



The theory and practice of fatliquoring

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Fatliquoring is an important step in the process of leather manufacture, as it is intended to lubricate the leather fibres. This results in softness and pliability and, at the same time, improves the mechanical properties of leathers.

The preliminary beamhouse processes remove most of the natural oils from the hides and skins, so after tannage the leather does not contain sufficient lubricants. Without oils, it consequently dries to a hard structure.

Fatliquoring is the most common method of lubrication, where the leathers are treated with emulsions of lubricating oil in an aqueous medium. A fatliquor emulsion deposits specialised oils within the leather, and this is absorbed on and into the fibres and fibrils. When the water is subsequently removed, the oil remains to lubricate and improve the physical properties of the leather, such as the break, stretch, stitch tear, tensile strength and comfort.

These fatty substances in water-soluble or emulsified form may be anionic or cationic. Fatliquors are usually anionic (*negatively charged*), with the most common water-soluble fatty substances being soaps. The water-solubilising group is either the carboxyl or the sulfonic group, and both convert the fatty radical they have entered into an anion. The presence of polar and non-polar groups in the oil helps to determine the affinity of the oil towards water. A polar group (*hydrophilic*) is one that has a natural ability to orient itself and dissolve in the water phase. Such groups are -COOH, -OH, -SO₃H, -Cl. A non-polar group (*hydrophobic*) tends to dissolve in the oil phase, typically -CH₃, -C₂H₅, etc.

An emulsion is the dispersion of one liquid in another, where both liquids under normal circumstances are quite immiscible. The emulsifiers, which are similar anion-active compounds, orientate themselves in a thin interfacial layer around the dispersed globules of water-insoluble fat. This imparts the hydrophilic group facing the water with a distinctly negative surface charge, so the water-soluble fatty substances are stable in the dispersion.

An emulsifying agent, with polar and non-polar groups, can form an emulsion of oil in water. The non-polar portion enters the oil phase while the polar portion enters the water phase, with the emulsifier initiating a mutual blending of oil and water. Normally the polar portion is stronger to bring about solubility. The fat or oil in an emulsion is dispersed in the form of particles in the water medium and retains some of its natural identity. The particle size of the emulsion can be classified as follows:

- When the particle size is larger than one micron, it is called a coarse emulsion
- When ranging from one millimicron to micron, it is called a colloidal emulsion

Most emulsions used in fatliquoring leather fall into the coarse category, however, when smaller than one millimicron, the fatliquor can be considered well-dispersed. The smaller the size of the oil particles in an emulsion, the greater the available surface area.

In fatliquoring, where penetration and combination are desired, the particle size is of considerable interest; and the smaller the particle size the more stable the emulsion, as the oil is in intimate contact with the water. For this reason, many emulsions are run through a homogeniser to reduce the particle size. In addition to polar compounds, protective colloids such as gums, starches and proteins may be used to prepare oil-in-water emulsions. Protective colloids can disperse the oil into finer particles to stabilise the emulsion, which will better penetrate into the leather to provide lubrication.

The concept of ionic charge

The ionic charge on leather influences tanning, re-tanning, dyeing and fatliquoring. This concept is extremely important in the selection of a fatliquor for a specific purpose.

Chrome-tanned leather carries a positive charge, whereas vegetable-tanned leather carries a negative charge. A chrome-retanned leather carries a negative charge at the surface, and to the limit of the penetration of syntans or vegetable extracts. Similarly the dyeing process can also alter the charge.

According to the charge on the leather, and the requirement of the finished leather, the fatliquor composition must be carefully considered in order to achieve the required leather properties. The pH of the leather at the time of fatliquoring plays an important role in the way the oil is fixed and distributed through the cross-section. This means that the neutralisation prior to retanning needs to reduce the strong positive charge to the extent that the negative dyestuff ions, and later the similarly charged particles of the fat emulsion, are not taken up on the surface too rapidly and unevenly.

Nevertheless, raising the pH alone is not sufficient, because an increase above the iso-electric point will affect the quality of leather. In addition, the kind of salts used for neutralising has an influence, as the acid radicals of these salts show a pronounced tendency to enter a stable linkage of the chrome complex.

An alkali such as sodium bicarbonate is not an ideal agent, because in practice this can lead to dirty staining on the flesh side, and a darker colour in the looser-grained flanks. These disadvantages may be avoided to a great extent if alkali salts with a buffer action are used, as these anions display a pronounced complex activity. This buffer-neutralisation protects those places where basic chrome compounds have accumulated. This results in a fuller dyeing of the grain, a cleaner and brighter flesh side,



and firmer flanks with a good cutting value.

When processing nappa garments, gloving and suedes, the well-neutralised leather after retanning and initial fatliquoring are crusted, and this helps the most appropriate selection of leathers for various purposes. During drying, the complexes are stabilised by the entrance of anionic radicals into the inner-sphere, and an exchange of anions. The dried leather now displays only the lower polarity of the collagen. In practice, this means that after wetting back, the dyeing and fatliquoring differs strongly from that of freshly tanned chrome leathers. The fatliquors and dyes have much less affinity, because of the more uniform and anionic charge on the leather, with these products therefore they penetrate more deeply and provide uniform penetration.

In the fatliquoring of vegetable-tanned leather, the fatliquors do not play such an important role. The usual anionic fatliquors are absorbed by this similarly-charged material more slowly and often less completely than a chrome-tanned leather. A subsequent addition of acid is often required in order to fix them, and the addition of cationic auxiliaries will improve the fixation.

After the anionic fatliquor and fixation, a surface fatliquoring with a cationic fatliquor at lower pH can also fix the anionic fat and stops the migration of fats to the surface. This topping with a cationic fatliquor produces a higher surface oil concentration, which assists greatly in setting, and vacuum drying, and gives greater grain lubrication.

Sometimes non-ionic emulsifiers are used to stabilise cationic fatliquor. Such fatliquors slow down the rate of exhaustion and increase the penetration into the fibres. Non-ionics (*generally of the ethylene oxide condensate type*) are quite stable in salt solution, and are added to many commercial cationic fatliquors. So for gloving leather—where one needs very good run—this type of cationic fatliquors can be used in appreciable quantities, both in the pickle and chrome tanning, to obtain very good oil penetration and exhaustion.

Multi-charge fatliquors are classified under two categories:

- With mixed emulsifiers
- Amphoteric fatliquors.

The amphoteric type of emulsifier is one where both the positive and the negative groups are present in the same molecule, and is usually achieved by introducing amino and carboxyl groups simultaneously into the same molecule.

Fatliquor stabilising agents

Non-ionic/anionic surfactant compounds are used as stabilising agents for fatliquors. The non-ionic surfactants are reaction products from fatty alcohol and ethylene oxide, whilst anionic surfactants are manufactured through the sulfonation or sulfation of fatty alcohols.

As these products are often used at the fatliquoring stage, they can influence the final leather to a considerable degree. In particular, any free and low ethoxylated fatty alcohols can exert a negative influence on fogging characteristics. Therefore before using a fatliquor stabiliser in the fatliquoring process, its influence must be tested.

Types of oils

Fatliquoring agents are produced from natural and petrochemical-based raw materials. Natural-based fatliquors are

manufactured from natural raw material as triglycerides - unsaturated fatty acids with one (*Oleic*) to three (*Linoleic*) double bonds or saturated (*Stearic*) fatty acids. The important sources of these triglycerides are fish oils, neatsfoot oil, animal oil and waxes (*fatty alcohol + fatty acids esters*). Lanolin, fatty alcohols and tallow, etc can also be hydrolysed.

Fatliquors can be manufactured from the following raw materials:

BIOLOGICAL FATTY SUBSTANCES

- *Vegetable oils*: Linseed oil, nut oil and wood oil are classified as dry oils
Rape oil, maize oil, sunflower oil, soya bean oil, cotton seed oil and rice bran oil are classified as semi-drying oils.
Olive oil, castor oil and groundnut oil are classified as non-drying oils
- *Vegetable Fats*: Coconut fat, palm kernel fat and palm oil fat
- *Animal oils*: Marine animal oil, seal oil, whale oil, dolphin oil, fish oil, sardine oil, menhaden oil, cod liver oil, lard oil, and neatsfoot oil
- *Animal fats*: Beef and mutton tallow, lard, butterfat, bonefat and horse grease
- *Waxes*: Carnauba wax, bee's wax and wool grease.

(It should be noted that the use of some marine products is limited due to conservation requirements)

NON-BIOLOGICAL / SYNTHETIC OILS

Paraffin waxes, mineral oils, olefins, processed hydrocarbon, synthetic fatty acid esters and waxes, fatty alcohols, alkyl benzene.

CLASSIFICATION OF OILS

In leather fatliquoring, the above-mentioned oils are classified as follows:

- Untreated oil, fat and waxes
- Emulsified oils and fats
- Sulfonated oils, fats and fatty alcohols
 - (a) Sulfated products (-C-O-S bond, ester-like)
 - (b) Sulfonated products (-C-S bond, true sulfo-acids)
- Chlorinated oils and fats
 - (a) Chlorinated products
 - (b) Sulfo-chlorinated products
- Oxidation products of oils and fats

Reactions in the production of fatliquors

- *Sulfating*:
(i.e.) fatty substances + Sulfuric acid $\Rightarrow$ R-O-SO₃H
- *Sulfiting*:
(i.e.) fatty substances + O₂ + NaHSO₃ $\Rightarrow$ R-SO₃Na
- *Sulfochlorination*:
(i.e.) fatty substances + SO₂ + Cl₂ + H₂ $\Rightarrow$ R-CH-SO₃H

$\begin{array}{c} | \\ \text{Cl} \end{array}$
- *Esterification and hydroxyethylation*.

Sulfated oils are prepared by reacting the oils with sulfuric acid in suitable proportions under controlled temperatures, followed by washing and neutralisation. Sulfation takes place as the ➤



result of the reaction of the hydroxyl group or the addition of sulfuric acid to the ethylene linkage.

Sulfonated oils are produced by subjecting the oils to reaction with sulfuric acid of a higher concentration at relatively higher temperatures, along with strong sulfonating agents such as chloro-sulfuric acids.

The sulfited oils are produced by the oxidative sulfitation of oils—passing air through a mixture of oil and bi-sulfite solutions at the required temperature. The process does not involve washing or neutralisation as in the case of sulfation. The water emulsion of sulfonated and sulfited oil fatliquors shows better electrolyte stability compared with sulfated oil.

In sulfited oils there is a genuine sulfonic acid group with a C-S bond, which cannot split off. In the production of these oils, which are commonly called sulfited oils, alpha oxylsulfonates are formed as the by-product, mainly in the $-SO_3$ sulfonation. Sulfonation can be carried out until adequate water emulsifiability and emulsion stability is reached. The emulsion becomes more resistant to water hardness, electrolytes, mineral tanning agents, etc.

The sulfited oils and the $-SO_3$ sulfonated oils yield emulsions which are more resistant to electrolytes than the sulfated oils. With the increasing emulsifier content, the fatliquoring effect of sulfonated oil generally becomes drier, and suited to fatliquoring suedes, nubuck, etc. The solvent extractability also generally decreases when the emulsifier content increases.

Sulfited oils produce a softer fatliquoring effect than sulfated or $-SO_3$ sulfonated oils. The softness is increased with the use of neatsfoot oil, lard oil, sperm oil or fish oil. In the sequence of sulfition, sulfation and $-SO_3$ sulfonation, the feel of leathers becomes drier and firmer.

The type of emulsion and technical properties of the fatliquor depends on the degree of sulfonation, type of raw material, choice of chemical processing and the technique of manufacture. This enables the development of a wide variety of fatliquoring agents with very specific properties.

The degree of sulfonation of natural raw materials does not generally exceed 40%, as the softening properties decrease at higher values. However, a sulfonation degree of around 60% is not uncommon with synthetic fatliquoring agents. In this case the chain length of the raw material significantly influences the technical properties: long-chained paraffin produces better softening and filling effects, whereas short-chained ones serve better as wetting agents.

Synthetic fatliquors

The classification of 'synthetic' is liberally used to describe anything from mineral oil to ethoxylated phosphate esters. Most synthetic-based raw materials are available as by-products of other industries such as the petrochemical and detergent sectors.

Medium molecular weight paraffins—which are capable of being chlorinated or sulfo-chlorinated (*oxidised paraffins and paraffin sulfates*)—are quite often used in mixtures with naturally available oils in order to adjust the dry handle often associated with synthetic fatliquors. The advantages they have over the natural oils are that they tend to be almost odourless and exhibit little tendency to fatty spues and discolouration. They are produced by the sulfonation of paraffins, and in contrast to glycerides they are less chemically reactive, as they are not manufactured using sulfuric acid or sulfites.

Polymer fatliquors

The lubricating acrylic syntan, first introduced to leather manufacture in the late 1980s, has proved to be a breakthrough in leather technology. It is a polymer that retans and fatliquors leathers in one step. This quality is derived from the chemical union of specific retanning and lubricating properties, and is not a physical blend of retanning agents and a fatliquor.

Lubricating acrylic syntans define a new class of hybrid polymer that gives leather extra benefits besides filling and softening. Depending on the product, other advantages can include waterproofing, grain tightening and low fogging, with these value-added qualities giving the user a competitive and technological edge. The products are user friendly, and are compatible with each other and with available retans and fatliquors.

These products basically comprise a backbone chain with attached carboxyl and other functional groups and side chains. By modifying the backbone composition, molecular weight, end use pH, and the functional groups, polymers can be designed to give specific performance to the leather.

These products are self-emulsifying and have a high affinity for chrome-tanned leathers. They form stable complexes on penetration into the fibre structure, thereby providing a low-level extractability. Other advantages are high light fastness, heat resistance and improved physical properties. These fatliquors are useful for the manufacture of automotive leathers where a low volatile content is crucial, and for garment leathers where a low specific weight is required, as well as resistance to washing and dry cleaning.

Waterproof fatliquors

Waterproofing agents are structured in a similar way to normal fatliquors. They consist of hydrophilic components for emulsification, and hydrophobic components for waterproofing properties.

The hydrophilic components are soaps or phosphates, either as monomers or polymers, identified by hydrophilic carboxyl group (COO^-). The hydrophobic components are fats, waxes or silicones.

In normal practice, waterproofing applications take place using an aqueous medium. The waterproofing agents are compatible in water in the form of an emulsion to allow it to be used.

At the end of the application, to obtain water repellency, the water compatibility must be converted to a strongly hydrophobic effect. This can be readily enacted, as the fats or phosphates initially used as the hydrophilic components can form water insoluble compounds by capping with mineral tanning agents.

Fluoro chemicals are perceived as primarily waterproofing and oil repellent chemicals. They are used on the surface of the leather to give repellency.

Solvent fatliquor

The principle of chemical bonding in the presence of an organic solvent is used in so-called 'solvent fatliquors'. Solvent fatliquoring is based on introducing the oil into the leather in a high boiling solvent. This solvent will displace the water in the leather, leaving a solution of the solvent and the oil. As the solvent slowly evaporates, the oil remains absorbed in the fibres. The solvents used are Diethylene Glycol (*Cellosolve*) and various mono alkyl ethers of diethylene glycol or dipropylene glycol, diacetone alcohol, etc. ►



The amount of these polar substances needed is only 15% to 25% of the amount of water taken as a dispersing medium. The solvent fatliquors are used in particular for maximum softness with minimum fatliquor for light leathers, very soft leathers, namely gloving or clothing softies, and milled softies. They are also useful as a re-fatliquoring agent.

Water insoluble neutral oils

These are the raw oil components added to the fatliquor to modify the character of the leather. They are classified as a natural oil, mainly raw neatsfoot oil, or a blend of oils and synthetic oils.

Synthetic oils are based on synthetic esters, blends of synthetic esters, or synthetic oils based on chlorinated hydrocarbons. They have fat values of 100% cold tested, and medium viscosity. They have no unsaturated compounds and therefore have very good light fastness, and as a result of the polar structure, are fixed by the leather fibres.

Synthetic oils do not cause any fatty spue and can even inhibit other fatty spues. This is because they are capable of dissolving solid fatty acids, which may be formed by both natural grease, or from common fatliquors, because of the action of acids or bacteria.

They can be used with anionic fatliquors, multi-charge fatliquors, and in cationic fats to improve the lubrication properties, with some long chain hydrocarbons and synthetic ester oils used for pull-up leather and oily nubuck. In this situation they are normally used undiluted by a roller coat to obtain the pull-up effect with a pleasant touch.

Fatliquoring in practice

The fatliquoring of leather depends on the following factors:

- Preparation of the leather—degree of neutralisation, retanning, etc.
- Concentration of the fatliquor.
- Types of fatliquor and the blend ratio.
- Temperature, pH and time of the fatliquoring.
- The degree of lubrication and the penetration into the leather.

The influence of fatliquoring is associated with the softness of the leather, with the fatliquor formulations usually comprising several raw materials to produce the required properties of softness, feel and handle. The behaviour of the fatliquor emulsion must be taken into account within the fatliquoring drum, which, assuming careful preparation of the emulsion, involves the quality of water, drum revolution, temperature, pH, etc.

Fatliquor combinations should be mixed well by stirring before dilution. Careless addition of water when diluting the fatliquor results in a coarse emulsion, which gives an irregular surface deposition of the fat. The correct procedure is the addition of hot water during constant stirring, ensuring that the emulsion is homogeneous before the addition of further water.

Differences of appearance provide indications of the fineness of the particle size. Oils in semi colloidal emulsion are almost in solution and appear as opalescent or almost transparent dispersions. Cloudy dispersions up to milky dispersions are of increasing particle size, i.e. the milkier the appearance the coarser the particle size.

The particle size influences the ability of the emulsions to penetrate and disperse within the fine structure of the fibre. The consistency of results demands that the fatliquor is always correctly emulsified before addition to the drum.

THE EFFECT OF TEMPERATURE ON THE EMULSION BEHAVIOUR

High temperature fatliquoring will result in a controlled degree of instability in the system, which will induce a deposition of fat onto the leather fibre. Another important impact of temperature is to reduce the viscosity of any high melting point of components of the fatliquor mix such as waxes, etc. If the temperature falls, these will tend to become pasty and deposit on the grain surface causing greasy handle. Consistent results and batch-to-batch uniformity demand that exact temperatures are known and controlled in the drum.

THE INFLUENCE OF ELECTROLYTES

The polar group dissociation is influenced by the quality of the process water in the fatliquoring bath. Process water contains electrolytes in the form of calcium and magnesium salts, sometimes even sodium salts, so it is essential that the quality of water is controlled.

Water-soluble polyphosphates in solution will give poly anions, and these have the ability to form complexes with multivalent cations. This improves the dispersion of dyes and fatliquors.

THE EFFECT OF MECHANICAL OPERATIONS

The agitation of molecules in the emulsion by thermal energy or by mechanical means, (*in the drum*) results in a coarser emulsion. The extent to which this happens depends on the drum speed, drum loading and the float.

To obtain a leather with temper and spring, the fatliquor should not penetrate completely. This is managed by adjusting the neutralisation so that the centre zone remains less lubricated. This may even result in the inner-fibres setting stiffly without any lubrication in the final leather. In such a case, the emulsion breaks and deposits the fat in the outer layers before penetration into the central zone. The effect is assisted by high temperature, long float and a lower quantity of fatliquor.

However, to produce leather with a mellow handle, each fibre must be relaxed, flexible and separated after drying, and given a coat of lubricant to allow unrestricted movement. The thorough and uniform penetration of fatliquor is possible, provided that the cross-section of the leather has a uniform pH. This means the neutralisation, retanning, and other pre treatment, should be uniformly penetrated throughout the structure.

Merely, using more fatliquors without preparing the leather will not result in softness as the fat is distributed in the wrong place. When the exhaustion of fatliquor is completed, fixation is achieved by the addition of formic acid so that a low pH is achieved below the isoelectric point.

THE SIGNIFICANCE OF CATIONIC FATLIQUORS

The types of cationic fatliquors are as follows:

- Highly cationic, high dispersion, low softening for use in mineral tanning and in dyeing.
- Highly cationic, low dispersion, high softening for gloving leathers for use in the chrome tanning and in rechrome.

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- Low cationic, low dispersing, high softening for multi-charge combinations.
- Low cationic, medium dispersion, and a waxy touch to assist mechanical operation.

THE EFFECT OF HORSING AND PILING LEATHERS BEFORE DRYING

Fatliquors have polar groups, and the molecules of the lubricating fat display some affinity towards the collagen. This attraction is usually relatively weak compared with the tannin or dyestuff, and it needs time for molecular accommodation to take place. For this reason, after the completion of retannage and fatliquoring, 24-hour ageing by piling the leather wet on a flat platform—or horsing up—is very beneficial.

Premature drying will induce fatliquor migration to the surface during samming, setting and vacuum drying. The greatest loss is by samming and setting after fatliquoring without a sufficient laying period and, as a result, a firmer, flatter leather is formed.

THE EFFECTS OF DRYING, CONDITIONING AND STAKING

After setting out and drying, the leather is relatively firm and therefore needs conditioning then staking to soften. Conditioning allows moisture to enter the fibre bundles, thereby rehydrating them so that they become more flexible. At a moisture content of 28% to 30%, the leather is taken for staking for mechanical softening, where it is normally essential to maintain a uniform break and a soft and full handle.

Under-conditioning results in torn fibres, loose bellies and a loose grain. Over-conditioning allows easy softening in staking, but the leather then dries hard when the moisture is removed in second-time drying due to the fibres becoming stuck together.

The staking operation varies according to the leather requirements. For leather bags, dry milling might be required after staking to separate the fibres and loosen the structure to obtain a very soft and fluffy leather.

Floater leathers require a loose grain and this occurs when the upper and inner layers of the hide have significantly different structures, appearing as if they no longer truly interconnect. After retannage and fatliquoring, the crucial stage for floater is the drying method. Toggle drying maximises the weakening of the junction between the grain and the flesh, so that the pattern that is developed on milling will be bold and pronounced.

Vacuum drying with subsequent hang drying results in a smaller milling grain. The trend of wet milling to a near dry state, with subsequent hang drying, is another option for achieving a bold pebble grain.

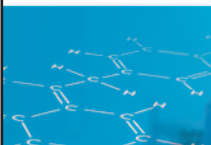
Reliability and uniformity: the key to success

Fatliquors are the key to modern high quality leathers. The outcome and reliability of the critical stage of fatliquoring is highly reliant on careful attention to good practice. It is also fully dependent on the selection of the raw materials and the quality control applied during the manufacture of these essential products.

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