



The theory and practice of direct pickle/chrome liquor recycling

MINIMISING THE CHLORIDE/SULFATE AND CHROMIUM ION
CONTENT FROM PICKLE/TANNING

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In World Leather May 2007, a list was given of 45 papers that had been published which addressed various aspects of salinity that arise from leather manufacture. A CD was also made available holding all of these papers, but to make the compendium as complete as possible, some papers that were still awaiting publication were included.

This was an unusual step, but, with consideration to the growing environmental pressures that tanners are facing, and to make the compendium comprehensive, it was considered right to include this material.

The following is one of the papers that was awaiting publication, and concerns the reduction of chloride, sulfate and chromium that arises from the pickle/tanning process as a result of recycling.

CSIRO was at the forefront in the investigation of this technology and its introduction into commercial use.

When reading this paper, it should be remembered that the original report was produced before the technology became widely established and although it has been subject to a technical edit some minor details will have changed by now.

The information set down is, however, fundamental to the highly successful technology and this is probably the most informative study that has been written on this subject.

When the investigations into recycling of pickle/chrome tanning floats first commenced, the feasibility of the process was tested using a variety of techniques for the separation and characterisation of the chromium complexes present in tanning liquors. This led to the important conclusion that the poor exhaustion rate observed in practical tanning was not due to the presence of inactive chromium complexes (which might have had serious implications in recycling if present), but was simply a mass action effect.

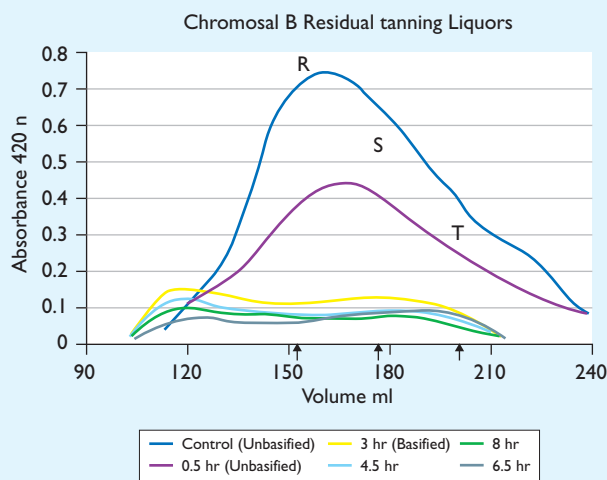
Complexes were shown to be taken up by the hide from solutions of Chromosal B from across the entire molecular weight range and charge distribution in the liquor throughout the tannage as shown in *Panel 1*.

The rates of uptake at different points (R, S, and T) across the molecular weight distribution were similar in each case as shown in *Panel 2*. As a confirmation, it was also shown that the residual chromium complexes present after a normal tanning run were readily and completely bound to the freshly-pickled hide.

The recommended recycling system

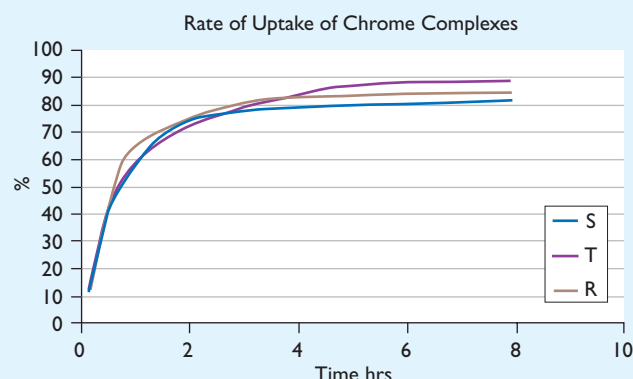
The method developed for hide processing involved the use of spent chrome liquor as a basis for the preparation of the pickle liquor for the following pack of hides.

Panel 1: Gel filtration of the residual tanning liquor at various times throughout the reaction of hide with Chromosal B





Panel 2: Rate of uptake of chromium complexes at three points in the gel filtration patterns



Before presentation to the delimed/bated hide, the spent liquor is reconstituted by addition of the full amount of acid normally used in pickling together with a reduced amount (normally ca. 75%) of the normal masking agent and a low level of salt if necessary.

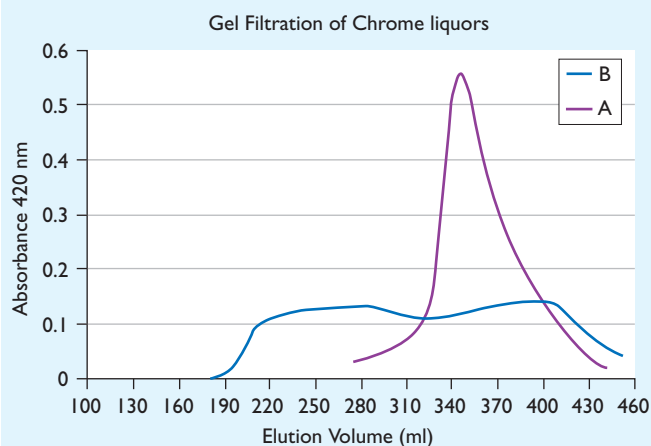
After the first cycle (i.e. a normal tanning run), it is not necessary to add neutral salt to the liquor provided certain conditions are observed (*discussed in following sections*).

The delimed/bated hide is pickled with the reconstituted liquor for the desired time, after which the calculated decreased amount (normally ca. 75%) of the chrome reagent is added directly to the pickle float to provide the usual total chrome offer.

For basification (where necessary), the amount of base is again decreased in proportion to the decrease in the amount of chrome reagent added.

It is an important principle of this method that, by the addition of the pickle acid before the presentation of the recycled chrome liquor to the delimed/bated hide, the low pH (ca. 1) prevents excessive chrome binding to the outer layers of the hide as the acid penetrates ahead of the chromium complexes. The faster penetration of acid is illustrated in this system by the slight temporary swelling of the hide which can occur early in the pickling stage (*discussed in following sections*).

Panel 3: Typical gel filtration patterns of a chrome liquor throughout recycling



A) freshly reconstituted at the start of tanning,
B) spent liquor at the end of tanning

Characteristics of recycled chrome liquors

Before discussing some of the practical aspects of the process in the tannery, it is worth considering the characteristics of a recycled chrome liquor as they clearly illustrate the scientific rationale involved.

THE NATURE OF THE CHROME COMPLEX

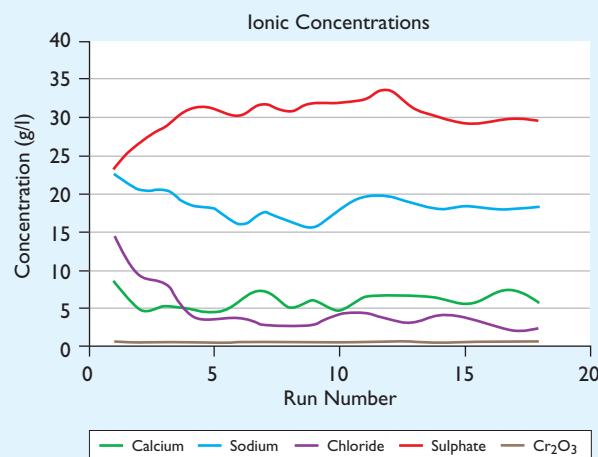
First, there is no observed change in the nature of the chromium complexes present in the liquors over repeated cycles, either at the start after the chrome addition or at the end of tanning. This is shown in *Panel 3*—see curves A and B—by Sephadex gel filtration, cellulose acetate ion-exchange chromatography and absorption spectra.

This shows that there is no build-up of inactive species, and tanning is performed with essentially the same chromium complex system in all cycles.

CHANGES IN THE CONCENTRATION OF SULFATE AND CHLORIDE

The level of dissolved salts in the spent tanning liquors does not increase on recycling and equilibrium is reached so that the concentrations of the various components stabilise after about the third cycle. This is shown in *Panel 4*.

Panel 4: Concentrations of Sulfate, Sodium, Chloride, Cr_2O_3 and Calcium in the residual liquors after reuse for 18 cycles.



This shows that:

- The calcium concentrations remain essentially constant throughout
- The chromium concentrations remain essentially constant throughout—indicating an essentially constant chromium uptake in the leather
- The sodium and chloride ion concentrations fall to a constant level
- The sulfate ion concentration increases to a constant level
- There is a progressive change from a chloride- to a sulfate-based pickle

The method relies on the utilisation of the dissolved sodium sulfate to repress swelling during the pickling and tanning stages. Correct adjustment of this neutral salt concentration in the recycled liquor is a key factor in ensuring the production of leather of at least comparable quality to normal production ➤



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Panel 5: Analytical results for spent chrome tanning liquor during a successful recycling trial in a commercial tannery

Run No.	Na (M)	Cl (M)	SO ₄ (M)	Ionic Strength	Specific Gravity (g/ml)
1	0.983	0.406	0.241	1.176	1.064
2	0.883	0.259	0.280	1.131	1.057
3	0.891	0.237	0.298	1.160	1.060
4	0.804	0.121	0.324	1.110	1.061
5	0.784	0.099	0.325	1.093	1.060
6	0.696	0.110	0.314	1.031	1.054
7	0.748	0.079	0.332	1.077	1.058
8	0.713	0.087	0.321	1.042	1.053
9	0.683	0.079	0.331	1.043	1.054
10	0.778	0.127	0.330	1.112	1.056
11	0.861	0.127	0.336	1.166	1.058
12	0.857	0.099	0.349	1.176	1.060
13	0.804	0.084	0.323	1.090	1.058
14	0.787	0.121	0.312	1.078	1.057
15	0.791	0.107	0.306	1.061	1.055
16	0.774	0.079	0.305	1.036	1.055
17	0.778	0.056	0.314	1.045	1.056
18	0.800	0.073	0.309	1.054	1.055

The Ionic Strength (and Specific Gravity) of the liquor was relatively constant throughout, resulting in leather comparable to the normal production.

(discussed in following sections).

Organic masking agents, such as formate, used in the recommended decreased amounts also reach an equilibrium concentration. In addition, both the pH and Specific Gravity of the liquors should be stable throughout repeated cycles.

THE REDUCED NEED FOR NEUTRAL SALTS

Further consideration of the salt contents of recycled liquors highlights a major advantage of this system over other alternatives. When compared to other systems—conventional tanning, chromium precipitation/re-use or ‘high exhaustion’ systems—there is a considerable decrease in the amount of neutral salt used in processing and in the neutral salt concentration appearing in the tannery effluent.

Throughout recycling, the total neutral salt concentration in the spent pickling/ tanning liquor is lower than in a conventional tanning process. This is shown in *Panel 4*, and is shown in more detail in *Panel 5*.

This reduction is the result of the replacement of sodium chloride with sodium sulfate which is more effective in repressing swelling at corresponding concentrations than sodium chloride. This liquor is then re-used rather than being discharged into the effluent as in other systems.

This is particularly important when processing is being carried out in inland areas as there is still no effective and economical

method for the removal of high levels of neutral salt from industrial effluents.

Characteristics of leather produced from recycled liquors

In Australia, there was some initial resistance to full-scale implementation of chrome liquor recycling from the industry. However, this was gradually overcome by illustrating that leather quality is unimpaired when the system is used correctly.

The process has now been used, for many years, by tanneries processing a few hundred hides per week to units processing around 12,000 hides per week. Observations in these tanneries have confirmed that leather quality can in fact be improved by recycling.

Careful attention has been paid to factors such as general appearance, colour, feel, grain quality, grain draw, veininess, Lastometer load/distension and other physical properties, chromium and ash content. The general conclusion is that the leather is at least of comparable quality to that produced by the conventional tannery process.

This is hardly surprising when it is considered that the tanning takes place in essentially the same system as a conventional tannage, except for the substitution of a sulfate pickle system for the more normal chloride system. This latter factor is thought to be involved in the improvements reported in leather quality from a recycled system e.g. a smoother grain and a more even chromium distribution throughout the cross-section.

The general experience in tanneries is that leather quality also becomes more consistent. This is partly because recycling requires more careful monitoring and control of the tannage than was often used previously.

A special mention should be made about colour as, although the ‘wet blue’ leather in some of our trials was noted as showing a slightly deeper blue colour than normal, this has not been observed in other trials. In practice any such effect is not apparent in the finished leather and there have been no reports of problems arising from this.

It should be noted that the above comments do not only originate from our own and the Australian industry's experience. The chrome liquor recycling process described in this paper is being used extensively and successfully in tanneries throughout most other regions of the world.

The importance of neutral salt concentration

Although the chrome liquor recycling process was already well-established in laboratory, commercial scale trials and full industrial implementation, the importance of neutral salt concentration in the recycled liquors was highlighted.

During early trials in some tanneries, a temporary downgrading in leather quality occurred whereby the ‘wet blue’ or finished leather showed characteristics which were traced to a small degree of swelling during pickling/tanning. This can occur when:

- There is inadequate control of the neutral salt concentration. This can arise under several circumstances such as where there is inadequate drainage of the delime/bate wash liquor before pickling.
- Where chrome-tanning agents containing low percentages of sodium sulfate are used.
- Where particularly low float levels (e.g. 30%) are used in tanning. ➤



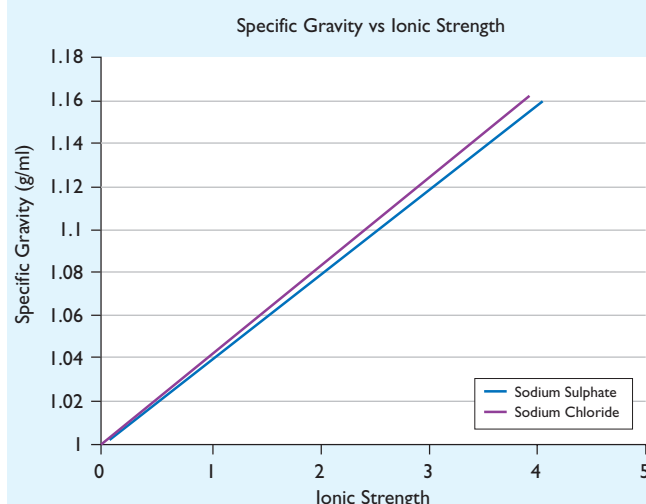
The degree of swelling of the hide during pickling/tanning is controlled by the Ionic Strength of the liquor defined as:

$$I = \frac{1}{2} \sum c_i Z_i^2$$

where c_i is the molar concentration and z_i is the charge of each ion present in the solution—such as sodium, chloride and sulfate. To ensure that the degree of swelling of the hide during pickling/tanning in a recycled liquor is the same as that in a non-recycled system, the Ionic Strength of the pickling/tanning liquor should be the same at comparable stages during the process. The monitoring and control of Ionic Strength in recycled liquors can be carried out simply by monitoring the Specific Gravity of the liquor.

Although the salt in the liquor changes progressively from, essentially, sodium chloride to sodium sulfate during recycling, by coincidence the specific gravities of solutions of sodium chloride or sodium sulfate are almost identical at the same Ionic Strength. This is shown in *Panel 6*.

Panel 6: The relationship between Specific Gravity and Ionic Strength for simple solutions of sodium chloride and sodium sulfate.



This correlation applies equally to complete pickle systems as shown in *Panel 7*. This means that Specific Gravity is a direct measure of Ionic Strength in the recycled system irrespective of whether the liquor is:

- Essentially a chloride pickle system as in the first cycle
- Sulfate pickle system following the establishment of equilibrium after 3-4 cycles
- A mixed chloride—sulfate system as in the intermediate cycles (or where the addition of some sodium chloride is necessary)

It is therefore only necessary to work to the same Specific Gravity levels in the recycled liquor at comparable stages during pickling/ tanning. This achieves the same control over swelling as in the normal process and the operation of this principle is illustrated in *Panel 7*.

In an early tannery trial, the combination of parameters used

in tanning resulted in a relatively constant Ionic Strength (and Specific Gravity) of the spent liquor throughout repeated recycling. There was no necessity to add sodium chloride after the first cycle (*Panel 5*).

It is known from tannery trials using different procedures that have resulted in a drop in Ionic Strength (and Specific Gravity) that acid swelling has occurred. This was reflected in the properties of the leather produced—such as an increase in plumping, a rubbery feel, chrome-stained areas and excessive firmness in the finished leather and a drop in Lastometer readings. In this event the problem was rectified by adding a small amount of salt to raise the Specific Gravity to normal levels.

It should be noted that it is also important to avoid the use of excessive salt, as 'negative' swelling will adversely affect the leather quality.

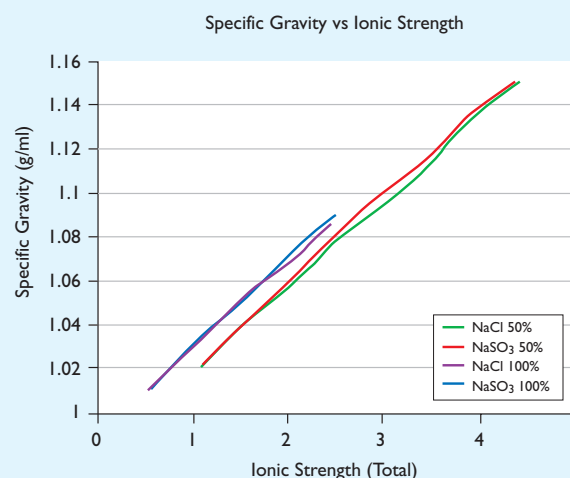
However, consistency can be ensured by working to the same Specific Gravity as in the normal tannery process at comparable stages. (*Note: the presence or absence of sulfuric acid makes a substantial difference to Specific Gravity*).

Other observations on chrome liquor recycling

A number of other observations have been made during the introduction of the chrome liquor recycling process into industry:

- There may be a small temporary degree of swelling of the hide despite the presence of an adequate salt concentration at the start of pickling. This has no apparent adverse effect on leather quality. If desired, this can be controlled by drumming any additional salt found necessary with the residual liquor before adding the acidified recycled liquor. This is preferable to adding any salt directly to the recycled liquor during reconstitution.
- Occasionally, a tannery has inadvertently added less than the normal amount of sulfuric acid to reconstitute the recycled liquor ready for pickling. This can cause chrome staining on the hide, which does not occur if the full amount of pickle acid is used (and the salt level is correct).
- Some chrome staining of leather can occur during the processing of relatively large loads of hides. If the time ➤

Panel 7: The relationship between Specific Gravity and Ionic Strength for typical pickle systems at two float levels using either sodium chloride or sodium sulfate, sulfuric acid and sodium formate.





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taken to add the reconstituted pickle liquor to the delimed/bated stock is excessively long, this can be simply overcome by the use of an enlarged piping and pumping capacity.

- Tanneries do not always ensure that 'control' and 'test' runs are performed under comparable conditions and misleading results can be obtained.
- In Australia, tanneries using the recycling process have had no problems in meeting the local requirements for discharge of chromium in effluent, but particular care is necessary with the process where very low effluent levels (e.g. 1 mg per litre) have to be met.
- To minimise any increase in volume of the recycled liquors, the following details should be taken into account:
 - i] Ensure relatively complete draining of the delime/bate wash liquor before pickling
 - ii] Use solid chromium reagents rather than liquors for addition to the pickle float
 - iii] Use solid basifying agents (where necessary) such as magnesium oxide
 - iiii] Use 98% sulfuric acid and powdered or undiluted formate when reconstituting the liquor

In practice, there can be a volume of chromium-containing liquor accumulated, which cannot be recycled. Over and above the volume recovered from the tanning drum, there is residual chrome arising from draining before samming, the samming machine and from washings from the dyeing/retanning process. These can be treated with a base such as magnesium oxide for precipitation and re-use.

General requirements for direct chrome liquor recycling

It is not the purpose of this paper to give detailed practical recommendations for chrome liquor recycling but rather to present the important principles involved. The actual method of implementation will vary from tannery to tannery but, in summary, provision should be made for:

- The segregation and separate collection of the used chrome liquor after tanning
- Adequate (and consistent) draining of the processing drum or other vessel
- Collection of chromium-containing liquor liberated during 'horsing' and samming of the leather
- Suitable storage of the spent chrome liquor

- Regular removal of coarse solids from the recovered liquor and periodic removal from the storage tank of the accumulated fine solid sludge and surface fats: careful attention to these factors will allow indefinite re-use of the liquor
- Reconstitution of the recovered liquor with acid and a masking agent (and salt if necessary) before presentation to the delimed/bated hide
- Analysis of the liquors (pH, Specific Gravity, chromium content) at appropriate stages in the process

The advantages of direct chrome liquor recycling

The method of direct pickle/chrome liquor recycling has many benefits, which have led to its successful adoption by the tanning industry. The following are regarded as advantages:

- The method is very flexible and is applicable to the production of a wide range of leather types using a wide range of formulations, processing chemicals and vessels, and is capable of indefinite operation.
- The method is effective in reducing the concentration of the chromium appearing in tannery effluent. This is important not only where stringent restrictions have to be met, but also where tannery effluent is used to irrigate land. It should also be noted that the possibilities for economical utilisation of tannery sludges are extended by the exclusion of chromium.
- The concentration of neutral salts such as sodium chloride and sodium sulfate appearing in the effluent can be substantially reduced. The process is ideally suited for inland processing where controlling salinity is a serious problem.
- With proper control, there is no loss in leather quality using the recycling system and quality can, in fact, be improved in some respects.
- There are major savings in the cost of the chrome-tanning process when compared with conventional processing and even further savings when compared with alternative solutions to environmental responsibilities. ♻️

Acknowledgements

The original CSIRO documents that have been used in this publication made reference to more than 60 papers. These were published before recycling was in common use, and this information is now generally accepted. For this reason these references have not been included in this paper.

Wet blue goes green

A final year student, Sun Lei, at the British School of Leather Technology has been investigating possible substitutes for salt (*sodium chloride*) in the pickle for his dissertation. The study investigated the use of potassium and ammonium cations combined with sulfate and phosphate anions. The use of ammonium, phosphate and sulfate salts may seem a strange combination as they are considered pollutants in their own right, but a well designed biological effluent treatment plant should be capable of removing these from wastewaters.

Sodium chloride, on the other hand, is difficult and expensive to remove, and cannot be treated biologically.

The pickled material was chrome tanned and favourable results were achieved with potassium and ammonium phosphate. The salts, however, produce an aquamarine green colour in place of the traditional blue. Physical and chemical testing is ongoing and plans are underway to optimise the offers and test these pickle salts on glutaraldehyde tanned material. ♻️

In-house edit