



Fatliquors and fatliquoring: a brief insight *Part 2*

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The history of leather-making, the development and functions of fatliquoring and the definition of a fatliquor were discussed in Part 1 of this paper, published in World Leather October 2007.

Part 2 continues the overview of this complex subject, providing insight into the fatliquoring process, and the avoidance of problems within applications.

The fatliquoring process

The fatliquoring process is central to the handle and properties of leather. At present, the global consumption of fatliquors stands at approximately 400,000 tons per year. In comparison, the consumption of syntans stands at 250,000 tons, and dyestuffs at 150,000 tons.

In almost all situations fatliquors are designed to be applied to leather in the form of an aqueous emulsion that is an 'oil in water emulsion'. In practice this is best achieved by adding the fatliquor to 4-5 times its own volume of water at approximately 50°C.

THE PARTICAL SIZE OF THE EMULSION

A fatliquor emulsion can be of various particle sizes. If the emulsion is coarse it will have a particle size of around 100nm and will have a milky appearance. In this situation, the penetration of these fatliquors is restricted to the surface of the leather. If the particle size is around 30nm, then the emulsion is translucent, and because of the smaller size these can generally penetrate more deeply into the fibre structure. Emulsions of 5nm are classified as micro-emulsions; they are relatively clear and give good penetration. Examples of these three emulsion types are shown in *Panel 5*.

THE STABILITY OF THE FATLIQUOR EMULSION

The stability of the fatliquor emulsion has a direct effect on the penetration through the cross section of the leather. In the case of sulfated oils the degree of sulfation or combined SO_3 is of critical importance. The emulsion stability is influenced by several factors including the presence of charged ions, neutral salts and the level of acidity both in the leather and the fatliquoring bath.

The stability to acids is very important as chrome tanned leathers are acidic and can easily split in an unstable emulsion. Insight into this effect can be gained by the acid titration of an emulsion to the point where the emulsion is broken and this is often used as a simple quality control test of fatliquors during their development and manufacturing.

The combined SO_3 can generally be described as the 'in-situ' emulsifier within a sulfated oil and as such, depending upon the

quantity present, will affect the characteristics of the final fatliquor and its performance on leather.

If the $\text{C}:\text{SO}_3$ or degree of sulfation is high, then quite a large proportion of the lubricant has been converted to emulsifier and will form a clear or translucent emulsion due to the fine particle size of the oil globules being unable to scatter light.

The converse is true for oil sulfated to a lower degree, in that the oil particle size in the emulsion will be much larger and, as a consequence, produce a milky type of emulsion.

In leather-making terms the quantity of $\text{C}:\text{SO}_3$ or emulsifier in a sulfated oil can be loosely described as the fuel to drive the dispersed oil droplets into the leather. As fatliquoring progresses, the emulsifier is used up as oil is carried into the leather and deposited onto the fibres, resulting in the depletion of the emulsifier within the system. This depletion has the effect of increasing the oil particle size, resulting in a less stable and quite often milkier type of emulsion.

This reduction in emulsion stability has the effect of depositing more oil within the leather and, as a consequence, exhaustion of the fatliquoring bath is accomplished. However, during the latter stages of fatliquoring this oil is more likely to be

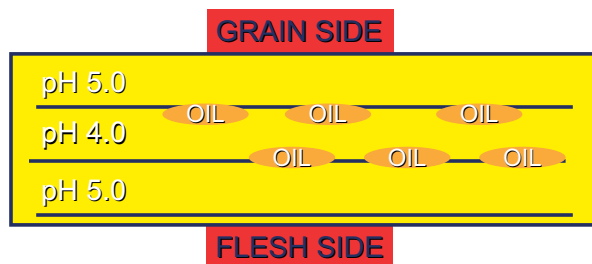
Panel 5: Fatliquor at various process stages





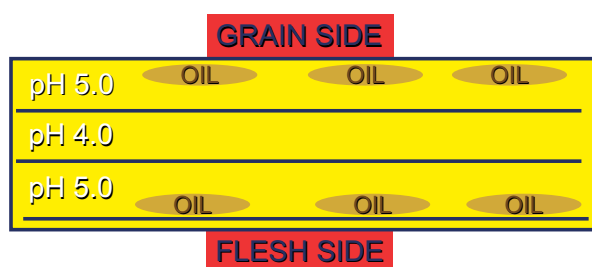
Panel 6: The penetration of fatliquor into leather

PENETRATION OF A HIGHLY SULFATED FATLIQUOR WITH HIGH EMULSION STABILITY



Gives a soft leather with a dry handle

PENETRATION OF A LOW SULFATED FATLIQUOR WITH LOW EMULSION STABILITY



Gives a firm leather with a waxy handle

deposited on the outer surfaces of the leathers as opposed to inside.

The emulsifier, which in the case of sulfated oils is negatively-charged or anionic, will also—to a greater or lesser extent—undergo fixation to the leather fibre. This is dependent upon the charge being exhibited by the leather in relation to the emulsifier.

The system is obviously not quite as simple as the foregoing suggests and will be dependent on many factors. These include the temperature, time, mechanical action, tannage, retannage, neutralisation, salt and electrolyte concentration within the float, and the type and quantity of fatliquor being used.

However, in general terms, highly sulfated oil will tend to penetrate the leather creating a softer leather with a dry surface, whereas a low sulfated product will penetrate less creating a firmer leather with a waxier handle as illustrated in *Panel 6*.

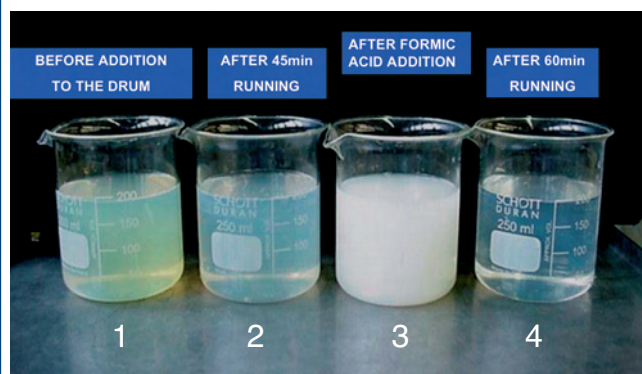
EMULSION CHANGES WITHIN THE FATLIQUORING PROCESS

During the fatliquoring process changes occur in the emulsion as shown in *Panel 7*. This shows samples of a fatliquor emulsion taken at four stages.

1. The fatliquor emulsion before it is added to the drum.
2. The fatliquor emulsion after a running time of 45 mins. Although much of the fatliquor has been taken up by the leather, some still remains in the float.
3. The float after lowering the pH with formic acid, resulting in a further reduction of the emulsion stability with increasing particle size and a milkier appearance
4. This technique ensures a good exhaustion of the fatliquoring bath as shown in this example, and helps fix the oils within the leather.

With reference to both *Panels 6* and *7*, it is clear that the emulsion stability plays a crucial part in the success of the fatliquoring process and the final leather qualities.

Panel 7: Examples of emulsion type



Most fatliquors should exhibit sufficient take up within the first 20-30 minutes running time. Longer floats and lower temperatures will tend to decrease the uptake of fatliquors. With higher temperatures and lower floats the converse is true.

The type of tannage or retannage will also greatly affect the performance of a given fatliquor.

A heavily vegetable retanned leather, possessing less affinity for an anionic fatliquor than full chrome, will tend to exhibit a dry handle and a floating grain surface unless the fatliquor blend is adjusted to have a higher proportion of neutral oil present.

In addition the type, colour and quantity of dyestuffs all have a marked effect upon the behaviour of a fatliquor. Direct dyes of large molecular size and high hydrogen bonding fixation tend to produce firmer leather than a simple monosulfonated acid dye. Moreover, the use of large amounts of dyestuff for through-dyed leathers has the effect of introducing high salt concentrations into the bath which, depending upon the type of fatliquor, may have an adverse effect upon its emulsion stability.

The effects of fatliquoring during piling and leather drying

Having completed fatliquoring the story is not quite ended. The oil or lubricant present in the leather will displace moisture from the fibre and, depending on the prevailing conditions, tend to spread along the fibre and penetrate further.

This release of water is often illustrated by the water-pearling effect seen in fatliquored leather. Also, freshly fatliquored leather that often appears greasy when removed from the drum is grease-free after overnight piling. It is therefore advantageous, wherever possible, to allow the leather to achieve equilibrium by piling the rinsed leather for a period of time.

During the subsequent drying process the loss of water increases the inter-fibrillary spaces in the leather matrix, thus favouring migration into these voids. In addition, the increase in temperature reduces the viscosity of the oils, and this encourages the movement and spreading of the lubricant along the fibre.

If the leathers are vacuum dried, then there is migration to the surface in contact with the heat. On the other hand, toggle drying causes the fats to migrate deeper into the leather structure. It is also noted that the choice of fatliquor influences the drying rate and that a fatliquored leather dries more rapidly than a unfatliquored leather. ➤



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The influence of fatliquors on the physical properties of leathers

The fatliquoring process is crucial to the development of the physical properties of the leather, particularly the aesthetic properties such as softness and handle. Other properties such as the grain break characteristics, looseness, and the penetration/adhesion of finish can also be strongly influenced by the fatliquor selection. The correct choice of fatliquor can help to improve the tear strength and help to maintain the tensile strength. And good grain lubrication improves the lastometer values.

Problems associated with fatliquoring

Problems that may be associated with a poor choice of fatliquor are set down in *Panel 8*.

Panel 8

Problems that may be associated with a poor choice of fatliquor

- Fatty stains
- Dark flanks and belly areas
- Unlevel dyeings
- Hard leather
- Poor rub fastness
- Poor and loose grain
- Poor finish adhesion
- Area loss

However, many of these problems can be avoided if the correct emulsification techniques are employed in the tannery. For example:

- Most fatliquors are designed to produce oil in water, not water in oil emulsions. Such emulsions are best prepared by adding the weighed and mixed fatliquor blend to ideally 4-6 parts its own volume of water at 50°C.
- In extreme cases where a small quantity of water is added to the fatliquor, an inverted (i.e. water in oil) emulsion can be produced. On further dilution, by adding to the drum, this may cause the emulsion to break down and deposit oil on the surface of the leather. This results in patchy uneven fatliquoring.
- The temperature of the water used is also very important in preparing fatliquor emulsions. Boiling an emulsion is one of the easiest ways of breaking the micelle structure, with the effect of a reduction of emulsion stability, and uneven fatliquoring and inconsistent results.
- In many tanneries the emulsification techniques employed in fatliquoring leaves much to be desired with the use of live steam and broom handles being commonplace. Under such conditions it is often more expedient to add the fatliquor directly to the drum in its un-emulsified form. However, correct preparation should, if possible, be practiced in order to ensure consistency and reduce problems in the tannery.
- The quality of the fatliquor also affects leather properties that are not immediately obvious. For example, fatliquors that contain large quantities of highly unsaturated components such as fish oil will oxidise due to heat and/or



Panel 9

The storage and use of fatliquors

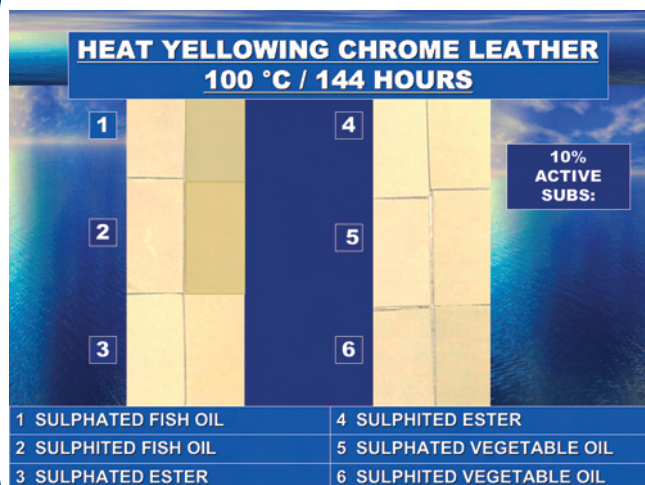
The way that fatliquors are stored and the way that emulsions are prepared can strongly influence the outcome of the fatliquoring process. The following is given as good practice:

- Follow the manufacturer's guidelines.
- Store fatliquors at between 5° and 40°C if possible.
- Mix fatliquors together before emulsifying.
- Add the fatliquor to water, not water to fat.
- The water temperature should not be more than 50° to 55°C.
- The fatliquor-to-water ratio should be 1:4 to 1:5 by volume.
- If possible use soft water.
- Do not allow the emulsion to stand for a long time.

ageing and become yellow. Under extreme conditions this may lead to the oxidation of chrome III to chrome VI in the leather.

- If the fatliquor contains high quantities of aromatic components such as certain types of mineral oils they will turn yellow on exposure to light. An indication of these potential problems is shown in *Panel 10*.

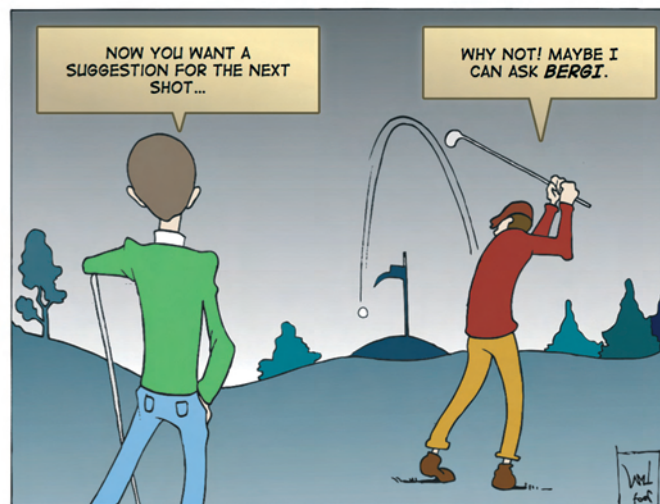
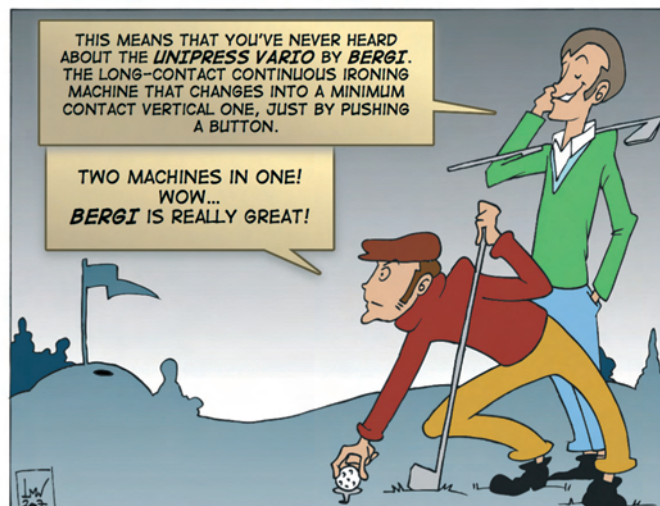
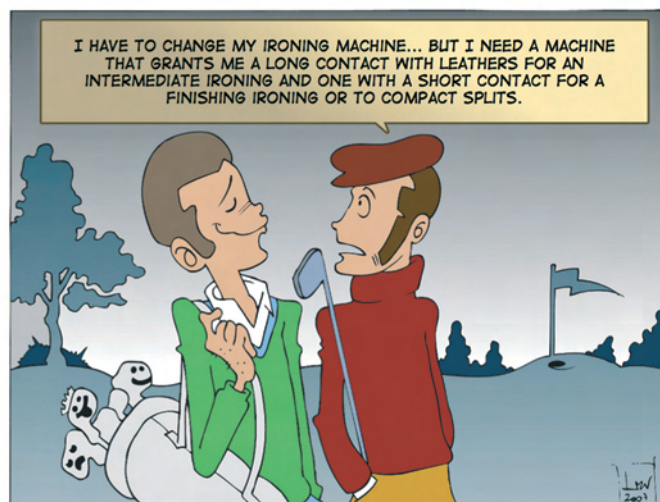
Panel 10



In this example, the fatliquors used in making the leathers were produced by sulfating or sulfiting different raw materials. The samples to the left in each pair are the reference samples; the samples to the right were exposed to heat.

The sensitivities of fatliquoring

It is clear that fatliquoring is a sophisticated operation. To ensure uniformity, the tanner needs assurance regarding the quality and consistency of supply. There must also be a very careful appraisal of the property of fatliquors by the tanner. It must also be recognised that any changes in retannage and to a certain extent dyeing will have an effect on the fatliquoring process. If these changes are considerable, then the fatliquoring blend will almost certainly require modification.



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