

The use of non-swelling acids in pickle to minimise the chloride content in wastewaters

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In our industrialised society, responsibility for environmental protection is becoming more and more important. Not surprisingly environmental awareness has grown in leather production as it has elsewhere. Tough official regulations governing effluents, waste air and solid waste disposal provide the legislative background to this environmental sensitivity. To meet specified limit values products and application methods must measure up to stringent requirements. Optimum exhaustion of products, environmental compatibility of the by-products formed, and avoidance of waste are very important. Compliance with stricter effluent legislation and landfill regulations is a severe challenge to both the leather industry and the industry supplying it with chemicals. In a look-ahead leather factory, environmental protection is therefore every bit as important as leather quality, productivity and profitability.

Most effluent pollution arises in the beamhouse and within chrome tanning. In this situation the high chloride, sulfate and chromium concentrations present in exhaust processing floats play a central role. Sodium chloride is used in both curing and pickling, and in tanning the non-fixed chromium and sulfate pass into the effluent.

Against this background, and motivated by the widening discussion of pollution generated by salts and heavy metals, existing techniques can be optimised to reduce these problems. In pickling the replacement of mineral acids and a reduction in inorganic salts by non-swelling organic acids has proved effective.

Pickling with non-swelling acids and reduced salt content

Skins are mainly acidified within pickle using sulfuric and formic acids. To avoid acid swelling and a weakening of the skin, large amounts of neutral salts are added as they repress swelling. This is the traditional method used, but causes heavy chloride pollution. The obvious alternative is to use a low-salt pickling system.

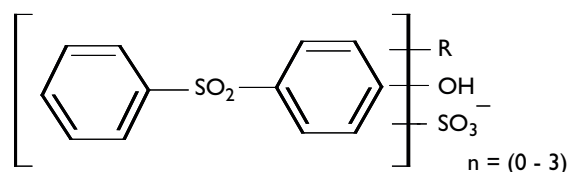
G. Otto created the term "non-swelling acids" for a large

number of aromatic sulphonic acids in 1957. Specifically noted were mononuclear, binuclear and polynuclear sulfonic acids, as these become firmly anchored at the charge centres within the skin due to their dipolar properties. In this event they stabilise the skin and inhibit the uncontrolled uptake of water. This prevents acid swelling.

The chemistry of non-swelling acids

Modified aromatic polysulfonic acid (condensed arylsulfonic acid) can be used as a non-swelling auxiliary^[Legend 2] so that pickling can be performed with less salt. The simplified molecular structure is shown as *Figure 1*.

Figure 1: Simplified structure of condensed arylsulfonic acid



Combination within the skin structure occurs similar to that of a syntan. An electrostatic bond is formed between the collagen and the polysulfonic acid. This can be seen as intermediate between a traditional synthetic auxiliary and a vegetable or synthetic replacement tanning agent.

The exhaustion of the non-swelling acid is excellent. In practice the skins remain non-swollen with growth marks in the neck remaining decidedly flat. It is also noted that a skin stabilisation occurs, and this results in a rise in shrinkage temperature of about 10°C when compared to the traditional pickling process. In addition this technique offers improved handling within subsequent mechanical processes such as samming, splitting and shaving.

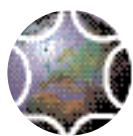


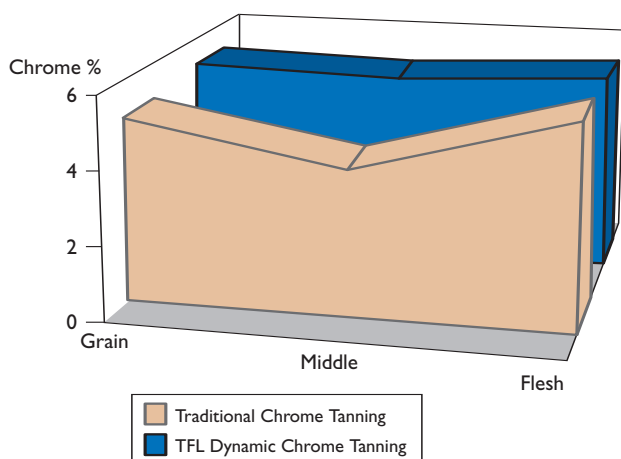
Figure 2: Guideline formulation:
Bovine hides:Weights on fleshed weight

50 %	Water 20°C	
3.0 %	Sodium chloride, Run 15 min	> 3.0 - 3.50 Be
0.0-0.5 %	CORIPOL PL(1), Run 15 min	
0.5 %	Formic acid 85% Run 15 min	
1.8 %	Sellatan P liq.(2) Run 15 min	> pH 3.0 - 3.3
5.0 %	Chrome 25/33	
0.0 -0.1 %	Aracit 4A Run 120 min	
0.3 %	Cromeno FB, Run 640 min Reqd: pH 4.0, temperature 40°C, pass boil test Wash	

Legend: Products by TFL:

- (1) Coripol PL - acid stable fatliquor that could be included to produce a finer grain.
- (2) Sellatan P - aromatic polysulfonic acid as non-swelling acid.
- (3) Cromeno FB - basifying agent.
- (4) Aracit 4A - Preservative

Figure 3: Chrome distribution throughout the cross-section



Benefits from improved chrome diffusion and fixation

The technique enables a reduced offer of formic/sulfuric acid to meet a suitable pH for tanning. A standard recipe is given as Figure 2.

The actual chrome tanning process may not need to be significantly changed, and in practice the process must be adapted to the tannery needs. However, the process is improved

Panel I

Minimising the chloride and sulfate content

The major problems that remain in treating tannery effluents are the presence of sodium chloride and sulfate. In processing 1000 kg raw hide approximately 300 kg of inorganic salts are released as indicated:

- 200 kg salt as sodium chloride from curing
- 20 kg sodium chloride/sulfate from beam-house chemicals
- 40 kg sodium chloride from pickling
- 37 kg sodium sulfate from chrome tanning
- 3 kg sodium chloride/sulfate from wet-end chemicals.

Raw hide is mainly preserved (in global terms) using more than 20% common salt on the raw weight. In many tanneries, skins are now put into work in the fresh, cooled (green) state, and in this event more than 200 kg salt in the effluent can be avoided per tonne of raw hides.

However, sodium chloride is also used in pickling. In traditional pickling and dependent upon the float, 6-20% sodium chloride, and up to 0.7% formic and 1% sulfuric acid are used. By using non-swelling acids the salt content as chloride can be significantly reduced, and the sulfate content arising from sulfuric acid.

as the chrome (or other tanning agents) can diffuse within the skin more easily before forming a stable bond with the collagen.

Within the traditional chrome tanning process the exhaustion of chrome was fairly low, and attempts have been successfully made in the past few years for improvement. If, however, the uptake is irregular or an over-fixation on the grain occurs these leathers can be very difficult in terms of a uniform colouration. Often a great deal of chrome is released by these "over-fixed" leathers in the retanning, dyeing and fat liquoring floats, and this is detrimental to an even uptake and distribution of these products.

The technique presented, however, can enhance chrome fixation when compared with a conventional chrome tanning process. The entire cross-section of the skin can be uniformly tanned as illustrated in Figure 3.

A practical approach to reduce inorganic salts

Considerable progress has been made in reducing the level of inorganic salts arising from the pickling process using non-swelling acids. The results presented are based on methods and recipes carried out in production, and seen as useful for tanners facing problematical chloride levels in their effluent. The process improves grain flatness and tightness of the wet blues and the finished leather shows more uniform dyeing characteristics due to improved chrome distribution. 

Acknowledgements

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