

Getting better fatliquor exhaustion

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Many discussions have taken place in the industry recently around the topic of putting the chemicals in the leather, and not in the effluent waste. A chemical company is certainly not in the business of feeding the effluent treatment plant, considering most of their research and development takes place on leather trials.

Fatliquor that is not absorbed by the leather will enter the effluent plant and will need to be broken down if the effluent is to be classified as non-polluting. The chemical oxygen demand (COD) is a measure of this pollution power. Monitoring the COD allows you to monitor the fatliquor uptake.

The emulsion

The emulsion is a special category of a mixture used in the tanning drum. When a non-polar substance such as an oil is placed into a polar solvent like water, then, the two are incompatible and will not mix. Depending on the density, either the oil will float on the top or it will form at the bottom of the container. If the mixture is agitated, the oil will rapidly break up into little balls of oil (called oil droplets) and when the mixing is ceased the droplets begin to re-coalesce. They are attracted together by their mutual hatred of water, known as hydrophobic bonding.

As soon as a soap or surfactant is added, the droplets will get smaller until they form microscopic droplets; known as micelles. A schematic representation of a micelle is seen in Figure 1.

There are several other very interesting ways of making a micelle, in addition to just adding a soap. A chemical supplier can use a modified oil to achieve the fatliquor. To do this, the neutral oil is treated with a certain chemistry that can add a charge to parts of the emulsion. The most common way of treating a fat in the tanning industry is to add a sulfonate ($-SO_3^-$) or a sulfate group ($-O-SO_3^-$). The addition of these charged groups makes regions of the fat become charged or polar, allowing their association with a polar solvent like water.

The treated fat/oil will distribute itself in the micelle so that the hydrophobic groups are buried deep inside the structure, while the charged hydrophilic groups stick out into the water. The surfactant will be dispersed halfway between the modified oil, in the Stern layer or at the fringes of the double diffuse layer. Counter ions that are opposite to the charge of the modified oil/soap will associate with the negative charges (if it is an anionic fatliquor) of the soap or of the modified oil. The charge of the soap or modified oil allows the

micelle to have stability and to be repelled from other micelles, ensuring stability of the emulsion.

Counterions added as part of the formulation or attracted from the hide/skin or added as part of the water or process chemistry will be stuck in the double diffuse layer or will firmly bind to the modified oil.

Fatliquor components

The amount of each component is what makes a fatliquor distinguishable from other fatliquor products. If a tannery wants to develop a leather that is immediately distinct from other leathers, all they need do is to blend their own fatliquors in-house and the chemical companies or competitor tanneries can never copy their formulation unless they have a recipe and a fatliquor formulation.

The components of fatliquor are most commonly water, modified oil, neutral oil, surfactant/stabilisers. So, it is not uncommon to see a fatliquor given extreme storage conditions, or poor compatibility, separate into four layers. Fourier transform infra-red analysis with attenuated total reflectance (FTIR-ATR) allows a sample of the fractions to then be placed onto the instrument and infra-red light bounced off the fatliquor surface.

The resulting trace can then show what kind of functional groups are present in the fatliquor fractions. C-O, C=O, C-C, C-H, N-H, S-O, O-S-O, groups can all be examined using the device and the quantity will allow a researcher to predict the behaviour of the oil.

The soap or surfactant itself will be a fat dissolving type that has a hydrophilic/lipophilic balance that penetrates as a fat droplet and then carries some of the neutral oil in a fashion that is like the modified oil. The more hydrophilic groups are added, the less the soap will penetrate the droplet or be associated with the Stern Layer, and the more the surfactant will be in the double diffuse layer and will play a stabilising role for the emulsion. If a soap is added that has a higher lipophilic to hydrophilic ratio, then the chemical will act like a modified oil and will associate with the neutral fraction. Sometimes a surfactant that is of opposite charge or is even a non-ionic charge is added to provide stability. These polar non-charged groups, dipoles for instance, can allow emulsions but are not that sensitive to counterions.

Neutral oil

The neutral oil is the component of the fatliquor that binds very well to collagen, if allowed. The neutral oil is the component responsible for the plasticisation of the fibre, the increase in strength and,

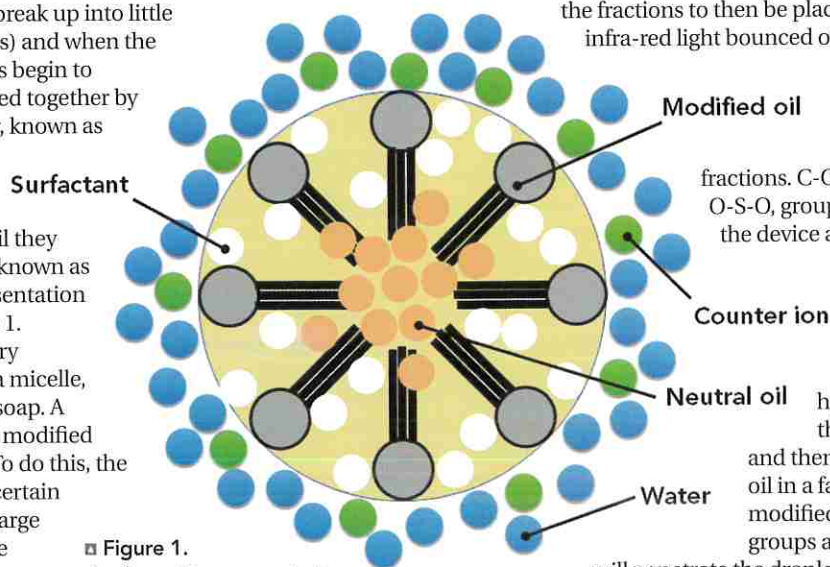


Figure 1. A schematic representation of a fatliquor micelle.

ultimately, in the prevention of fibre sticking. The nature of the neutral oil has been investigated many times in the leather industry. Certain neutral oils, some plant oils, tend to be drying types; meaning they are quite volatile, will evaporate out of the leather over time, leaving the leather harder, flatter, and dry to the touch.

A waxy ester type oil, like those seen in fish oils and sperm whale replacement oils, tend to nourish and lubricate the leather enhancing the touch and feel. The neutral oil will not like being in water and will immediately bind together in the middle of the micelle, getting as far away from the external water as possible.

The neutral oil can also provide a safe refuge for hydrophobic dyes, retanning materials, and other fats that do not like being in water. A tried and tested way of getting a hydrophobic dye penetrated into the leather structure is to dye with the fatliquor and the use of a liposomal type transfer into the fibre stratification will be achieved relatively easily.

When the time is right, the emulsion will be broken and the water and the non-polar oils will immediately separate. The neutral oil will

Acids (H^+), sodium (Na^+), potassium (K^+), hard water (Ca^{2+} , Mg^{2+}), or metals (Cr^{3+} , Al^{3+} , and Zr^{4+}) will create havoc in an emulsion system. The metals can also be used at the end of fixation to "cap" the fats and oils, see Figure 2C.

Two-component system

The possibility of the emulsion breaking in the drum is something that must not be eliminated by the tanner. When the time is right, the tanner wants the emulsion to be unstable and should coat the fibres as seen in Figure 2. If either one of the scenarios (seen in Figure 2) is achieved in the drum, the COD will be lower.

The difficulty for tanners and chemical suppliers is that the logistics of chemical manufacture, transport, storage, and logistics of chemicals means that premature emulsion instability is a very real scenario. The premature splitting of the fatliquor in the drum is equally a difficult situation to deal with. Progressively, tanners have been buying fatliquors that are more stable than ever, specially to prevent fatliquor splitting while in storage and to eliminate time and effort in stirring the flow bins prior to decanting.

To achieve these levels of stability, tanners have either been adding a stabiliser or emulsion assist chemical together with their fatliquor, have been using very high temperatures in the drum, or they have relied on the chemical supplier to add additional quantity of stabilisers or surfactants to achieve the stability of product.

When the time now comes to break the emulsion during fixing, the tanner adds the normal quantity of acid and the result is the fatliquor only partially breaks, and the unsplit emulsion is discarded with the effluent instead of being taken up by the leather. The tanner, when feeling the final leather, adjusts the formulae to add more fatliquor to achieve the correct level of softness; creating a double problem.

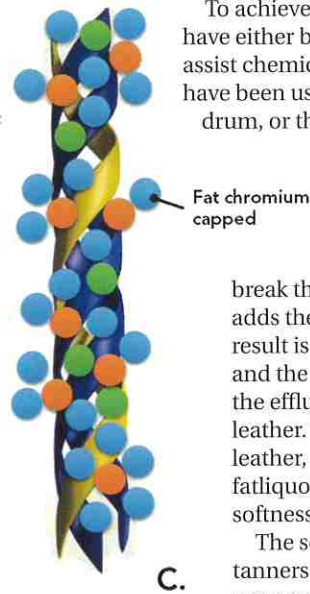


Figure 2. Three types of emulsion breaking. A. The ionization of the collagen or charge of the chromium. B Hydrophobic bonding or smearing. C. Metal capping of oils.

rapidly attach to any hydrophobic groups on the collagen in a hydrophobic bonding arrangement. This smearing of oil onto the collagen allows the fibres to release after drying, see Figure 2B.

Emulsion breaking

The counterions are the largest destabilisation factor for an emulsion. Second will be the effect of temperature. Low temperatures lower the energy of the system, preventing effective micelle repulsion. The solubility of the polar fractions will also be depressed. The ionization of the leather can also result in emulsion instability, as the modified oils and polar surfactants are removed, see Figure 2A.

If the concentration of counterions is raised, particularly the polyvalent ions, the ionicity of the double diffuse layer will be lowered. The repulsion between micelles is lowered and the aggregation of the micelles occurs.

If the non-polar fraction of the emulsion is raised too high, then the micelle size will increase. The Stern Layer and double diffuse layer will flatten and more non-polar groups will be exposed to the water. Exposure of the non-polar groups also allow binding to the flesh and grain side of the leather, binding to other micelles, and an inversion of the micelle. As soon as the centre of the micelle is exposed then the emulsion will break, see Figure 2B.

The solution to this problem may be that tanners will need to return to a scenario that was commonly used from the 1950s to the late 1980s in shoe upper tanneries; they used to blend their own fatliquors through the combination of a low stability modified oil, a small quantity of high stability modified oil, and then they bulked up the fatliquor to the desired level of instability through the use of a raw/neutral oil (or at the very least a very low stability fatliquor), usually a natural lubricating fatliquor.

These two or three component systems allowed the exact level of fatliquor instability so that penetrating into an incompletely neutralised leather, or through the addition of a quantity of acid, resulted in the complete exhaustion of a small quantity of acid. The correct exhaustion of the fatliquor meant a much more effective COD and, more importantly, the optimised level of product in the manufacture of the leather.

Conclusion

In this article, the stability of fatliquor has been addressed. The description of the stability of a fatliquor is discussed, the components of the system and a detailed look at how the tanners and chemical companies work together to achieve the desired softness in leather has been highlighted. Scenarios of why this could be problematic have been presented and the possible solution, that is the use of a two or three component system, has been proposed by the author. ■

References: Burgess, D. (1993) General aspects of fatliquoring; an introduction to the application and chemistry of fatliquoring. J. Soc. Leath. Technol. Chem. 78: 39-43.