



The real cost of a kilo of salt

Papers have been presented in World Leather since May 2005 with focus on salinity-related problems. The objective is to bring together a series of papers to assist tanneries in reducing the environmental impact of their manufacture, and help secure their future. Salinity is the unresolved component in wastewater treatment, but considerable work has already taken place to help minimise this difficult problem. The following paper is an amended version of the original CSIRO publication of the same name. It describes a series of investigations that were made in the 1990s into salt-free pickling systems, based on phenol sulfonic acid preparation.



A salt-free pickling regime for hides and skins

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In the conversion of hides and skins to chromium tanned leather, an intermediate pickling (*or acidification*) step is normally performed. This enables the even penetration of chromium into the collagen matrix. Traditionally, the acidification is achieved using a mineral acid such as sulfuric or an organic acid such as formic or a mixture of the two. Salt, usually sodium chloride, is added to restrict the swelling of the collagen in the acidic medium. This pickling process is both inexpensive and very effective but it suffers in that high salt concentrations in the tannery effluent can be a serious environmental problem, in particular where the tannery cannot discharge its effluent to a marine environment.

Over the past 40 years, several studies have shown that, in the absence of salt, organic sulfonic acids can suppress the swelling that occurs in pickling¹⁻⁵. This concept has culminated in the commercial availability of several preparations as salt-free pickling agents. However, many of these products are either ineffective below pH 3, or impart undesirable characteristics to the resultant pickled stock.

The following paper describes a series of pilot studies to investigate salt-free pickling systems based on phenol sulfonic acid preparations. These investigations were made on hides, sheepskin pelts, and woolsheep, and the successful findings were subsequently performed on full commercial scale

The Phenol sulfonic Acid preparation

Two different methods of production were used to create two product variations:

PREPARATION No 1: OLEUM PREPARATION

Oleum (*at 65%*) was slowly added to phenol (*1:2.2*

phenol:oleum equivalent) over 4 hours, with stirring and cooling in ice, so that the reaction temperature was kept below 80°C. The reaction mixture was then warmed to 80°C and left to stir at that temperature for 12 hours. The mixture was cooled and water added to make up a 60% solution of product.

PREPARATION No 2: SULFURIC ACID PREPARATION

Concentrated sulfuric acid was added to phenol (*1:2.2 phenol:sulfuric acid equivalent*) so that the temperature was kept below 80°C. The reaction mixture was then warmed to 120°C and left to stir at that temperature for 5 hours, and maintained at that temperature for 5 hours. The mixture was cooled and water added to make up a 60% solution of product.

The salt free pickling of hides, sheepskin pelts, and woolskins

The details of the trials performed are summarised as follows, the percentage chemical offers being based on the delimed pelt weight.

FULL THICKNESS HIDES

Three different sets of conditions were investigated

The standard acid/salt pickle (as control)

Delimed hides were drummed with 25% water at 25°C, then 6% sodium chloride and 0.5% sodium formate added, and run 10 mins. 2.4% sulfuric acid in 10% water was then added, and drumming continued to achieve the pickle conditions as required by the comparative salt-free process.



The salt-free equilibrium pickle

Delimed hides were drummed with 25% water at 25°C, and 0.5-1.0% sodium formate was added. Drumming was continued for 10 mins before addition of 6% phenol sulfonic acid No.2 preparation diluted in 10% water. Drumming was continued for a further 2 to 3 hrs, then 0.6-1% sulfuric acid in 10% water added to further adjust the pH as required.

Drumming was continued for a further 12 hrs. The pH of the pickling liquor ranged between pH 1.5-3.0, depending on the extent of deliming of the hides and the amount of sulfuric acid added. The cut showed full penetration of the acid to bromocresol green. The running time for the control (*the standard pickle*) was based on these times and also achieved full acid penetration.

The salt-free non-equilibrium pickle combined with chrome tannage

Delimed hides were treated with phenol sulfonic acid No.2 preparation, followed by a sulfuric acid addition as in the previous example.

Drumming was continued for a further 30 mins and 8% chromium tanning agent was then added. Full penetration of the chromium was achieved after 5 to 7 hrs. The pH of the tanning mixture was then raised to 3.5 to 4.1 using magnesium oxide.

SHEEPSKIN PELTS

The salt-free equilibrium pickle combined with chrome tannage

Delimed hides were drummed with 25% water at 25°C, and 0.5-1.0% sodium formate was added. Drumming was continued for 10 mins before addition of 3.5% phenol sulfonic No.2 preparation. The pelts were drummed for 60 mins at which time acid penetration was close to completion.

0.4% Formic acid was added, and after running for 30 to 60 mins. followed by an offer of 8% chromium tanning powder. Full penetration was achieved after 2 hrs of drumming. The pH was raised to pH 3.5 to 4.1, using magnesium oxide over 3 hrs, and the pelts drained and washed.

WOOLSKINS

The salt-free pickle

Two different techniques were used:

- The woolskins (50-75mm wool length) were drummed (2rpm) in water (20l/skins, 25°C) containing sodium formate (2.5g/l). The sodium formate was used to both mask the chromium in the subsequent tannage and also to partly neutralise any excess acid in the preparation.

After 1 hr, phenol sulfonic acid No.1 preparation was added (15g/l). The skins were drummed intermittently for 18 hrs till acid had fully penetrated (*to bromocresol green*). Full acid penetration of a standard pickle took place after a similar

Panel 1: Compositions of phenol sulfonates under various sulfonation conditions

Sulfonation acid mixture	Mono Sulfonate (%)	Di Sulfonate (%)	Tri Sulfonate (%)
65% Oleum (Preparation 1)	40	60	Trace
Conc. sulfuric acid (Preparation 2)	50	50	0
Excess concentrated sulfuric acid	50	50	0

Panel 2: Swelling of hides and skins in salt-containing and salt-free pickling systems

Acid used	Increase/decrease in weight (%)	
	Woolskin [§]	Pelt/hide [#]
Sulfuric acid only (no salt)	70 to 90	30 to 40
Sulfuric acid with salt (standard pickle)	-35 to -40	-8 to -12
Phenol monosulfonic acid (purified, min. H ₂ SO ₄)	20 to 30	-6 to -8
Preparation 1 (65% oleum)	-30 to -40	-8 to -11
Preparation 2 (concentrated sulfuric acid)	0 to 20	-4 to -9
Preparation 2 with 3g/L sodium carbonate	-15 to -20	—

[§]Per cent weight gain (loss) is based on green, shaved woolskin weight.

[#]Per cent weight gain (loss) is based on delimed hide/pelt weight.

time span. The final pH was 2.7.

- The woolskins (50-75mm wool length) were drummed (2rpm) in water (20l/skins, 25°C) containing sodium formate (2.5g/l) and sodium carbonate (2.5g/l). Phenol sulfonic acid No.2 preparation was added (15g/l). The skins were drummed intermittently for 18 hrs till acid had fully penetrated (*to bromocresol green*). Full acid penetration of a standard pickle took place after a similar time span. The final pH was 3.1.

The salt-free non-equilibrium pickle combined with chrome tannage

Two different techniques were used:

- The woolskins (17mm wool length) were drummed (2rpm) in water (10l/skin, 25°C) containing phenol sulfonic acid No.2 preparation (50g/l). The skins were drummed for 1 hr and drained well. The final pH was 1.5.

To the pickled skins was added recycled chromium liquor (10l/skin, specific gravity 1.03) which had been reconstituted to a chromium concentration of 30g/l with chromium tanning powder. The skins were drummed for 2 hrs then intermittently 2 mins/10 mins for a further 4 hours or until full chromium penetration was achieved. Drumming was continued for 4 hrs, during which period the pH was then raised to 3.6 - 4.0 with 10% sodium bicarbonate solution. ➤



A SALT-FREE PICKLING REGIME FOR HIDES AND SKINS

- The woolskins (50-75mm wool length) were drummed (2rpm) in water (30l/skin, 25°C) which contained phenol sulfonic acid No.2 preparation (50g/l). Drumming was continued for 1 hr and the skins were then drained well. The final pH was 1.2.
To the pickled skins was added recycled chromium liquor (10l/skin, specific gravity 1.03) which had been reconstituted to a chromium concentration of 20g/l with chromium tanning powder. Processing was then the same as described in the previous trial.

The composition of Phenol Sulfonic Acid preparations

Proton NMR analysis of the two phenol sulfonic acid preparations showed that the ratio of sulfonates was dependent on the sulfonating conditions as shown in *Panel 1*.

The pickling investigations

As expected, swelling occurred when sulfuric acid alone was used and deswelling was observed when salt was included in the pickle. Deswelling also occurred when phenol sulfonic acid preparations were employed, as shown in *Panel 2*.

Previous workers¹⁻³ in the field reported that phenol-4-sulfonic acid did not suppress swelling in the salt-free pickling of hides and skins. None of these reports studied the efficacy of phenol-2,4-disulfonic acid. Since the preparations of phenol sulfonic acid in this investigation were always mixtures, the efficacy of these preparations in a salt-free pickling regime must therefore have been due to either:

- the lack of free sulfuric acid in the pickling mixture or
- the possible greater efficacy of the phenol-disulfonate (or

even the trisulfonate) over the mono-sulfonate which are present in the preparations (No.1 and 2) and absent in the previously studied preparations^{1,2}.

The greater effectiveness of the 65% oleum (No.1) preparation (For example, as indicated in *Panel 2* preparation No.2 could be used to pickle sheepskins in long floats) suggests that the ratio of di- to mono-sulfonates was important as the disulfonate predominated. The observation that a mixture synthesised using phenol and a large excess of concentrated sulfuric acid invariably resulted in the swelling of the hides or skins, was also relevant.

This observation helped explain the failure of previous workers in the field¹⁻³ to observe any suppression of swelling with commercial phenol-4-sulfonic acid. These preparations probably contained a large excess of sulfuric acid.

In contrast, when the requisite stoichiometric quantity of 2 moles sulfonating agent (sulfuric acid) to 1 mole phenol was employed, the resultant preparation was effective as a salt-free pickling agent. This preparation consisted of an approximate equimolar mixture of the mono- and di- sulfonates as well as minimal quantities of free sulfuric acid.

With the concentrated sulfuric acid preparation (preparation No.2), considerable swelling was observed in the salt-free pickling of woolskins in conventional, long floats (20 l/skin). This could be ameliorated by addition of sodium carbonate as this, in effect, appeared to neutralise some of the excess sulfuric acid, which seemed to be a problem at these float levels. Alternatively, reducing the float to 10l/skin and using 50g/l of the preparation was found to eliminate swelling.

The pickling of hides could be achieved in a process, which

Panel 3: Reducing salts and sodium ion in tannery waste waters

High salinity in irrigation water causes high osmotic pressure. This results in reduced water availability and retarded growth of crops. In addition, high concentrations of sodium can adversely affect the soil structure by causing dispersion of clay. Salts and sodium ion are commonly added to wet-blue processes, but work by CSIRO has shown that in practice these effluent loads can be minimised. These developments include:

- processing green hides
- reducing floats and chemical consumption
- reusing lime liquors in conjunction with hair saving processes
- carbon dioxide deliming
- direct recycling of chrome liquor

The quantities of salts consumed in basic processing, change to salt-free hides, and the use of recycling in unhairing and conventional pickle/tannage are generalised in Item 3/1.

The content of this panel have been extracted from the paper entitled "Clean Technology Challenges" presented by Catherine Money, CSIRO, IULTCS (XXV), India, 1999.

Item 3/1 The minimisation of salts and sodium ion achieved in wet blue manufacture

Process		% Salts		% Sodium	
		Basic process	Recycle process	Basic process	Recycle process
Soak	Salted hides	14.0		5.60	
Lime/Unhair	1.0% NaHS (70%)	1.0		0.30	
	1.5% Na ₂ S (60%)	1.5	0.75	0.55	0.27
	2.5% Ca(OH) ₂	2.5	2.25		
Delime	1.0% CO ₂	-			
	1.0% (NH ₄) ₂ SO ₄	1.0			
	0.5% Na ₂ S ₂ O ₅	0.5		0.10	
Pickle	6.0% Salt	6.0	2.00	2.50	0.80
	1.0% HCOOH	1.0	0.75		
	1.0% H ₂ SO ₄	1.0			
Tannage	8.0% Chrome Powder	7-8	5-6	0.8	0.5
	0.7% MgO	0.7			

A SALT-FREE PICKLING REGIME



mimicked the conventional acid/salt regime. Generally, 4% of the phenol sulfonic acid mixture based on green weight of the hides, or 6% based on the delimed weight was added in place of the conventional pickling acid and salt. To further lower the pH of the pickle (*when required*), dilute sulfuric or formic acid was added with no observed deleterious effects. pH levels as low as pH 1.2 were achieved in the absence of any added salt and with no observable swelling.

Full scale trials

Full scale industrial trials using full thickness cattle hides (10 tonnes) and employing the salt-free phenol sulfonic acid mixture (*preparation No.2*), produced leather, which was indistinguishable from conventional leather production.

Pelts could also be pickled in a similar manner. However, the phenol sulfonic acid mixture (*preparation No.2*) together with sulfuric acid (*to lower the pH*) could not be satisfactorily employed for a storage pickle despite the low pH levels achieved. In the absence of salt, incubation at 35°C of pelts pickled to pH 1.5 resulted in extensive degradation in approximately two weeks.

The advantages of the non-swelling acid pickle process

The acid-free pickling process described offers the following advantages over the conventional salt/acid process:

- It is sodium chloride free, and results in significant reduction in the salinity of tannery effluent.
- The pickling acid penetrates hides and skins as rapidly as the conventional salt/acid pickle.
- The preparation can be readily used in conjunction with the mineral and organic acids used in the conventional salt/acid process.
- The salt-free pickling process is compatible with conventional pickling and chromium tanning regimes.
- The pickle stock obtained by the process is similar to that obtained by conventional salt/acid pickling.
- Chromium tanned hides obtained using the salt-free pickling process on an industrial scale have proved to be indistinguishable from those produced conventionally.
- The pickling formulation is biodegradable⁷.

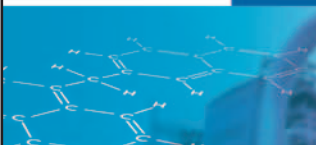
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- *The technology is subject to PATENT: Patent, WO 9606953 - A1, 7 March 1996*

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