



Fatliquors and fatliquoring: a brief insight *Part 1*



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The history of leather-making, the development and functions of fatliquoring and the definition of a fatliquor are discussed in the first part of this paper.

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

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The history of leather-making

The manufacture of leather is an ancient profession. The beginning is lost in time, but one of the earliest written records of the employment of skins of animals is contained in the book of Genesis in the Old Testament of the Bible where it states: "God made clothes out of skins for the man and his wife."

The first method of tanning was in all probability that of rubbing the skins of animals with other parts of animals found close at hand such as dung, brains, milk and fats. Such an operation is closely related to what we now know as oil or Chamois tanning.

What our ancestors could not have known was that dung had enzymatic properties, brains contained lecithin, a material that has emulsification as well as softening properties, and that fats contained unsaturated components in their structure, which, under certain conditions, could oxidise to form aldehydes and thus exhibit a leathering or tanning effect.

Dated from around 5,000 BC, coloured leather artefacts have been found in Egyptian tombs, and some of the earliest records of recipes for tanning have been found in Sumeria (Iraq) dated at around 800 BC. This particular recipe involved the treatment of fresh ox hides with, water, flour, beer and wine, alum, oak galls and beef tallow.

Although the craft of leather-making was well-established, there was a general expansion throughout Europe during the 8th and 9th centuries. In 1768 a patent was issued for the first tanning drum, and in 1820 the first splitting machine was invented.

At around this time chemical development began shaping the methods of manufacture. In 1834 the first sulfated oil was produced by Runge. In 1856 William Henry Perkin synthesised the first synthetic dye 'Mauve' from 'aniline' an extract of coal tar. Like many other great discoveries this one was also fortuitous as at the time he was looking to find a cure for Malaria.

It was only towards the end of the nineteenth century that chrome tannage began to play a major role in the production of leather, with the utilisation of the two-bath chrome tannage using dichromate as patented by Augustus Schultz in 1884, followed by the first one-bath chrome tannage from Martin Dennis in 1893.

Significantly, it was the incorporation of a fatliquoring emulsion made from raw oils and soap in place of the traditional

currying or stuffing process that achieved the final breakthrough in the successful production of chrome tanned leather.

Further discoveries followed including Dr. Otto Rohm's development of bating agents from pig pancreas in 1904, and in 1913 Stiasny's invention of the first synthetic tanning agent.

The development and functions of fatliquoring

Essentially, fatliquoring is a development of the last century. Early fatliquors were based on mixtures of natural oils and soaps. Other fatty materials which were capable of forming water in oil emulsions such as degreas and lanolin were also widely utilised. Egg yolk, which contains lecithin, was also of great value, particularly in the fatliquoring of gloving leathers. Often soaps and flour were used within these mixtures as a means of forming coarse emulsions and imparting a certain degree of colloidal stabilisation.

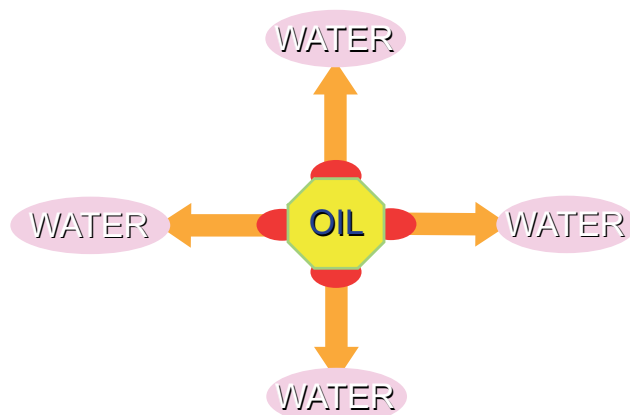
Tanned leather in its wet condition is relatively flexible. Chrome tanned leather more so than vegetable leather but, as water is removed during the drying stage, cohesion of the fibres takes place. This results in a hard, intractable leather which is difficult to re-hydrate. This phenomenon is more noticeable in chrome leather than in vegetable tanned leather, mainly due to the fact that chrome leather does not contain interfibrillary 'fillers' such as non tans and insolubles which have the effect of cushioning and separating the fibres.

By introducing a lubricant into the leather the fibres are kept apart during drying and frictional forces within the fibre weave are reduced, thus allowing the fibres to move laterally over each other. In essence, fatliquoring is a simple lubrication phenomenon. How and with what this is achieved is a somewhat more complex and contestable matter.

In former times damp leather was treated with water insoluble oils and fats by means of hand swabbing or stuffing. Later the development of kickers and drums allowed the fur and leather dresser more flexibility.

However, conditions for uptake and penetration of such lubricants were largely dependant upon the moisture content of the leather. Too wet and the oil merely spread unevenly over the surface of the skins, too dry and the spreading would not take place.

With the correct conditions, the water insoluble oil spreads

**Panel 1: Oil in water emulsion**

evenly over the damp fibres eventually displacing moisture within the fibre weave. Heat and mechanical action help to speed such operations through a reduction in the viscosity of the oil and the removal of moisture. This facilitates even distribution and penetration of fat throughout the cross section.

This process of currying or stuffing was a highly skilled operation. This entailed the use of mixtures of cod oil, sperm oil, tallow, waxes and fatty acids and the currier's experience in judgement of the time, temperature and quantities of the components to be used. Variations were also made to the viscosity of the stuffing blend from summer to winter.

With the exception of the fur industry and a few specialised heavy leather manufacturers currying has, to all intents and purposes, been superseded in the leather industry by fatliquoring, that is the treatment of leather by 'oil in water emulsions'.

The definition of a fatliquor

A fatliquor:

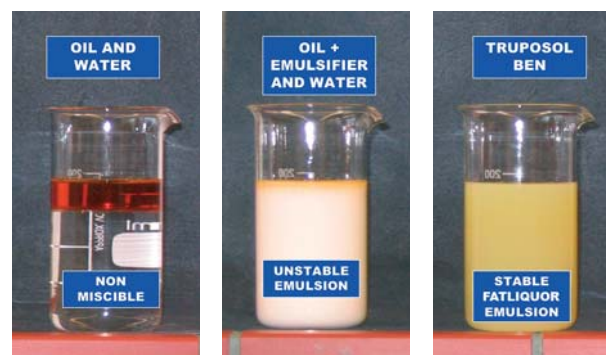
- is a chemically modified water emulsifiable lubricant
- is capable of softening leather by reducing the frictional forces between the fibres
- provides partial bonding of the emulsifier and the lubricant to the substrate

Emulsification is central to the success of the process. In many fatliquors this can be achieved by chemically modifying the lubricant or oil through the process of sulfation or sulfition. This is in order to incorporate hydrophilic groups within the structure, thus facilitating oil in water emulsions to be produced, as indicated in *Panel 1*.

The emulsion stability of a fatliquor is dependent on many factors. This includes the degree of sulfation or sulfition undertaken in manufacture, along with the addition of other emulsifiers or stabilisers that may be incorporated in the fatliquors formulation.

A highly stable fatliquor emulsion will often appear translucent due to the extremely finely dispersed oil globules being unable to scatter light. The converse is true for a less stable emulsion which will appear milky due to the larger oil particle size and may—on prolonged standing—show signs of separation, such as creaming or free oil on the surface.

These three states are illustrated in *Panel 2*.

Panel 2: Examples of emulsion stability**Panel 3: Fatliquor bases**

Animal Oils	Lard Oil Skin Grease Tallow Neatsfoot
Vegetable Oils	Rape Oil Soya Oil Coconut Sunflower Groundnut
Fish Oils	Cod Oil Sardine Oil Caplin Oil Orange Roughy Herring Oil
Synthetic Oils	Fatty Esters Paraffinic Oil Oxo Alcohols Alkyl Benzene Chlor Paraffins
Waxes	Lanolin Paraffinic Waxes Polyeth: Waxes Sperm Oil (1978)

Fatliquor categories and groups

The types of raw materials used in the production of fatliquors can be classified into the following categories:

- Animal oils
- Vegetable oils
- Synthetic oils
- Waxes

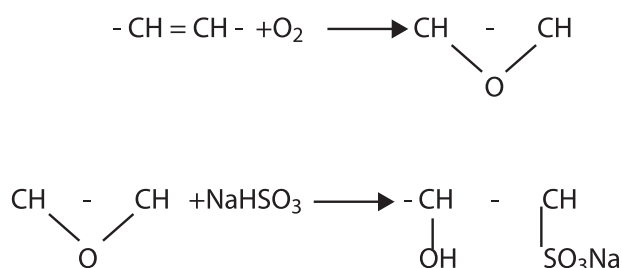
Some of the raw materials used within these different categories are listed in *Panel 3*.

Generally speaking fatliquors can be divided into four main groups: ➤



FATLIQUORS AND FATLIQUORING: A BRIEF INSIGHT

Panel 4



- Anionic: based on sulfated and sulfited products
- Cationic: based on quaternary ammonium compounds
- Amphoteric: based on fatty acid amides
- Non-ionic: based on ethoxylated fatty adducts

The production and development of fatliquors is not dissimilar to the art and science of leather-making, where the skill and experience of the formulator is of great importance. The product not only has to meet the requirements of the tanner in terms of the handle and feel of the leather, but must also conform to the various physical and chemical specifications required in today's modern leather-making world.

ANIONIC: SULFATED AND SULFITED OILS

Although the process of actual sulfation has changed little in 170 years, the choice of emulsifiers available has meant that manufacturers can build or design fatliquors to suit the requirements of individual leathers and process situations. It is not uncommon for a fatliquor to be made up of several different components and emulsifiers, depending upon the prerequisites involved.

Sulfated oils, although suitable for many requirements within the tannery, have the disadvantage of not being stable to heavy metal salts such as chromium and aluminium. During the 1950s a second, and today widely used, class of fatliquors was developed, that of sulfited oils.

Sulfited oils differ in their chemistry to sulfated oils in that the sodium salt of a sulfonic acid is produced as opposed to a sulfate ester. These oils are manufactured by reacting sodium bisulfite or meta bisulfite with an unsaturated oil—fish oils along with

certain vegetable oils being amongst the most popular. The reaction takes place more readily if the oil is first partially oxidised by air blowing or aeration as indicated in *Panel 4*.

The oxidation and sulfition of oils

In addition to their increased emulsion stability, sulfited oils undergo far less chemical modification and hydrolysis, thus maintaining a higher proportion of neutral oil available for lubrication. This, plus their increased molecular size due to oxidation, has the effect of producing a leather with exceptional softness and a mellow surface.

Their disadvantage is that when used in large amounts they can highlight loose areas and may add weight to the leather. Sulfited oils are often, therefore, used in chrome tanning where they will, if sufficiently stable, help promote a smooth grain and good softness.

CATIONIC AND NONIONIC OILS

Cationic oils are generally produced by blending a cationic emulsifier such as quaternary ammonium compounds with raw oil. They are quite often supplied in the emulsified form and can be used in chrome tannage or, more probably, as a final top fatliquor in order to modify the surface, handle and appearance. This applies to leather destined for paste drying, or high gloss writing effect suedes.

Non-ionic oils possess no charge. Like cationic oils these are produced by blending a non-ionic surfactant with raw oil or by ethoxylation. Their use is generally limited to areas where good wettability coupled with natural grease dispersal is required, for example in first-way fatliquoring of woolskins and the crusting of suedes. However, care should be shown in their deployment as they exhibit little fibre substantivity and can lead to leather which wets out too readily on the finishing table.

Non-ionic surfactants of the ethylene oxide condensate types are, however, quite often added to sulfited oils by the manufacturer in order to improve emulsion stability. This is for use under severe conditions such as pickling and tanning. 

Information and acknowledgements

- The author's current position incorporates product management of the Trumpler Fatliquor and Dyestuff business as well as responsibilities as group technical manager of Trumpler International's subsidiaries.
- Section "The history of leather making", acknowledgments to "Chrome tannage in the nineteenth century" by Roy Thompson.

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