

Reducing salinity in the pickle-tanning process

Part 2

Dr Ramón Palop, Cromogenia-Units S.A., Spain

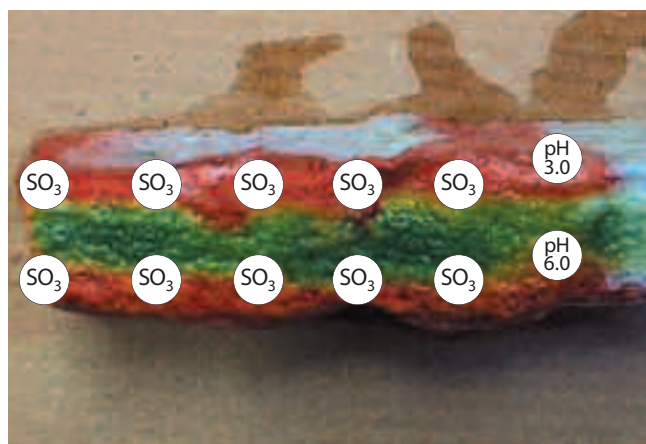
Salinity is a cause for concern in tannery waste waters as it is unaffected by effluent treatment and more than 25% of salinity can be generated from the pickle-chrome tanning process. Part 1 of this paper discussed the role of salts in the chrome pickle-tanning process, and investigations into their elimination or reduction by the use of non-swelling acids. Based on the initial findings, the investigation continues in Part 2.

Many permutations using non-swelling acids and reduced levels of salinity in pickle were used in the initial investigations. Although the results were encouraging, the leathers were limited by an irregular penetration of chrome through the cross section, a colour difference between the grain and flesh parts after dyeing, and a slightly shrunken grain appearance.

Study of the pickled hide before the addition of chrome showed a pH value of 3.0 on the grain and flesh sides, with penetration to 1/3 of the section. These values are due to the strong negative charge (SO_3^-) arising from the sulfonic groups of naphthalene and naphthol sulfonic acids (low molecular syntans) used as the non-swelling component - Product (d) - and sulfuric acid. This is illustrated in Figure 15, where the skin section is shown after 3 hrs treatment with Product (d), then 2 hrs pickle with sulfuric acid.

When chrome salt at 33°Sch is added, although the pH is 3.0,

Figure 15: Cross section after 3 hours with Product (d) + 2 hours with sulphuric acid



Acid penetration using Universal Indicator and Bromo Cresol Green

and a high level of sulfonic groups, there is some chrome fixation. Penetration continues through these surface layers to the outer parts of the zone where the pH is 6.0, and the negative charge typical of hide at that pH. The chrome quickly fixes in this zone, but this makes complete and uniform penetration towards the central part of the leather difficult as a barrier of strong positive charge is developed.

This causes irregularities, as observed in the initial investigations. However, it was considered that more uniform distribution could be achieved by using a strongly masked chrome of low basicity in the formulation. This was investigated as shown as Figure 16, using complete delimed and bated bovine hide.

Figure 16: Pickle with minimised salt content in conjunction with masked chrome

- 60 % water at 25°C
+ Salt to provide 0°, 1°, 2°, 3°Be
- 1.0 % Sodium Formate
Run 15 min
- 3.0 % Product (d)
Run for 30 min
- 0.6 % sulphuric acid (1:10)
Run for 30 min
Samples taken for assessment
- 3.0 % masked chrome salt^(F)
Run for 2 hours
Samples taken for assessment
- 5.0 % masked chrome salt^(F)
Run for 2 hours
- 0.7 % Basifying agent^(A)
Run for 8 hours
Temp 42°C, pH 3.9
Shrinkage temperature 100°C

(A) Plenatol HBE (F) Cromosal BS



Figure 17: Water absorption (%) in relation to salt concentration °Be

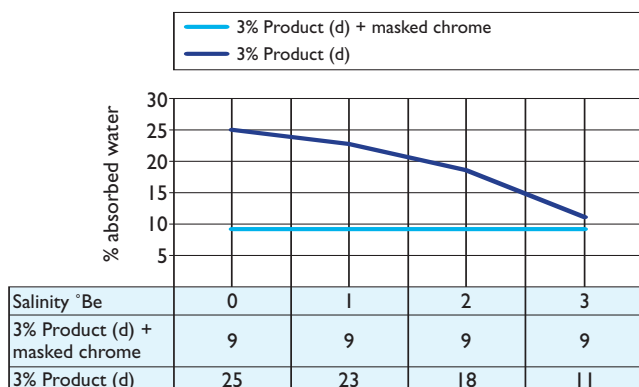
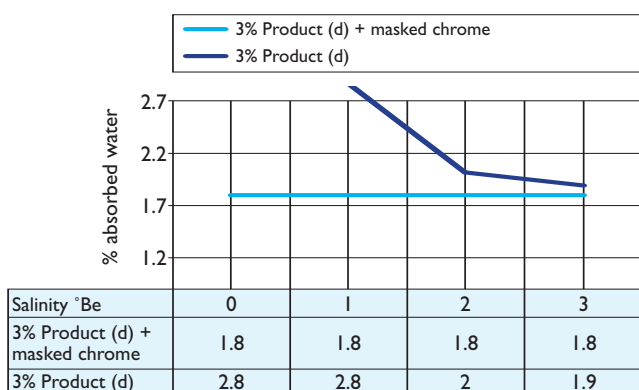


Figure 18: Thickness variation in relation to salt concentration °Be



Samples were taken at the stages identified in Figure 16. These samples were used to measure the percentage of water absorbed in relation to the salt concentration before the addition of the chrome, and the effects after 2 hours run. The findings are given as Figure 17 where it is shown that the masked chrome reduces the percentage of the water absorbed, maintaining it at a constant level irrespective of initial salinity.

Compared with just using Product (d), the masked chrome reduces the thickness that results from acid swelling where salt concentrations are less than 3°Be. This makes the leather stable throughout its structure and is shown in Figure 18.

The effects of process variations

Although it appears that leathers can be successfully produced without using salt to inhibit acid swelling, the effects were studied where the process was disrupted as might occur in manufacture. With reference to the process used in Figure 16, and in the absence of salt, four variables were investigated:

- After the 30 min run in Product (d), lay for 10 hours (equivalent to an overnight lay)
- After the 30 min run in sulphuric acid, lay for 10 hours
- Run the process without introducing the laying periods of 10 hour
- Use the Reference process, but with a salt concentration for pickle of 6°Be. (As given in Figure 19).

Figure 19: Reference pickle-tannage

- 60 % water at 25°C
Salt to 6°Be
- 1.0 % sodium formate
Run for 15 min.
pH 8.3
- 1.0 % formic acid (1:10)
- 0.9 % sulphuric acid (1:10)
Run for 3 hours
Penetration at pH 3.0
- 7.0 % Chrome salt 33°Sch
Run for 2 hours
- 0.7 % Basifying agent
Run for 8 hours
Temp 42°C, pH 3.8
Shrinkage temperature 100°C
(Process as Part I Figure 10)

Figure 20: Water absorbed in relation to process variable

Parameter	Variables			
	(i)	(ii)	(iii)	(iv)
Water absorbed %	22	58	8	8
Thickness mm	2.7	4.3	2.4	2.4

The findings are given in Figure 20.

This indicates that:

- during the 10-hour lay Product (d) continues to penetrate and cause some protection, but the inherent acidity generates some swelling.
- The 10-hour lay after the 30 min run in sulfuric acid allows acid penetration into the inner areas of the pelt. However, this rate of penetration is more rapid than that of Product (d). Product (d), therefore, is not available to inhibit a strong irreversible swelling. This swelling remains after the tannage.
- When no laying periods are introduced, the masked chrome penetrates rapidly and stabilises the protein throughout the whole thickness of the leather. This is shown by the lack of both water absorption and increase in thickness.

Conditions for the elimination of salt in a pickle-chrome tanning process

Further comparisons were made between the reference process and another tanning variation that ensures fast chrome penetration. The details are given as Figure 21:

Samples taken at the various stages show that:

- 30 min after the addition of Product (d), the bath is at pH 3.9, and the section pH 8.3.
- 30 min after the addition of sulphuric acid, the bath is at pH 2.6, and the section pH 8.0
- 30 min after the addition of the chrome alum the bath is at pH 3.0, and the section pH 7.0.
- 60 min after the addition of the chrome alum the bath is at pH 3.5, and the section pH 6.5. In addition a slight blue colour was visible throughout the section as a result of the chrome fixed.



Figure 21: naphthalene / naphthol sulfonic acids + masked chrome

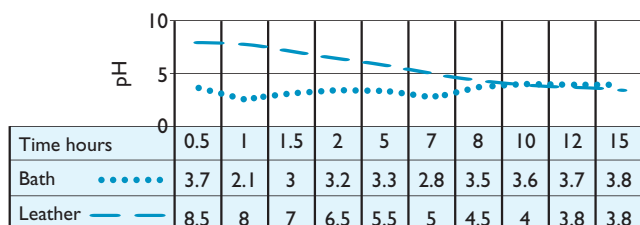
- 30 % water at 25°C
- 1.0 % Sodium Formate
Run 15 min
- 3.0 % Product (d)
Run for 30 min
- 0.6 % sulphuric acid (1:10)
Run for 30 min
- 3.0 % Chrome alum^(G)
Run for 3 hours
- 5.0 % Chrome salt 33° Sch
Run for 2 hours
- 30 % water at 50°C
Run 15 min
- 0.4 % Basifying agent^(A)
Run for 8 hours
Temp 42°C, pH 3.9
Shrinkage temperature 100°C

(g) Chrome alum: $\text{Cr}_2\text{O}_3 = 15\%$, Bas = 0°Sch

- Immediately after the 5% addition of chrome 33°Sch, the bath is at pH 3.6, and the section pH 5.5. A blue chrome colouration was uniform throughout the section.

These changes in pH are summarised in *Figure 22*:

Figure 22: Curves showing pH in the bath and in the leather during tannage



The hides were measured at four different points. This showed that the more empty areas such as the shoulders and butt were slightly thicker in the new process than in the reference, and appeared more compact and level than the reference leathers. These substance measurements at the end of process are given as *Figure 23*.

Analysis of the bath showed significant differences. A reduction in chloride content from 7.16 g/l to 0.17 g/l was achieved, and reduction in the Cr_2O_3 in the bath from 1.9% to 1.2%. The distribution of Cr_2O_3 in the leathers also changed from Reference vs. new process - grain 4.1% to 4.6%, middle 3.8% to 4.8%, flesh 3.0% to 4.7%.

The leathers were subsequently shaved to 1.4 mm, then

Figure 23: Comparing final thickness values

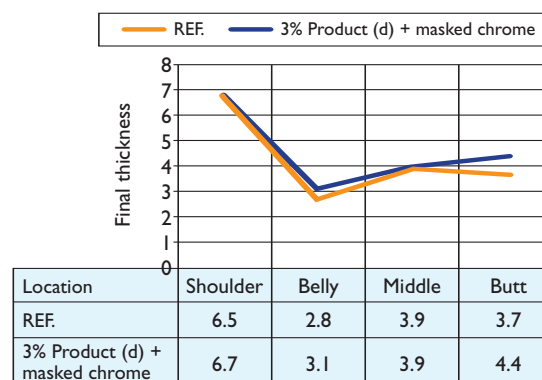


Figure 24

Figure 24

	Colour		Feel (IUP-36) (0-8)	Tensile Strength N/cm ²	Tearing resist. N
	Grain	Flesh			
REF.	40	37	5	2,000	91
Product (d) + masked chrome	36	33	5.1	2,050	95

neutralised, dyed and fatliquored as previously (*Part 1 Figure 8*). When the new process is used, the colour (L^*) is slightly darker, but the colour differential between the grain and flesh on both leathers are similar as shown in *Figure 24*. The physical properties are slightly improved with the new process, and the leathers slightly more compact.

Summary of findings

- Within a conventional chrome tanning process, it is possible to reduce the salinity within pickle from 6°Be as normally employed to 2°Be, by using selected non-swelling acids (low molecular syntans.) In this situation, a reduction in salinity below 2°Be results in acid swelling and fibre weakening.
- Among the products tested as non-swelling acids, a mixture of naphthalene and naphthol sulfonic acids provided the best results.
- When using these systems the balance between the pH of the pickle bath and throughout the skin section throws different values to a conventional formic/sulfuric acid pickle.
- The avoidance of common salt in the pickle-chrome tanning process is possible if selected non-swelling acids are used coupled with modifications within the chrome tanning process. In this situation fast chrome penetration is required using either low basicity/highly masked chrome salts, or masking agents with chrome tanning agents of low basicity and high masking capacity. ☺