



Vegetable tannage of heavy leathers

Colin Jones, Northampton, UK

The vegetable tanning process is flexible and can produce leathers with a very wide range of characteristics. Heavy hides can be converted into heavy, firm types of leather with high abrasion resistance such as sole leathers for footwear. Small skins can be used for outlets such as hard wearing leather goods that might require intricate embossing, or soft flexible leathers.

Over and above properties dependent upon the type of skin or hide, the characteristics of these leathers are highly dependent upon:

- the nature of the individual vegetable tanning material selected
- the percentage of tannin offered
- the levels of acids and salts in the tannage

The tanning mechanism

The principal tanning reaction is brought about by weak multi-hydrogen bondings which form between the many phenolic -OH groups in the vegetable tannins, and the countless oxygen and nitrogen atoms in collagen found in the peptide groups.

Vegetable tannins also carry a weak anionic charge due to the presence of acid carboxyl groups. Hence, there is also the possibility of electrostatic bonds being formed with the opposite positively charged amino groups in collagen. This type of attraction increases as the pH falls below the iso electric point. It has also been suggested that attraction can occur between the hydrophobic parts of vegetable tannins and collagen with the exclusion of water.

However, the difference in structure, substance, and the user requirements of hides and skins leads to quite different approaches to tanning light and heavy leathers.

The manufacture of heavy leathers

Heavy leathers, such as sole leathers and equestrian leathers, are produced from hides and sold by weight. The leather yield or rendement is dependent on:

- The amount of tannin within the fibre structure. These tannins are both chemically bound to the fibre and deposited in-situ within the hide structure
- The level of filler material, such as magnesium sulfate, glucose, or china clay, introduced in post tanning

Vegetable tannage originated in pit systems. These have evolved and are still used, although faster methods have been developed based on drum tanning techniques. However, for the best insight into the intricacies of vegetable tanning, pit tanning methods should be considered first.

The pit tanning system

If leathers are to be firm, deliming is limited to either the

removal of free surface lime by washing with water, or the removal of bound lime from the surface by deliming with boric acid and sodium bisulfite. The full deliming of the alkaline plumped hides is then completed using previously used tan liquors. These are relatively non-astringent (mellow) in the pH range 3.5 - 4.0.

Because of the small molecular size of the acids present in these liquors, there is faster penetration into the fibre structure than the vegetable tannins. This acid penetration causes the nature of the fibre swelling to change from one of alkaline plumping to a controlled level of acid swelling. The slightly acid swollen fibre structure is subsequently fixed and stabilised by the slower moving anionic charged tannin particles. As the pH falls from strongly alkaline to mildly acidic conditions, the electrical charge also changes from anionic to a more cationic state. This is more reactive with anionic vegetable tannins.

This system of tannage may be viewed as a two-stage process.

1. To achieve penetration, and uniform distribution of tannins through the cross section. This achieves fibre stability to swelling/deswelling, to pH change, and osmotic effects.
2. To increase the level of tannin fixation and deposition.

The greatest levels of uptake at the second stage can be gained by:

Increasing the concentration of tannin - this is usually up to 21% or, in terms of hydrometer readings, 140°Bk or 18°Be.

Increasing acidity - minimum pH 3.2 to increase electrostatic fixation to a maximum acid concentration 400m.mols/l. It is noted that weak organic acids in vegetable tan liquors are almost entirely in the form of undissociated molecules (not detected by pH but titration to pH 6.5 with a standard alkali). These molecules have a lyotropic effect, opening up hydrogen bonds in collagen and thus creating sites for vegetable fixation.

Increasing astringency - through the selection of tanning properties coupled with agents that provide acidity.

Increasing temperature (up to a limit of 37°C) - this is dependent on acid concentration, as a rise in temperature increases the lyotropic effect of the weak acid. A rise of only 2-3°C above the limit can result in a loss of physical properties, short fibre and darkening in colour (oxidation).

The role of salts in vegetable tanning

Salts play an important role in tanning. In the initial stages the content is normally 200-300 m.mols/l^(Legend 1), being sufficient to control acid swelling, and so allow tannin penetration. Approximately 3.0% salt concentration as common salt is required to prevent acid swelling in a normal pickle, but levels in a normal vegetable tanning system are equivalent to around half of this level. This allows a slight acid swelling to take place thus producing a firmer and fuller leather. ►



THE MANUFACTURE OF VEGETABLE TANNED HEAVY LEATHERS

If an excess amount of salts is present in the tannage, especially in the final stage, there is a reduction in tannin fixation. This causes a loss in yield, and a weakening and softening of the fibre structure. This results in a reduction in wear properties, and can produce a more water absorbent leather.

The selection of tanning materials

Typical blends of tanning extracts used are 70-80% catechols (i.e. mimosa and quebracho) and 20-30% pyrogallols (i.e. myrabolans, chestnut or valonia.)

Catechols form the major part of the blend because of their lower acidity and more rapid penetration. Pyrogallols due to their lower pH provide the astringency necessary to increase the tannin fixation. At the same time this influences the colour and feel of the resultant leather.

Pit and drum tannages

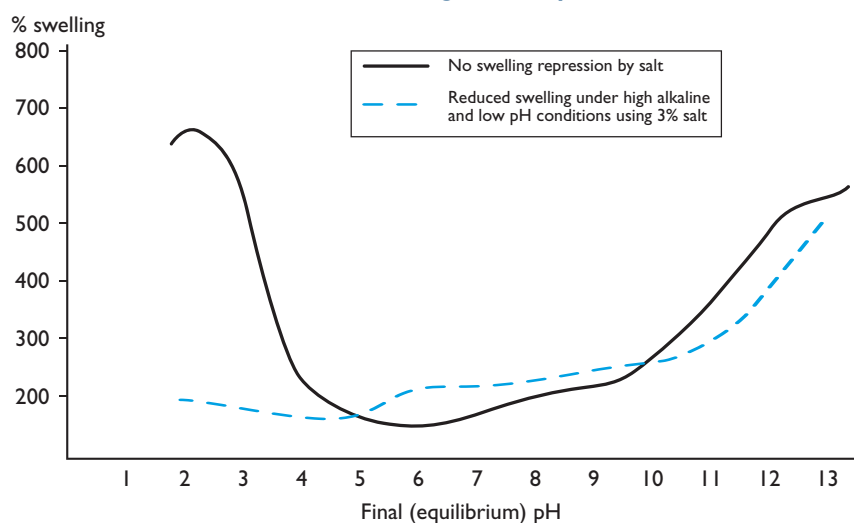
Pit tanning systems and drum processing provide two alternative approaches to tannage, and there are many variations depending on the vegetable tanning agents used and individual manufacturing techniques. However, basically, the uptake and yield of vegetable tanning materials on pit systems is greater than drum processing.

In the pit system, the tannage is performed by introducing hides to vegetable tannin blends of gradually increasing concentration. This is done by suspending hides from a frame, then lowering them into the first pit containing the most dilute tanning solution. As appropriate, the hides are lifted and introduced to the second pit containing a higher concentration of tannins. This is repeated until the final introduction to the tanning liquors of highest concentration.

As the hides move through the series of pits, there is a counter flow of tanning liquors as indicated in *Panel 4*. The blend in the final pit is freshly made, but after being used in the final stage in

Panel 2:

The swelling curve of pelt



Swelling in the pH range 0 - 14 in solutions of strong acid and alkali (hydrochloric acid and sodium hydroxide) in the absence of salt and as a 3.0% solution of sodium chloride. Swelling expressed as water uptake on dry pelt weight.

tanning, the liquor is pumped to the preceding pit. Here it is used as the penultimate tanning bath, and this progression continues until the liquor reaches the first tanning pit. By this stage the level of astringency and tannin content is very low, and after use the liquor is discharged.

This is a very materials-efficient system, but the counter flow system also provides technical benefits. As the tan liquor is offered to the final pit, the heavy molecules are the first to be taken from the solution by the hides. The smaller molecules remain, to be taken up by the newly offered hides in the initial tanning stages.

Because of their size and low affinity these small molecules can penetrate deep into the structure. However, as the hides are introduced to higher concentrations of vegetable extract in the latter stages of the pit system, molecules of a larger size displace the smaller molecules.

Pit tannages therefore absorb the larger molecules whereas no-float drum systems offer a broad spectrum of molecules, the uptake being representative of this conglomerate. A lower proportion of larger molecules is taken up by the hides, therefore, yields from drum processing are lower than pit systems.

Panel 1:

Discolouration of vegetable tanned leathers

Vegetable tanned leathers can easily show dark discolourations. This is mainly due to the following:

- An increase in initial pH, say from pH 5.0 to 8.0 will cause a rapid darkening due to oxidation. This affects catechols in particular
- Staining from iron. Complexes are formed with the vegetable tanning agents in the leather forming ink stains. Iron contamination may be from dust and even minute levels cause discolourations
- Mould growth on vegetable tanning liquors, or on inactive or piled leathers

Preventative measures include pre-tannages to create a lighter colour on the grain, the selection of vegetable tanning agents, bleaching syntans, oxalic acid or polyphosphates (Calgon)

Accelerating the penetration of tannins

For many years, heavy leathers of a very firm nature and thick substance (6-7mm) were produced. These commonly required 20 or more pits, and high leather yields up to 85% were possible. In these systems the hide structure is stabilised in the early stages by the mild tanning action of low-astringent tanning liquors used. When introduced to high concentration liquors this stabilisation minimised any dewatering effects, or any swelling due to an increase in acidity.

As the process became more rationalised, various techniques were used to accelerate tannin penetration. In pit systems these included:

- Deliming close to the iso electric point, pH 4.7 - 5.0 range. This provided the optimum conditions for penetration of vegetable tannins due to minimum swelling—hence large capillary spaces—electrical neutrality and a low affinity for tannins

**Panel 3:****Slow vegetable tannage in pits**

The hides are first introduced to weak used tan liquors. Tannage commences as the smaller residual vegetable tanning molecules penetrate the hides. The hides are moved by hoist into pits of increasing tannin concentration. In the final pits the tannin concentration is high, and there is a high uptake of large molecules to produce high yields. As the tannins are absorbed by the hides, the used liquors are offered to subsequent batches of hides in earlier stages of tanning, as found in classic counter-flow systems. In the image, the hides suspended from the frame in the foreground have recently entered the pit tannage, and some fixation of the vegetable tanning agents has occurred. In contrast, the tannage of the suspended hides at the far end of the pit system is almost complete. (See the movement of hides and counterflow of tanning liquors as illustrated in Panel 4). Image: Concerie Riunite GB S.p.A., Italy.

- Ensuring that the delimed pelt is in an iso-ionic condition with initial tanning liquors. If the salt concentration is between 200-300 m.mols/l in the pelt—that is similar to the concentration of solubles in the float—this will minimise volume changes in the pelt through osmotic effects

Within faster processing fewer pits are used. In this event the pits are reduced to, say, five with the concentration being typically 30°, 50°, 70°, 100°, and 140° Be. As these steps in concentration are great in comparison with long pit processes, dewatering effects due to reverse osmosis are problematic. The iso-ionic balance becomes critical, so that the salt content in the

effects. If not controlled the water losses can increase the float and dilute the initial tanning concentration by 20-30%.

Another option is to employ non-swelling acids, being acid syntans of small molecular weight. A pretannage throughout the cross-section stabilises the structure and prevents dehydration of the pelt during tannage, which would otherwise result in a reduction in volume, closing of the fibre structure, poor penetration, and case hardening. This treatment both reduces the pH and fixes the fibre structure.

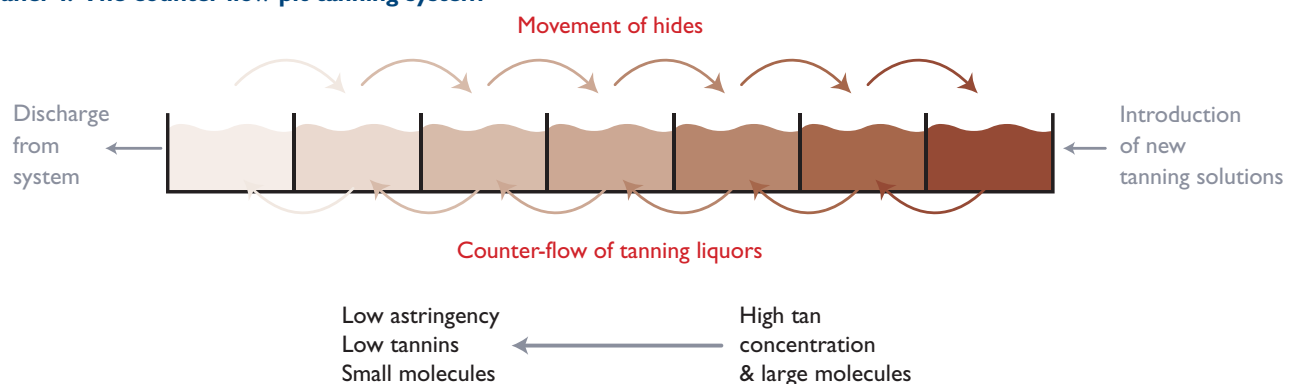
The quantities of offer are high, but can be reduced by using conventional syntans to 'condition' the structure. However, ➤

early pits needs building up to a suitable level, often using magnesium sulfate. A careful balance is needed between the dewatering effects of the tanning concentration, and acid swelling effects.

Drum tanning systems

More rapid methods have been developed based on drum systems. These offer the advantage of rationalisation, and involve no-float tanning methods. A combination of pre-tanning the grain with syntans and mechanical action ensures a rapid penetration of the tannins, and the tanning process can be reduced dramatically to three or four days. These produce more flexible leathers, but lighter in weight, with yields being around 70-72%. Nevertheless, the commercial advantages are significant, as less stock is required at any one time in the tanning stages.

In addition to complete deliming, the focus is strongly on controlling the osmotic balance. This is to prevent massive hide-volume losses due to water migration into the highly concentrated tanning solution. A technique known as conditioning can be applied where a high percentage of hydrophilic (water retaining) materials is introduced into the hide—such as sodium sulfate—to reduce osmotic

Panel 4: The counter-flow pit tanning system



THE MANUFACTURE OF VEGETABLE TANNED HEAVY LEATHERS

Panel 5:

The approach to rapid drum tanning

In the following guideline formulation many variations are possible, so the approach given should be taken as being very general:

Following a conventional liming and good fleshing, the hides may be rounded into butts, bellies, or shoulders for tannages appropriate to the different hide parts and end uses. In this example the butts are weighed, and slits may be made along the backbone to minimise creasing in tannage. The limed butts are then white-limed overnight to ensure a good opening of the structure, washed and drained.

CONDITION:	Drum speed 6-8 rpm No float 5.0% non-swelling acid (syntan) 0.1% Sodium bisulfite 2.0% Formic acid Run 4 hours <i>Required: Cross section completely delimed at pH 3.5</i> <i>Temperature limit 28°C</i>
PRE-TAN:	8-0 - 10.0% Replacement syntan Run until penetration (possible overnight) <i>Temperature limit 32°C</i> Drain, wash water at 25-30°C to remove neutral salts produced during conditioning
TANNAGE:	Drum: no float, 1-3 rpm (butts stiffen in tannage) 10.0 - 18.0% non-astringent powder vegetable tanning agent Run 2-3 hours <i>(good penetration required: cold soluble quebracho, mimosa, sweetened chestnut)</i> 18-0 - 10.0% astringent vegetable tanning agent Run 14-20 hours <i>(good fixation required: lower pH range vegetable tanning agents such as natural chestnut, myrabolans)</i> <i>Required: Full penetration of tannins</i> 1-2% syntan in final 30 minutes (to increase fixation and lighten colour) <i>Temperature limit 38°C</i>

The following points should be noted:

- Increased quantities of non-swelling acid may be used; this will enable a corresponding reduction of formic acid
- If the offer of non-swelling acid is increased, the offer of replacement syntan can be reduced
- The addition of the vegetable tanning agents may be split into several additions
- The total amount of tannins as pure tannins including syntans should be around 40%
- A residual float of 25-30% will develop. This is due to the replacement of chemically bound water within the hide structure by tannins
- The recycling of this liquor is not recommended due to oxidation
- If salts are not washed out after conditioning, the tan fixation will be reduced, and the leather characteristics will be spongy and water absorbent
- A small amount of slip agent or a high stability fatliquor may be added to aid hide movement

In this guideline formulation, the non-swelling acid syntan serves several purposes:

- Avoids the use of high levels of salts as a means to restrict swelling
- Combines deliming with pickling
- Stabilises the fibres to impede water movement. Initially acid swelling is avoided, then dehydration during tannage

if the levels of non-swelling acid are reduced this may generate a need for neutral salts to prevent acid swelling before fixation by the syntans. This fibre stabilisation also raises the shrinkage temperature enabling a higher initial temperature in tanning thus reducing the drumming time and risk of a pebbled grain.

Other important items to take into account include:

- Pretanning with anionic materials e.g. syntans or polymeric phosphates (Calgon) to block the positive charged amino groups
- Increased mechanical action and tighter temperature control
- Full opening of the fibre structure in liming, with good fleshing, to ensure good penetration of tannin molecules ranging from molecular weight 500 to + 6,000

Alternative conditioning methods

Alternative methods of simultaneous conditioning, deliming and pickle can also be used. For example 7.0% anhydrous sodium sulfate may be used to avoid movement of water, and 3.0% sodium bisulfate in three additions as the acid source for combined deliming and pickle.

It should also be noted that conditioning can also take place after a conventional pickle. With the cut showing 100% pH 3.3-3.5, the float is drained and 10% anhydrous sodium sulfate added, then run until full penetration is achieved. This is preferred to sodium chloride as it tends to be retained better within the pelt. This is followed by pre-tannage where mimosa powder might be used instead of a replacement syntan.

Other permutations using a salt free system include pre-tannage based on 5.0% solution of sodium polyphosphate (Calgon). This blocks amino groups thus improving the penetration of vegetable tanning, and sequesters iron, calcium and magnesium ions thus improving the colour.

This technique can be used on delimed and bated hides, but if limed hides are used then 1.0-2.0% sulfuric acid can be gradually introduced to reduce the pH. It is also noted that if the concentration of Calgon is reduced to say 3.0%, then salt will be needed to avoid acid swelling. This can be followed by either drum tannage, or a drum tannage in combination with pits. 🌐

Legend

1. 1 milli mole = - 1/1000 mole. The molecular weight of sodium chloride (common salt) is 58.5, therefore 58.5 gm/l NaCl = 1 mole solution or 1000 m/mols/l. 58.5 gm/l = 5.85% salt solution, that is approximately 6.0% concentration. A minimum of 3.0% of salt is required - that is in approximately a 500 m.mol/l - in a normal pickle to prevent acid swelling. The 200-300 m.mols/l from the vegetable tanning bath presented in the text is thus equivalent to around 1.5% solution as sodium chloride.

Additional Information

World Leather Publications: The manufacture of vegetable tanned light leathers: C. Jones, UK - Part 1 April 2000 p.80, Part 2 June/July 2000 p.37, Part 3 October 2000, Part 4 Feb/March 2000/1 p.32. *Heavy Leathers: preparation and drying methods* - April 1999 p.75. *Achieving the best from vegetable tanning extracts:* N. Cutting - Part 1 Dec/Jan 1996/7p.65, Part 2 Feb/March 1997 p.36 *Possible ways of streamlining vegetable tannage and the effects of these on capital investment:* H. Slaats, Bayer - Part 1 April 1995 p.57, Part 2 August/September 1995 p.67.