



Reducing salinity in the pickle-tanning process

Part 1 of 2

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The following paper describes a series of structured investigations with the objective of eliminating common salt from the pickle-chrome tanning process.

As pressures to reduce salinity in waste waters increase, the findings and descriptions provide a detailed insight into the technical issues that face tanners who seek to achieve this target.

The problem of salinity

On a global scale, salinity represents a major environmental problem. The availability of quality water is diminishing, and cause for widespread concern. Contamination of surface waters and the aquifer are increasing in many areas, rendering water that was previously available unsuitable for either consumption or land irrigation.

With regard to tannery effluent treatment, salinity remains the most difficult component to address. Sodium chloride, or common salt, is unchanged by effluent treatment as it simply passes through the system in solution. High technology offers reverse osmosis, but this simply produces one stream of treated effluent with a reduced level of salinity, and a second stream at a correspondingly increased concentration. The salt does not vanish, and remains in solution. Any option for treatment must therefore include evaporation, or possible relocation for marine discharge of treated effluents.

The emphasis is now on minimising salts within production. In this situation there are three sources that account for salinity: salt used in preservation, from the pickling-chrome tanning process, and residual from the manufacture of auxiliary products. Alternatives to salt preservation are possible, and salt minimisation by selection of auxiliaries, but salt discharge from pickle-chrome tannages can represent more than 25% of the salinity load.

Moreover salt elimination or reduction in the pickle-tanning liquors stands as one of the most technically difficult problems. This is because of the role of salt on the inhibition of acid swelling.

The swelling and deswelling of collagen

The great number of electrically-charged groups present in

Figure 1: The amphoteric character of collagen

High pH conditions	Low pH conditions	
OH^-	H^+	
$\text{H}_2\text{N}-\text{R}-\text{COO}^-$	$^+\text{H}_3\text{N}-\text{R}-\text{COO}^-$	$^+\text{H}_3\text{N}-\text{R}-\text{COOH}$
$^+\text{H}_2\text{O}$		
Anion charge	Iso-electrical point	Cation charge

collagen^(1,3,4) enable cationic behaviour at a low pH, and anionic behaviour at high pH, as indicated in *Figure 1*.

Starting from the iso-electrical point, if the pH is reduced by the addition of an acid (H^+), carboxyl groups lose their negative charge, while the amine groups remain positively charged. This cationic charge is the basis for "acid swelling".

Under alkaline conditions the reverse occurs, the amino groups being neutralised through the addition of alkali (OH^-). The negatively charged or anionic carboxyl groups prevail creating alkaline swelling.

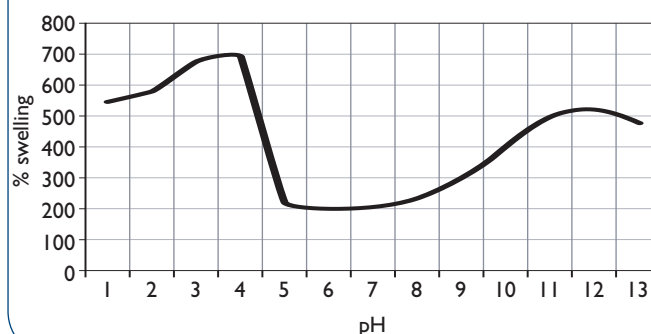
However, acid swelling is stronger than alkaline swelling as the loss of charge from the carboxyl groups - hence increase in cationic charge - only occur within a small pH margin. The highest swelling takes place at $\text{pH} = 3.5$, but at a very low pH (0.5-2.0) the ion rate is so high that it leads to a partial deswelling.

Under alkaline conditions the charges associated with guanidine and arginine groups (NH_3^+) are lost only at extremely high pH values, that is around $\text{pH} 13.0$. A typical swelling curve is presented as *Figure 2*.

The restriction of swelling by salt

The ability of salt to avoid swelling⁽⁶⁾ in strong acid solutions is in direct relation to its concentration and to its dissociation in ions. A 4% concentration of sodium chloride suffices to inhibit the swelling completely, but generally 6% is used in industrial practice as a preventive measure.

Figure 2: Swelling curve of collagen at different pH values





The ability of a salt to prevent swelling at a given concentration also depends on the kind of acid used.⁽¹¹⁾ This is because the degree of swelling produced by weak organic acids depends on their dissociation constant. For this reason, if using weak acids, it is often possible to use lower salt concentrations than required by strong acids.

Notwithstanding, the inclusion of sodium chloride in solution, the chloride and sodium ions being ionised, causes the chloride ion to pass from solution (the process bath) into the collagen structure by osmotic effect. The positive charges of the amino groups (NH_3^+) are thus neutralised, and the repulsion and swelling effects are avoided.

The use of sulfuric/formic acid combinations in the pickling process with common salt to repress swelling is well established. Even so, during the latest ten years, there have been many proposals involving the use of different types of sulfonic acids - that is low molecular syntans - as "non-swelling acids" to avoid swelling, and eliminate the need for salt.

Many papers deal with this subject,^(8,9,10,11,12,14) but the most outstanding was written by G. Otto,⁽¹³⁾ who studied the behaviour of 16 aromatic sulfonic acids and their neutral salts. Where sulfonic acids containing only one ring and increased dipolar activity were studied, acid swelling, that is the percentage of absorbed water, was diminished. However, sulfonic acids with two rings and a high dipolar activity repressed the swelling to a greater degree.

Investigation: minimising swelling under acid conditions

The non-swelling potential of four products were studied with the objective of eliminating salt within the pickling-chrome tanning process, being:

- Polyacrylic acid
- Naphtol 3-6-disulfonic acid
- P-hydroxydiphenyl sulfonic acid
- A blend of naphthalene and naphthol sulfonic acids

Figure 3: Standard process for measuring degree of swelling

- 80 % water at 25°C
- + Salt to provide 0°, 1°, 2°, 3°, 4°, 5°, 6°Be.
- 3 % Product - (a), (b), (c), and (d)
- Run 60 min
- Check thickness⁽¹⁾ & pH**
- 1 % formic acid (1:10)
- x % sulfuric acid (1:10)
- Run 180 min
- Adjust pH = 3.0
- Check thickness & drained weight⁽²⁾**
- 6 % chrome salt 33°Sch
- Run 120 min
- 0.7 % Basification^(A)
- Run 8 hr
- Final temperature 42°C
- Check thickness, pH & Ts**

⁽¹⁾ Thickness in four marked parts of each sample

⁽²⁾ Standard method used

^(A) Plenatal HBE

Figure 4: Percentage of water absorbed at pH = 3.0

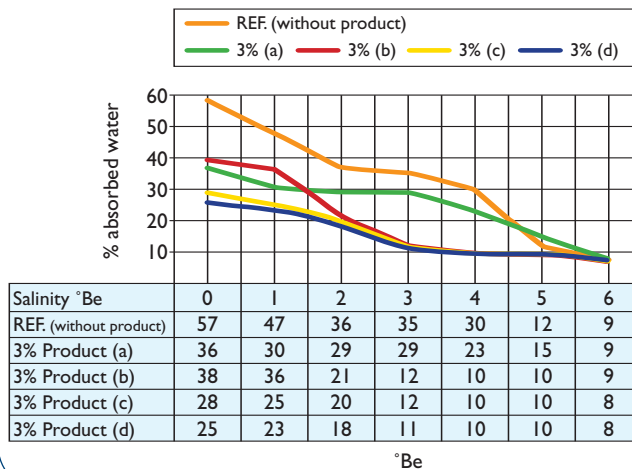
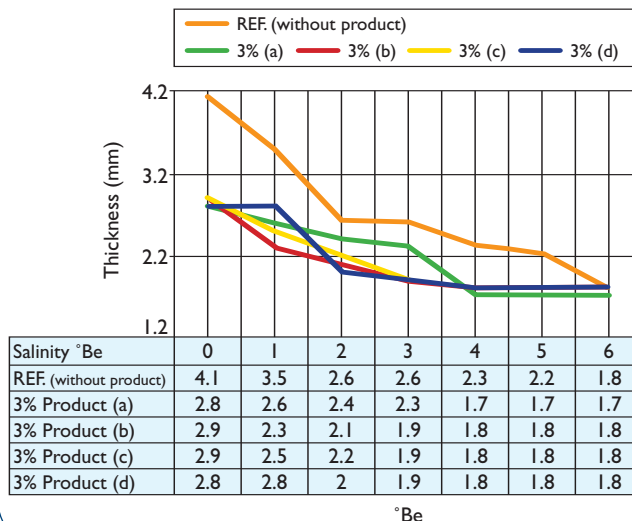


Figure 5: Thickness in pickle



In the initial stage, a pelt split to 3mm was delimed/bated, rounded and divided in to 450-g pieces, then processed in small drums using the method given as *Figure 3*.

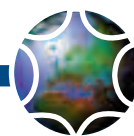
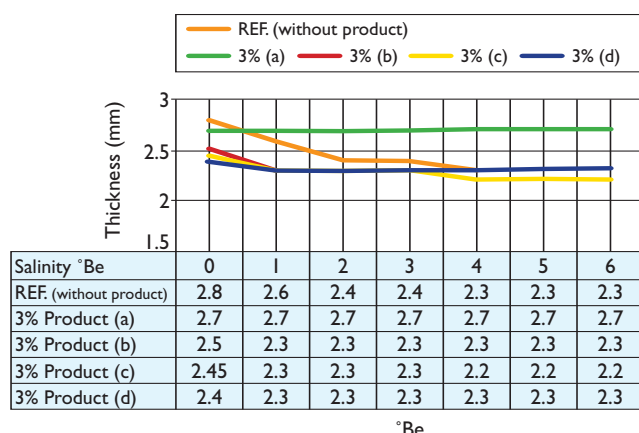
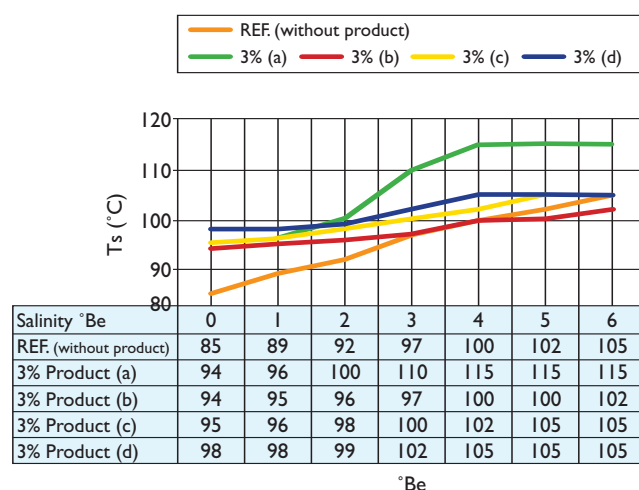
When creating the initial bath for each trial common salt was used at increasing amounts to study the effects of the different non-swelling products across a salinity gradient. The range commenced at 0°Be - being without any salt - to 6°Be reflecting the levels of salt in normal pickling systems.

WATER ABSORBED IN PICKLE AT INCREASING SALINITY USING NON-SWELLING PRODUCTS

The percentage of water absorbed at the end of pickle at pH 3.0 is given as *Figure 4*.

HIDE THICKNESS FROM PICKLE AT INCREASING SALINITY USING NON-SWELLING PRODUCTS

Based on a substance of 1.9 mm after deliming and bating, the degree of swelling was measured at the end of pickle. The findings are given in *Figure 5*.

**Figure 6: Final thickness in tannage****Figure 7: Shrinkage temperature variations**

HIDE THICKNESS FROM PICKLE AT INCREASING SALINITY USING NON-SWELLING PRODUCTS

The hide thickness was measured at the completion of tannage (pH 3.9), and the results are given in *Figure 6*.

SHRINKAGE TEMPERATURE VARIATIONS A RESULT OF PICKLE AT INCREASING SALINITY USING NON-SWELLING PRODUCTS

The shrinkage temperatures were measured at the completion of tannage (pH 3.9), and the results are given in *Figure 7*.

Observations from the studies

SWELLING AT THE END OF PICKLE

From the water absorption and thickness increase curves, *Figures 4 & 5*, there are four inferences:

- At values of 0°, 1°, and 2°Be, all four products reduce the swelling sharply.
- Starting from 3°Be, swelling values tend to become equal. This equality is reached at 6°Be
- The addition of any of the four products at 0°Be does not give the same values as a standard pickle at 5°-6°Be
- Further investigations are needed commencing 2°Be.

Figure 8: Standard Dye-fatliquoring process

Rinse: 200 % water at 30°C
0.2 % oxalic acid
0.2 % ethoxylated fatty alcohol^(B)
Run for 10 min. Run-off

Neutralise: 100 % water at 30°C
2.0 % sodium formate
0.2 % sodium bicarbonate
2.0 % neutralising agent^(C)
Run for 60 min. pH = 5.2
Drain, rinse for 10 min

Dye/Fatliquor: 50 % water at 30°C
2.0 % dyestuff
Run for 60 min
100 % water at 60°C
5.0 % sulphated triglycerid^(D)
5.0 % sulphochlorinated paraffin^(E)
Run for 60 min
2.0 % formic acid
Run for 60 min. pH = 4.0
Drain, rinse 10 min

Mechanics: Samm, Dry, Dampen, Stake, L* measurement

(B) Celesal DL (C) Retanal NS (D) Fosfol 50 (E) Fosfol SC-87

SWELLING AT THE END OF TANNAGE

From the findings summarised as *Figures 6 & 7*, the following observations are made:

Reference sample: The reference sample (without any product), at the end of tannage, shows that a degree of swelling remains between 0° and 3°Be. This becomes stabilised at Beame readings greater than 3°Be. However, the pieces from processing at 0°, 1°, and 2°Be do not reach an adequate shrinkage temperature. They break with the greatest ease.

Polyacrylic acid samples (a): These samples showed a deswelling effect during pickling, and become equal in thickness after tanning at all Beame levels, even showing greater relaxation in relation to the other samples. In addition, a greater amount of chrome is fixed, with higher shrinkage values.

This phenomenon is due to the fixation of the polymeric compounds, co-ordinated with the chrome, on the leather. It is exceptional behaviour, as the polymer provides both a non-swelling effect during pickle, and chrome fixing properties during tannage.

naphthol 3-6-disulfonic acid (b)

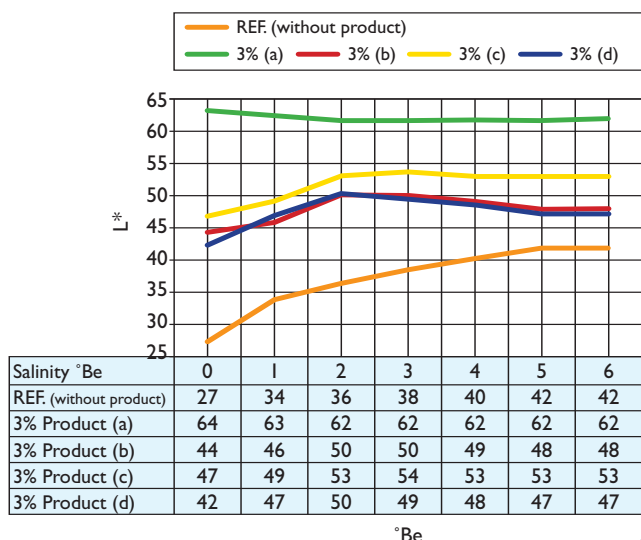
p-hydroxydiphenyl sulfonic acid (c)

a blend of naphthalene and naphthol sulfonic acids (d):

All of these products show similar behaviour as far as after-chrome thickness is concerned. Product (d) gives slightly higher values in shrinkage temperature.

The effects of dyeing and fatliquoring

Wet-blue pieces were shaved to a standard thickness of 1.4 mm, dyed and fatliquored in accordance with formulation given as *Figure 8*.


Figure 9: Intensity of colour


INTENSITY OF COLOUR AND GENERAL OBSERVATIONS

The intensity of colour (L^*) was measured and is shown in Figure 9.

Reference sample: All samples at 0°, 1°, and 2°Be show a very dark colour, are hard, and break easily. Samples 3° and 4°Be have a more uniform colour and an acceptable feel. Samples at 5° and 6°Be show a clean uniform colour, and provide the standard colour at 6°Be of $L^* = 42$.

Polyacrylic acid samples (a): All samples show very light, clean and uniform colour on the grain side. In general the feel is more compact than the Reference. However, the colour on the flesh side is deeper. This is because the polymer, which had not penetrated completely, was removed from the flesh side on shaving.

naphthol 3-6-disulfonic acid (b)

p-hydroxydiphenyl sulfonic acid (c)

a blend of naphthalene and naphthol sulfonic acids (d): Samples treated with (b) and (d) show similar behaviour as far as colour and feel are concerned. Product (c) lightens the colour more than (b) and (d). The colour difference between grain and flesh sides from (b), (c), and (d) is not so marked as (a). This means that a certain amount of product has reached the central part of the leather. The colour is lighter than in the Reference, but it remains within acceptable limits, particularly at values greater than 2°Be.

Taking all of the results into account the following conclusions were formed:

- Polyacrylic acid (a), despite its repression of swelling and its capacity to fix more chrome, would not be suitable on account of the sharp colour difference and lack of penetration.
- Product (d) could be a valid alternative at 2°Be. It represses the swelling sufficiently, gives a good shrinkage temperature, and does not reduce the colour too much compared with the Reference ($L^* = 50$ against 42).

Study of optimised conditions

Unsplit and complete delimited pieces (22Kg hide weight) were

chrome tanned using a conventional pickle (salt 6°Be), and a modified system using salt at 2°Be and the blend of a naphthalene and naphthol sulfonic acids as 3.0% Product (d) under optimum conditions. The techniques used are given in Figure 10.

Figure 10: Reference and modified pickle for chrome tannage

Reference pickle-tannage	Minimised salt pickle tannage
60 % water at 25°C	60 % water at 25°C
Salt to 6°Be	Salt to 2°Be
1.0 % sodium formate	1.0 % sodium formate
Run for 30 min. pH = 8.3	Run for 30 min. pH = 8.3
1.0 % formic acid (1:10)	3.0 % Product (d)
0.9 % sulphuric acid (1:10)	Run for 3 hours
Run for 3 hours	0.6 % sulphuric acid (1:10)
Penetration at pH 3.0	Run for 2 hours
	Incomplete penetration at pH 3.0
7.0 % Chrome salt 33°Sch	
Run for 2 hours	
0.7 % Basifying agent ^(a)	7.0 % chrome salt 33°Sch
Run for 8 hours	Run for 2 hours
Temp 42°C, pH 3.9	0.7 % Basifying agent ^(a)
Shrinkage temperature 100°C	Run for 8 hours
	Temp 42°C, pH 3.9
	Shrinkage temperature 100°C

In both of these processes, the pH in the bath was recorded, and penetration through the section using universal indicator (UVI) and bromocresol green (BCG). It is important to stress that these observations were carried out in the thickest parts of the samples, being the most representative for control purposes.

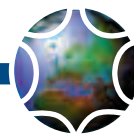
The development of the reference pickle is shown in Figure 11. This shows that after one hour the pH in the bath and inside the pelt is pH 2.2 and pH 5.0 respectively, reaching an equilibrium of pH 3.0 after three hours.

However, the situation develops quite differently in the modified process. Due to its acidity (pH = 1.2 at 10%), Product (d) acts as a strong acid so although the pH in the bath is pH 2.2 after one hour, the section remains unchanged at pH 8.5. After two hours the pH of the bath is 2.7, with a small decrease inside the leather to approximately pH 8.0. After three hours process, the pH in the bath is 2.9, and 7.5 inside the leather.

Despite being a strong acid, Product (d) only penetrates slowly. Moreover, two hours after the addition of sulfuric acid, the pH inside the leather is still slightly high at pH 6.0. These findings are presented as Figure 12.

Analysis of the residual float and the leathers show that chlorides are reduced to a third, total conductivity to a half, COD decreases slightly, residual chrome in the bath is similar, and a chrome content of 3.86% and 3.8% in the control and modified leathers respectively. The stratigraphic distribution of Cr_2O_3 in the modified process is worse than in the standard reference, and the results are presented in Figure 13.

The wet-blue was shaved to 1.4 mm, then neutralised, dyed and fatliquored with the standard formulation given as the

**Figure 11: pH change in the reference pickle bath**

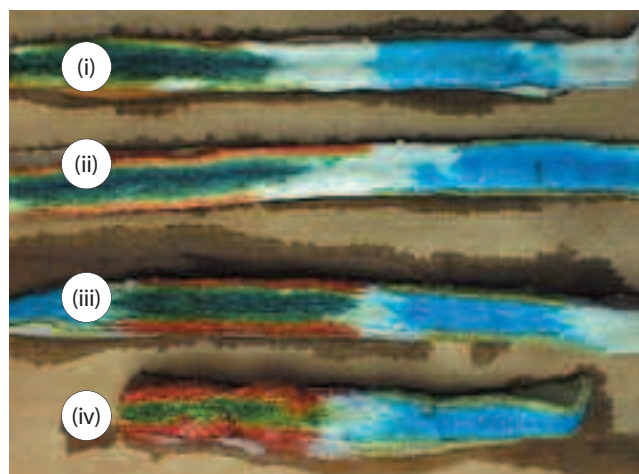
(i) 1 hour (ii) 2 hours (iii) 3 hours

Figure 13: Analytical data from the control and modified pickle-tannage

	Chlorides g/l	Conductivity Micro-Siemens/cm	C.O.D. ppm	Cr ₂ O ₃ (bath) g/l	Cr ₂ O ₃ (leather) %
Ref.	7.42	76,000	6,000	2.1	Grain-4.0 Middle-3.7 Flesh-3.9
Product (d)	2.5	38,000	5,600	2	Grain-4.4 Middle-3.0 Flesh-4.0

standard formulation *Figure 8*. This showed that compared to the reference, the colour (L*) on the grain side is lighter with the modified process, with a greater difference in intensity between the grain and the flesh sides. In addition the grain is slightly more shrunken and the tear strength slightly lower, although the feel and tensile strength is similar. Details of these results are presented in *Figure 14*:

At this stage of the investigation the following conclusions were formed regarding leathers from low salinity pickle systems incorporating the use of non-swelling acids

Figure 12: pH change in the modified pickle bath(i) 1 hour (ii) 2 hours (iii) 3 hours Product (d)
(iv) 3 hours Product (d) + 2 hours sulfuric acid**Figure 14: Values from the control and modified pickle-tannage**

	Colour		Feel (IUP-36) (0-8)	Tensile Strength N/cm ²	Tearing resist. N
	Grain	Flesh			
REF.	41	38	4.23	2,160	95
Product (d)	49	30	4	2,200	88

- Considerable reductions of salt in pickle are possible.
- Acceptable physical properties and handle are possible.
- The colour on the grain side can be acceptable, but the colour differential between the grain and flesh needs reducing.
- Further investigations are needed to develop working systems where salt is eliminated in pickle.

The investigation is concluded in Part 2, and will be published in World Leather May 2003