Dr. Boehme Kgl/Germany, COTANCE.
- 2) CRAFT 1999-70 615 and CRAFT EBV4-CT-2001-50 130
- 3) Wasserglass in leather production: K.H. Munz (Versuchsanstalt für Lederindustrie, Austria), S. Banaszak (Lederinstitut Gerberschule Reutlingen, Germany), G. Manzo, G. Grasso (Stazione Sperimentale per l'Industria delle Pelli, Italy): World Leather Aug/Sept 2004, p35-43.
- 4) Since this procedure does not increase the shrinkage temperature, no tanning action occurs.
- 5) From semi-technical trials it was found that the auxiliary offer (tanning and retanning materials, fat liquors and certain dyestuffs) could be by almost 30% without affecting the quality or handle of the final leathers. This improved uptake is significant in both materials cost reduction, minimisation of waste, and waste water treatment.
- 6) CRAFT ENV4-CT-2001-50 130 and INCO-DEV ICA4-CT-2002-10039.
- 7) INCO-DEV ICA4-CT-2002-10039.

Polyphosphates within salt-free pickle systems

Thomas Schauwecker, BK Guilini GmbH, Germany

Products based on condensed phosphates (polyphosphates) with different chain lengths, organic side molecules and pH values are used in the leather industry. Applications include the soaking of hides and skins, as a dispersant for lime during the liming process, avoiding lime blast, and within deliming and bating. In addition uses are found in neutralising, retanning and the removal of iron stains.

However polyphosphates have a tanning action, and can both increase the shrinkage temperature of pelts and provide stability to acid swelling. Moreover, polyphosphates are more effective when used in the absence of salt.

A basic formulation is given as preparation for vegetable or mineral-free tannage using fully delimed skins:

50-100 %	Water @ 22-28°C
1.5-2.0 %	Polyphosphate ⁽¹⁾ Run 20 to 40 mins
x %	Formic acid (diluted) 2 x 20 mins
y %	Sulfuric acid (diluted) 2 x 30 mins
	Run 40 min or until penetration

The amount of polyphosphate varies according to the float length and running time on the splitting thickness. The penetration rate is similar to common salt. The tanning action is slight at pH 6.0 to 6.5 but the rate of combination increases if

the pH is reduced. When acid is introduced to the system the polyphosphates—already penetrated in advance of the acid—start to combine with the amino groups.

In the absence of salt a full reaction is achieved, producing a tight, stable and compact structure. This is suitable as a pre-treatment for glutaraldehyde or other pretannage, vegetable tannage where there is a colour lightening, or synthetic tannages. Salt is not only unnecessary, but actually inhibits the uptake of these products.

The different chain lengths of the polyphosphates influence the softness and tightness of the final leather. If a salt-free polyphosphate pickle is used directly before chrome tannage a green colour develops, and when dried an undyed leather throws a grey coloration. This means that it is difficult to produce pastel shades. This may not be a problem with some volume dyeings or heavily finished automotive leathers. 

Legend

- 1) Coriagen CRII and V by BK Guilini GmbH.

Additional Information

Phosphates and their use in leather manufacture: Dr. T. Staffel, BK Guilini GmbH & G. Moog, Lederinstitut Gerberschule Reutlingen, Germany—World Leather April 1998.