



Challenges facing fatliquors today

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It is well known that a fatliquor is a blend of fats, oils and waxes (FOWs) designed for delivery of these materials to leather in aqueous medium. These FOWs are commonly added in the form of an emulsion mainly within the neutralising, dyeing and retanning sequences of leather processing, but, in addition, during pickling and tanning processes.

These FOWs may be untreated, or treated to a degree by aeration, sulfition or sulfation. The final products are also likely to contain emulsifying agents, additional stabilisers, water and miscellaneous products such as antioxidants and biocides.

As an emulsion, the fatliquor enables the penetration and lubrication of the fibre structure of a given leather in water medium to a required level. This process is not just reliant upon the properties of the fatliquor, but also on the raw material, neutralising process, the pH of the float and the leather, and upon temperature and mechanical action. Once the emulsion has penetrated the leather as required and then broken, the oils and waxes are deposited within the structure and coat the collagen fibres.

The role of drying

This coating of the fibres with the unmodified hydrophobic FOWs component helps to prevent the leather fibres from sticking together upon drying. Prior to drying, the water within the collagen matrix keeps the fibre structure apart: it acts as a lubricant and enables free movement within the structure. However, the drying operation removes this water, and the fibres are drawn together.

This is a fixation process and forces both the collagen fibres, and the chemicals that are bound within them to interact with each other. This takes place in two parts:

- Primary bondings are formed being both conventional and understood reactions. Here reagents are fixed in place by covalent and ionic bonds. These are relatively strong bonds, but few in number.

- Secondary bonds are formed as the fibre structure is brought more closely together. This forces additional bondings where hydrogen and hydrophobic bonds and dipole forces occur. These are relatively weak bonds but high in number.

In this drying stage, the oils and fat coated fibres are bound with very weak hydrophobic bonds, but because these are easily broken the fibres are able to slide by each other. The fibres do not stick together and this imparts flexibility and softness to the leather.

This lubrication also helps with a number of physical and tactile properties of leather. The physical performance is influenced by lubrication, and this can be measured in terms of tensile strength, extension under given load, and lastometer readings both of load and distension at crack and burst.

In contrast, the tactile properties such as handle are complex subjective properties and relate to the way that leather feels when it is manipulated. This combines the density, softness, compressibility, springiness, smoothness and stretchiness of the structure. This is easily understood by the tanner, but is very difficult to measure.

Fatliquor classifications

Fatliquors are normally defined according to the origin and nature of the oil (sulfited fish oil, sulfated vegetable, etc.) and by the nature of the emulsifiers (anionic, cationic, sulfited, sulfated, etc.)

- Natural: Animal and vegetable FOWs, e.g. lard oil, tallow, lanolin (wax), soya-lecithin and rapeseed oil.
- Marine: Cod oil, caplin oil, herring oil.
- Synthetic: Sulfosuccinate esters, acrylic acid esters, phosphate esters.
- Mineral: Paraffinic oils, paraffinic waxes.

Panel 1: Examples of blends of oil and water: non-miscible, coarse and fine emulsions



Non-miscible oil on water



Coarse emulsion (opaque)



Fine emulsion (translucent)



However, for the leather industry, synthetic and mineral oils are commonly classified together as they have similar contributions in leather. Some natural oils may be classified as synthetic following partial processing, such as re-esterification.

Emulsification and classification

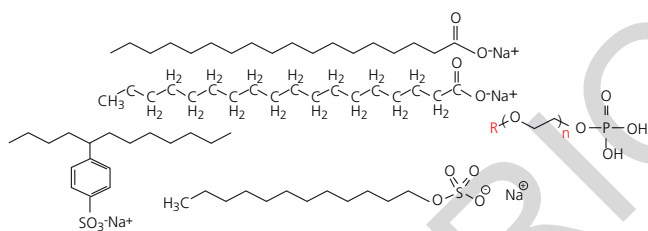
Fats, oils and waxes (FOWs) are hydrophobic and insoluble in water, and their emulsification is achieved with the use of surfactants. Here:

- A surfactant can be defined as a chemical that lowers the surface tension between two liquids (also solids-liquids), to enable the formation of an emulsion.
- An emulsion can be defined as a mixture of two immiscible liquids where one is suspended or dispersed in the other. Here, stability is usually achieved using surfactants aggregated in the form of micelles.

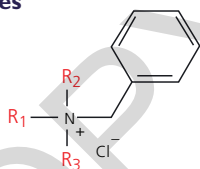
Examples of oil and water in a non-miscible state, and emulsified in coarse and fine emulsions are shown in *Panel 1*.

The nature of surfactants is complex, and fatliquors are commonly classified as anionic, cationic, non-ionic or amphoteric according to the nature of the surfactant. These are set down in *Panels 2, 3, 4, 5* respectively:

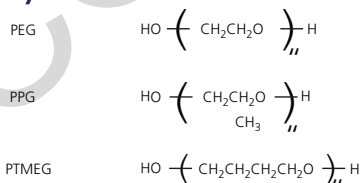
Panel 2: Examples of Anionic (-) Surfactants: Carboxylic (soap) sulfited, sulfated, phosphate esters



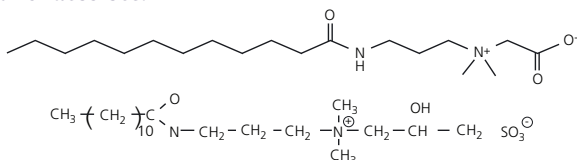
Panel 3: Example of Cationic (+) Surfactant: Quaternary amines



Panel 4: Examples of Nonionic Surfactants: Alcohols, polyethers



Panel 5: Examples of Amphoteric/Zwitterionic (+&-) Surfactants: Amides and carboxylates, Amides and sulfonates etc.



Specific requirements of fatliquors

In addition to meeting conventional leather making requirements - such as the ability to deposit oils and lubricate the fibre structure to meet specific tactile requirements and physical properties - fatliquors should also meet other basic needs. They should, for example, be expected to form emulsions with a reasonable degree of stability to chemicals and different hardnesses of water across a broad range of temperatures. They should also show good storage properties - up to say 2 years - at a temperature between 5° and 40°C, and not be too viscous for use within automated delivery systems.

There are issues with fatliquors but they should not have a negative impact. They should neither contribute excessively to fogging as determined by gravimetric and reflectometric methods, nor odour. In addition they should not negatively contribute to light and heat fastness properties, fat migration, or have an unwanted bleaching effect or reduce area yields.

Of considerable importance, they should be safe for transport and handling, and should not introduce, form or release substances of concern to both human health and the wider environment. In particular this includes halogenated hydrocarbons - short and medium chain chlorinated paraffins, polycyclic aromatics and alkyl phenyl ethoxylates (APEOs), among others. They should not contribute to the oxidation of trivalent chromium.

Sustainability

Sustainability and sustainable development have become synonymous from both a human and corporate perspective. This has been defined by the Brundtland Commission of the United Nations, 20 March, 1987 as "a development that meets the needs of the present without compromising the ability of future generations to meet their own needs".

The concept is complex and diverse, and the European Council in December 2009 confirmed that "Sustainable development remains a fundamental objective of the European Union under the Lisbon Treaty". The concept of this policy is set down in *Panel 6*:

Panel 6: The concept of sustainable development

Sustainable Development stands for meeting the needs of present generations without jeopardising the ability of future generations to meet their own needs.

In other words, a better quality of life for everyone, now and for generations to come.

It offers a vision of progress that integrates immediate and longer-term objectives, local and global action, and regards social, economic and environmental issues as inseparable and interdependent components of human progress.

Sustainable development will not be brought about by policies only. It must be taken up by society at large as a principle guiding the many choices each citizen makes every day, as well as the big political and economic decisions. This requires profound changes in thinking, in economic and social structures and in consumption and production patterns.



Sustainability has become a megatrend, and has empowered a rise in a range of “lists” in an effort to address substances of concern. Accordingly, a number of legislative bodies, NGOs and brands have established, or are in the process of establishing, “lists” that dictate:

- Substances of concern and restrictions regarding the presence of these chemicals during or after use.
- Chemical products that have been screened and certified for use by suppliers.

The two main types of lists are:

- Restricted Substances Lists (RSL) that identify undesirable substances in the final product and set limits for their presence.
- Manufacturer Restricted Substances Lists (MRSL) that identify undesirable substances utilised in the manufacture of the components used to make the final product and set limits for their presence.

These concepts and listings are given the closest attention in the development and supply by responsible fatliquor manufacturers.

Effluent arising from leather manufacture

Chemical oxygen demand (COD) is the most common indicator of the general quality of wastewater. It is used to reflect the amount of organic pollutants in wastewater and the associated effort required to remediate the effluent. It is well known that discharges from the beamhouse can contribute up to 75% of the COD load in leather manufacture with other contributions from the dyehouse that include retanning agents, dyestuffs, organic acids, and fatliquors.

The biochemical oxygen demand (BOD) is another tool used for measuring the quality of water. Whereas the COD is determined by chemical oxidation of a sample and represents the “maximum” oxygen demand, BOD is determined by bacterial action, commonly over a 5-day period, and is a measure of the biodegradable component of the COD contribution of an effluent. Effluents that have high BOD5 values will benefit significantly from biological effluent wastewater treatment plants as this not only lowers the BOD, but at the same time lowers the COD.

In this regard, a number of chemical products will be assessed for their biodegradability, i.e., while they may contribute to initial COD measurements, the values can be effectively reduced by biological effluent plants.

The biodegradability measurement

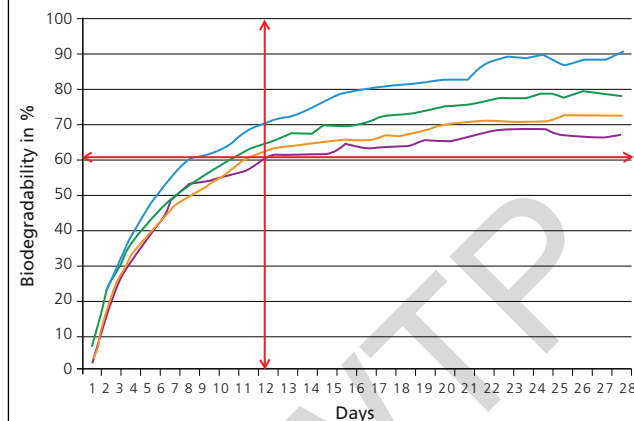
The biodegradability measurement, assessed by the OECD 301 (F) method, is quite different from the BOD value.

This refers to four categories when compared to the biodegradability of ethylene glycol as a standard (100%):

- Readily biodegradable: >60% within 10 days
- Biodegradable: >60% within 28 days
- Partially biodegradable: 20-60% within 28 days
- Poorly biodegradable: <20% within 28 days

The progressive biodegradation of four typical fatliquors over 28 days is given in *Panel 7*:

Panel 7: The biodegradability measurement of selected fatliquors



All four of the fatliquors represented in *Panel 7* would be classified as readily biodegradable.

The factor of biodegradability of fatliquoring residues from processing has led to improved uptake by better process control, innovations in fatliquor design, and ways to improve uptake that include the introduction of fixing agents.

Renewable resources

There are also challenges associated with the raw materials used in fatliquor manufacture in terms of renewable vs non-renewable sources of supply.

Here, renewable sourced materials derived from nature need to be sustainably managed and should ideally not compete with food production. Reputable fatliquor manufacturers want to use the highest quality oils available but this may not always be the most sustainable option. Ideally, the best quality industrial grade oils should be used, as long as the quality assurance requirements of the product are met.

Non-renewable sources include mineral and coal based raw materials, but these can provide leather properties that cannot always be achieved using renewable natural oils.

An additional challenge is the carbon and water footprint of both natural and mineral oils, and these cannot be influenced by the leather industry. Standard values based on data available are established for these chemicals, and the fatliquor manufacturers are limited to using raw materials with the lowest footprint values, or limiting the range of available oils and thereby customer choice.

These factors are driving the reuse of materials, in particular the innovative use of recovered and recycled raw materials and oils.

The way forward

- The development, production and selling of fatliquors is no longer a simple process.
- Challenges arise for tanneries and chemical companies alike as more lists of chemicals of concern to both the environment or to human health are established.
- Innovation is an instrumental aspect of modern chemical companies. This encompasses sustainable sources of oils and the development of biodegradable and high exhaustion fatliquors.
- Reliable chemical companies will ensure the strictest possible quality controls for all fatliquor raw materials and products as part of their customer service.