# Pickle-free low offer chrome tanning

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Historically, chrome tanning has been regarded as a highly polluting tanning method and the environmental negatives of this process have been well documented. Many alternatives have been introduced and adapted over the years to replace our industry's reliance on chrome, but recent developments and processes are now thought to have other environmentally negative effects, so it seems we are almost back to square one.

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What if it were possible to make chrome tanning much less harmful to the environment? What are the issues with chrome that have caused it to lose popularity over the years? The problems have been primarily associated with the high volume of chrome remaining in effluent, and the difficulties and costs associated with getting the residual chrome out of sludge and waste water before chrome III oxidises to become the very toxic chrome VI. This article will discuss a very simple method for chrome tanning hides, skins or splits, perfected by France based leather chemical makers, ATC. It offers a cost effective viable process that will reduce the amount of chrome powder used by a tannery by as much as 50%, and, at the same time, increase the chrome content of the leather. One of the major benefits of this process is that residual chrome in effluent water and sludge can dramatically be reduced.

Table 1 A traditional chrome tanning process

| Pickling / Tanning | Classic system | | |
|---|---|---|---|
| | % | Time | |
| Water | 50 | | |
| Salt | 6 | 15 | Bé 6.5 minimum |
| Formic acid | 0.8 | 3 x 20 | |
| | | 20 | |
| Sulphuric acid | 0.8/1 | 3 x 30 | |
| | | 60 | Check pH 2.8 /3.0 |
| | | | Check BCG full yellow |
| Adjust float to | 40 | | |
| complexing additive | 0.5 | 40 | |
| Add | | | |
| Chrome powder 26-33 | 6 | 60 | One shot only |
| Sodium formate | 0.5 | 60 | |
| Biocide | 0.15 | 60 | |
| Magnesium oxide | 0.5 | 8 hours | Final pH 3.7 / 3.9 |

Table 2 Pickle-free tanning system

| | ATC Actipickle NSA tanning system | | |
|---|---|---|---|
| | % | Time | |
| Water | 30 | | |
| Actipickle NSA | 2.0 | 90 mins | pH 4.5/5.0 BCG dark green |
| Actoil MDF | 0.5 | 60 mins | |
| Chrome powder 26-33 | 4.0 | 60 mins | pH 3.7-3.9 |
| Biocide M3 | 0.15 | 7 hours | |
| Finished | | | |

An additional bonus with this method is that the traditional pickling process is considerably altered making it possible to remove 'all' salt from this part of the leather making process, as well as removing the use of sulphuric acid, formic acid, sodium formate and magnesium oxide. This process enables the production of chrome tanned leather that will pass the boil test directly after an eight to ten-hour process, using up to 60% less chemicals. Moreover, the process can be completed much faster compared with traditional chrome tanning methods.

Table 1 shows a traditional chrome tanning process for split hides of substance to about 3mm. Variations of this method are used daily all over the world, and it is considered to be the normal process method to tan leather after the deliming process.

This traditional method gives a total run time of approximately 16 hours. Now, consider the process that ATC has developed, including for split hides of up to about 3mm. The Company has also developed the same technology for use on skins, splits, full substance hides and others, with some adjustments to the formulation as shown in Table 2.

The run time is less than 10 hours. The consumption of salt, sulphuric acid, formic acid, sodium formate, magnesium oxide is down to 0% and, most importantly, chrome powder consumption is lowered from 6-7% to 4%.

The process starts directly after deliming and incorporates a low, unheated, float system. It functions in mildly acidic conditions (between pH4-5), therefore, any danger of irreversible acid swelling is eliminated. The handling of potentially hazardous formic acid and sulphuric acid is removed. Further, salt is not required in the process since, even if the pH

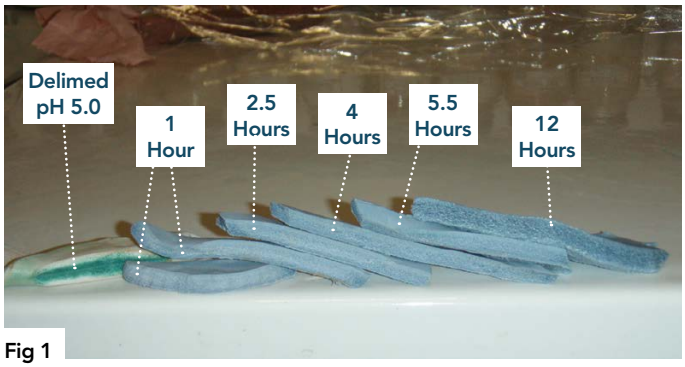


Fig 1


Fig 2

were to drop below pH3, the baumé mix of water and Actipikle NSA is above °bé 5.0 and, once the chrome powder is added, this rises further to °bé 10.0. Therefore, there is no risk of acid swelling. In some instances, especially where chromed leathers are traded around the world and drying out of wet-blue is a possibility, a small amount of salt can be added (around 1%-2%) to prevent any issues with wetting back of any dried leathers. However, where retanning follows the wet-blue process, all salt may be removed from the process, eliminating yet another contributor to effluent issues.

### The process mechanism

Actipickle NSA has a strong complexing effect with the chrome. The astringency of the chrome to the collagen fibres is masked and the chrome and Actipickle NSA complex is able to penetrate easily throughout the thickness of the hides or skins. In production, we have seen this process work perfectly on fully delimed hides of more than 8mm, where quick and even penetration of the chrome has been achieved.

As the chrome slowly reduces the pH of the liquor over time, the temporary complex between the Actipickle NSA and the chrome is broken, and the chrome becomes available again and fixes to the fibre structure of the hides or skins. Immediately, the Actipickle NSA is once again available, and quickly more chrome is found from within the liquor to form another complex; the process continues and repeats, taking chrome from the liquor each time, penetrating into the hides or skins and crosslinking the chrome to the collagen as the complex is once again broken. This process continues until the liquor contains no viable chrome content and exhaustion is complete. See Figures 1 and 2.

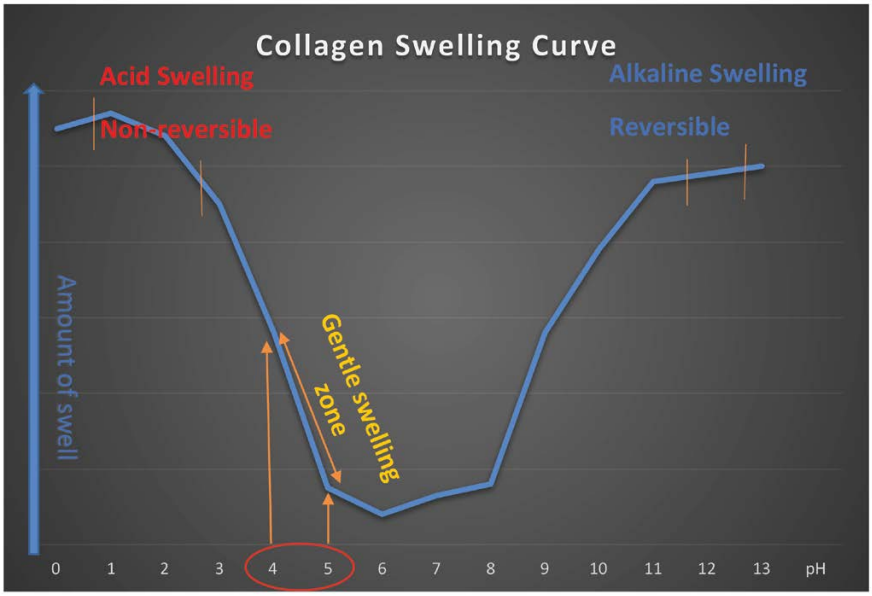


Table 3. Collagen swelling curve

### Production comparison results

One of the traditional methods to test the leather to ensure it has been correctly chrome tanned, is to perform a boil test or shrinkage test. The objective is to get a piece of leather that can withstand temperatures of greater than 100°C. This is a contentious issue in its own right and could be a subject for another full article. However, even when reducing the chrome offer from 6-7% down to 4%, with the ATC method, a shrinkage temperature test of above 100°C can be achieved directly after the tanning process; that is within as little as 9 hours.

Analysis of the leather and the liquor samples as a comparison make fascinating reading and can be seen in Table 4.

### Conclusion

The search for an 'environmentally safe' method to tan leather in an economic way continues. Until then, the use of chrome is inevitable. Maybe the answer to this problematic issue is to find a better way to use this proven technology? A process that can reduce the amount of chrome used while, at the same time, obtaining more of this potentially hazardous product to attach to the leather rather than sending it to effluent treatment plants, has to be an attractive concept.

Tanneries around the world that have already adopted this formulation method are already seeing the many benefits of this process: A reduction in chemical consumption of chrome, sulphuric acid, formic acid, salt and magnesium oxide. A reduction in the quantity of chrome or other harmful products, going into the effluent treatment plant. A reduction in the process time needed and an improvement in the actual tanned leather at the end of the process, and all for no extra cost.

Table 4 Chrome content and exhaustion

| | Traditional tanning (6% chrome powder offer) | Pickle-free tanning (4% chrome powder offer) |
|---|---|---|
| Leather $Cr_2O_3$ Content (%) | 2.7-2.8 % | 4.4 % |
| Final Liquor Sample $Cr_2O_3$ (%) Exhaustion Rate | 80-85% | 98% |