CHAPTER 17

Fatliquoring

17.1 INTRODUCTION

Contrary to popular belief, the primary function of fatliquoring is not to soften the leather: this is only the secondary function. The primary function of fatliquoring is to prevent the fibre structure resticking during drying. As the leather dries, the interfibrillary water is removed, allowing elements of the fibre structure to come close together, which consequently allows interactions to occur. In the limit, these interactions become strong, because they are created by the Maillard reaction. Therefore, it is essential for leather quality to prevent this happening.

Figure 17.1 shows the structure of a wet blue fibre.[1] The photomicrograph is the result of cryo-scanning electron microscopy: the sample is snap frozen in a slush of liquid and solid nitrogen at about –200 °C, then the temperature is allowed to rise a few degrees, so that the water can sublime away under vacuum to leave intact structure.

There are several aspects of the photomicrograph to note:

1. Collagenic materials are at their softest when they are soaking wet.
2. The photomicrograph is a representation of wet leather, *i.e.* no artefacts of drying are present.
3. The fine structure elements are fibril bundles: they indicate a high degree of opening up and the important level of the higher of collagen structure at which opening up occurs is at the level of the fibril bundles.
4. Taking points 1 and 3 together, the sites where lubrication is required are the fibril bundles: this implies that the conditions under which the lubricant penetrates the fibre structure are important.

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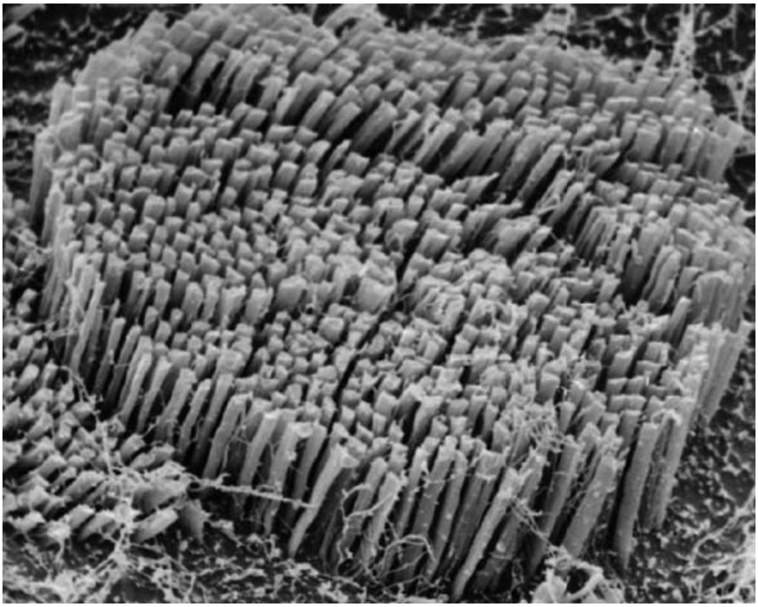


Figure 17.1 Cryo-scanning electron photomicrograph of wet blue leather.

Figure 17.2 shows a wet blue fibril bundle at higher resolution;[2] there are two aspects of this photomicrograph to note:

1. The structural elements are fibrils;
2. At the surface, where the sample is wettest, the fibrils are separated, but where evaporation of water can begin to take place it can be seen that the fibrils are much closer together.

The opening up processes apply also to the fibril bundles themselves, although it is probable, because of the close association of the fibrils, that the physical properties are derived from the ability of the fibril bundles to distort and slip when stress is applied. Those properties are the elements of handle, including softness, and strength. Handle is a complex concept, because it relates to the way the leather feels when it is manipulated: it is an algorithm that combines density, softness, compressibility, stiffness, smoothness, springiness and stretchiness, easily solved in the brain of the experienced tanner, but much less easy to quantify objectively. Strength is the ability of a material to resist breaking or tearing stress: in the case of leather, it is the ability of the material to dissipate stress over its volume by movement of the fibre structure. To be able to do this, two criteria must be met:

1. The fibre structure must not be stuck together by the adhesions created during drying.
2. The fibre structure must be lubricated to allow the elements to slide over one another.

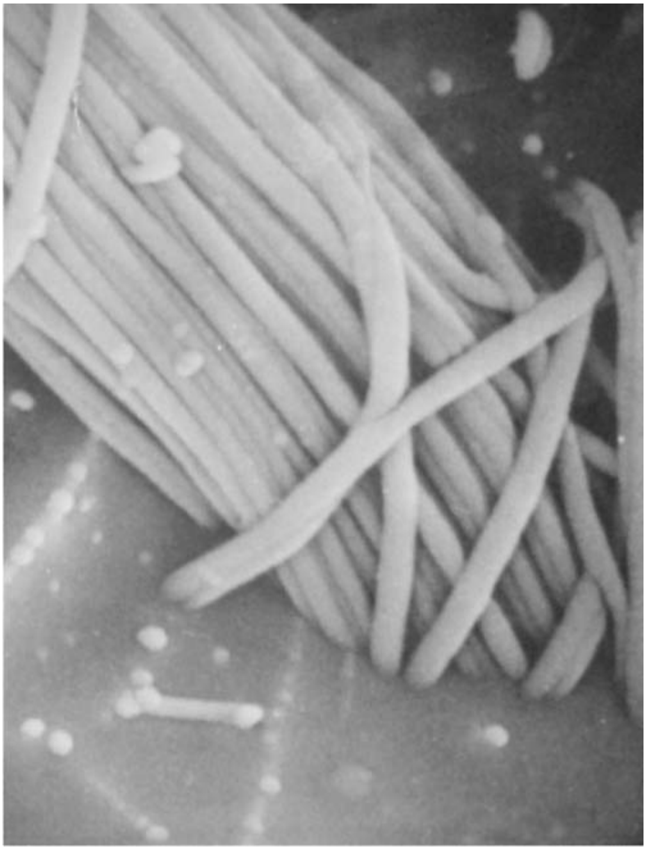


Figure 17.2 Cryo-scanning electron photomicrograph of a wet blue fibril bundle.

It is the purpose of the fatliquoring step to satisfy those criteria: it prevents fibre sticking during drying by providing an oil surface to the fibre structure, which then gives it the required lubrication. The effectiveness of the process step then depends on the degree to which the lubricant penetrates down the hierarchy of structure and its ability to allow contacting surfaces to slide. The photomicrograph in Figure 17.3 illustrates this, showing the effect of drying without lubricating; whereby the well opened up fibre structure is stuck together at the level of the fibril bundles.

Typically, the leather industry employs partially sulfated or sulfited oils, which might be animal vegetable, synthetic or, less commonly, mineral. Most commonly, the neutral oil is in the form of triglyceride (see below). Here, the so-called sulfo fraction is the emulsifying agent, keeping the neutral oil suspended in solution and thereby transporting it into the leather: it is the neutral oil that is the lubricant (see below).

Oil in water emulsions are created by the formation of particles, consisting of a small drop of oil, surrounded by an emulsifier/detergent/surfactant/tenside.

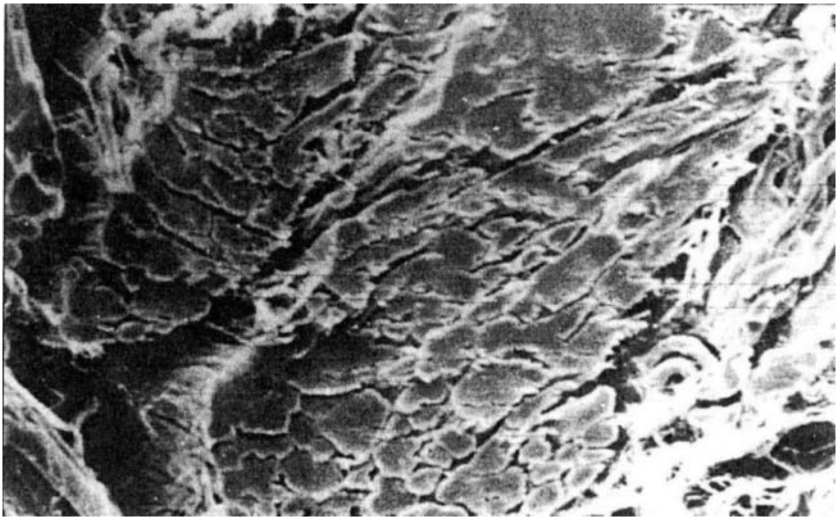


Figure 17.3 Chrome tanned leather: well opened up in the beamhouse, but dried without lubricant after tanning.

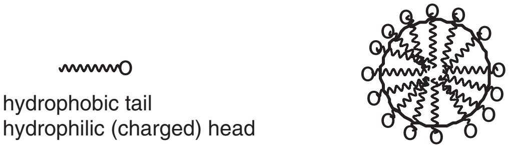


Figure 17.4 Model of an anionic oil-in-water emulsion particle.

The emulsifying agent has a hydrophobic part, which is dissolved in the oil, and a charged, hydrophilic part that interacts with the solvent (water), to keep the particle suspended (Figure 17.4).

The emulsion particles are prevented from coagulating or coalescing because they are held apart by the repulsing effect of the high charges on the surface. Any chemical reaction that reduces the charge on the particle surface will allow them to come together, allowing the neutral oil particles to coalesce. High temperature can drive the particles together, breaking the emulsion. An important mechanism to make this happen, which is exploited in leather making, is the ionic interaction between the sulfate/sulfonate group and the protein, in the way discussed in Chapter 15.

In the 1986 SLTC Conference the theme was fatliquoring: Waite reviewed the state of understanding at that time and summarised the important contributors to the mechanism, as follows:[3]

1. The charge on the leather (neutralisation dependent) can affect fatliquoring effectiveness;

2. Penetrating power depends on emulsion stability;
3. Particle size distribution an emulsion is a variable that influences stability and penetration;
4. Sulfonation (to make partially sulfited oils) imparts more stability than sulfation (to make partially sulfated oils);
5. Softness depends on the ratio of emulsifier fraction to neutral oil fraction;
6. Softening is influenced by the viscosity and interfacial tension of oils.

Points 1 and 2 emphasise the importance of pH in this process step: if the emulsion is anionic (which it usually is), the charge on the leather should also be anionic to allow penetration. Neutralisation of the substrate not only means pH adjustment through the cross section but also down the hierarchy of structure. The mechanism of fatliquoring can be expressed in simple terms as follows:

1. The neutral oil is transported into the pelt as an oil-in-water emulsion.
2. The emulsifying agent interacts with the leather, reducing or eliminating its emulsifying power.
3. The neutral oil is deposited over the fibre structure – the level of the hierarchy of structure depends on the degree of penetration.
4. The water is removed by drying, allowing the neutral oil to flow over the fibre structure.

The distribution of neutral oil determines the degree to which fibre sticking is prevented, which in turn depends on the depth of penetration of the emulsion, which in turn depends on the pH of the system and the particle size of the emulsion. Additional factors are the nature of the sulfo fraction carrier, sulfated or sulfited, the mechanism of distributing the oil, where the oil is distributed within the hierarchy of the fibre structure and the nature of the oil. It is this latter parameter that contributes to the softness of the leather: in general, the higher the viscosity of the neutral oil, the better are the lubricating properties. However, there is a limiting effect, which is the ability of the oil to be emulsified and hence carried into the leather: at high viscosities, the oil tends to deposit on the surface, leaving the leather empty.[4]

Clearly, from the analysis of the mechanism, the application of a fatliquor must incorporate the notion of creating as small an emulsion particle size as the formulation will allow. This is accomplished by applying the following conditions:

- High temperature of the diluting water: ideally heating the fatliquor to the same temperature as the water; this allows the oil to break up into small drops due to the decreased viscosity. Note, there is a limit to the temperature, since heating is a powerful mechanism of coagulation: a practical limit is 60 °C. This would be a maximum value to avoid damaging vegetable tanned leather, although chrome tanned leather is typically capable of withstanding much higher temperatures.

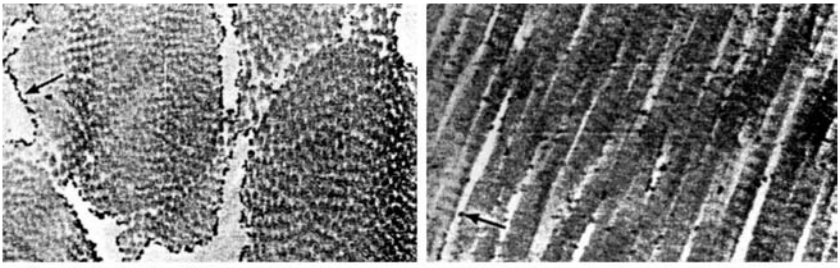
- Mechanical action: for mixing the fatliquor into water, mechanical action must be maximised, because this is the way the oil is dispersed into drops. Ideally, a motorised stirrer should be used, with the fatliquor added into the vortex. The common practice of adding cold fatliquor to hot water in a blue barrel, stirring with a broom handle, is not optimum and therefore best use will not be made of the fatliquor.
- Some tanners have favoured adding water to the fatliquor. In this way, a water-in-oil emulsion is formed. Continued additions of hot water reverse the emulsion to oil-in-water. There is no clear evidence to indicate that this a better way of optimising the eventual emulsion.

The particle size of the emulsion is determined by the degree to which the oil is converted into the sulfo derivative: the bigger the sulfo to neutral oil ratio the more solubilised the oil becomes and the particle size is reduced. Most fatliquor formulations contain about 50% neutral oil, 25% sulfo fraction and 25% water: this will produce emulsion particles of about 30 nm. Higher sulfo fractions can create micro-emulsions, where the oil is on the boundary of suspension and solubilisation, when the particle size is about 5 nm. Figure 17.5 shows the influence of particle size, comparing the typical emulsion with a micro-emulsion: the oil particles can be seen as black dots, visualised in transmission electron microscopy by osmium tetroxide.[1]

The relative effects of the neutral oil and the sulfo fraction were distinguished by separating the components of synthetic fatliquors and applying them individually.[1] For comparison of equal quantities of reagent, 20% fatliquor was compared with 5% sulfo fraction and 10% fatliquor was compared with 5% neutral oil. To allow the neutral oil to penetrate, it was formulated with either 5% non-ionic surfactant or acetone. Table 17.1 gives the results.

From Table 17.1:

- softness is conferred by the neutral oil, with no contribution from the sulfo fraction.
- the alternative ways of delivering the neutral oil appear more effective than the original fatliquor.



sulfated synthetic oil, 25nm

sulfated neatsfoot oil, 5nm

Figure 17.5 Penetration of oil emulsions, shown by transmission electron microscopy: 25 nm reaches the fibril bundles, 5 nm reaches the fibrils.

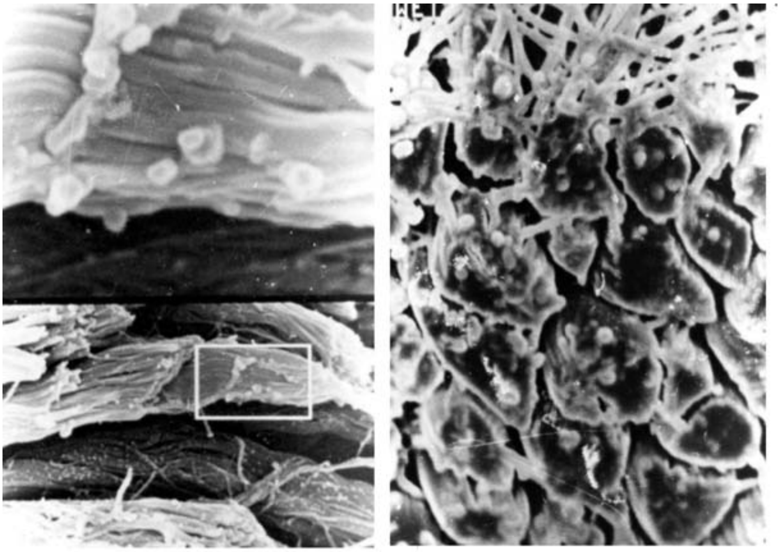
Table 17.1 Relative effects of neutral oil and sulfo fraction. The softness of the leather is measured by the loop test, where a lower weight/magnitude means softer leather.

Offers on wet weight	*Sulfited oil*	*Sulfated oil*
20% Fatliquor	44	56
10% Fatliquor	127	123
5% Sulfo fraction in water	450	590
5% Neutral oil in acetone	69	66
5% Neutral oil + 5% non-ionic surfactant	70	53
Controls:		
5% Non-ionic surfactant	164	
Acetone then rehydrate	781	
Water	1220	

It is clearly not feasible to use organic solvents in fatliquoring, but alternative emulsifying agents are of interest (Figure 17.6). An obvious feature of the emulsion of neutral oil and non-ionic surfactant is the instability of the emulsion: in attempting to measure the particle size by laser light scattering it was apparent that the rate of coagulation was faster than the rate of measuring particle size dimension. This raised the issue as to why the fatliquoring effect was so good.

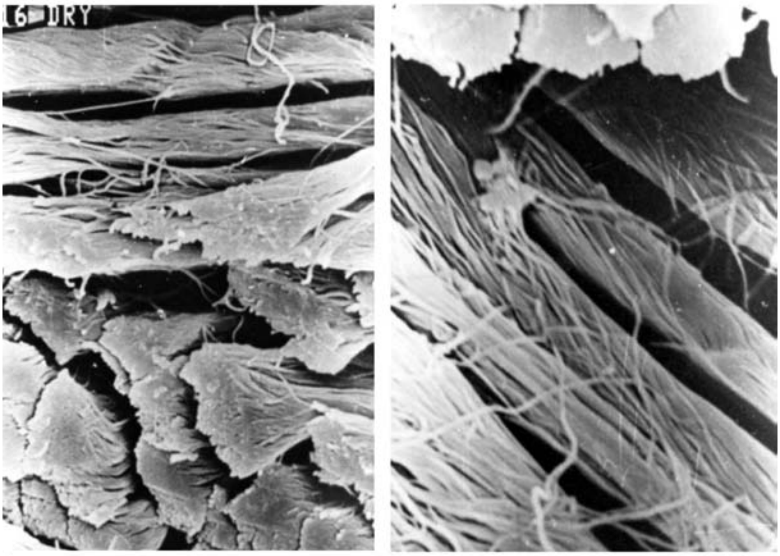
The wet leather fatliquored with sulfated oil has the appearance of droplets over the surface, which would be expected if the oil was deposited as emulsified drops. However, the leather fatliquored with neutral oil emulsified with non-ionic surfactant looks completely different: the surface is coated with what appears to be a water-in-oil emulsion. In both cases the dry leathers do not show any difference in structure, so the oil is assumed to be uniformly distributed in the regions where it was deposited. Therefore, it can be inferred that the unstable emulsion exhibits a different way of delivering the oil. Once a stable emulsion particle hits the fibre structure it is likely that the sulfo fraction will interact with it, depending on the charge conditions, causing the emulsion to lose its emulsifier and the neutral oil will be deposited: there is no mechanism for the neutral oil to move within the aqueous medium, so it is static until the water is removed in drying and it can flow over the leather surface. However, if there is residual emulsifier in solution, because of the weak emulsifying effect, continuous interaction can occur between the deposited oil and the solvent water, creating a water-in-oil system that allows the oil to flow over the surface in the presence of water.

Sulfated oils and sulfited oils can be compared. Sulfated oils are less stable and hence less penetrating because the sulfo fraction reacts readily with the leather, so the emulsions break easily over the leather. In contrast, sulfited oil are less reactive towards the substrate, so the emulsions are apparently more stable in the environment of the leather and hence the emulsion particles penetrate more deeply into the hierarchy of structure. For this reason the technological approach to fatliquoring is to use a mixture of the two types, to



Sulfated oil, wet leather

Nonionic surfactant and neutral oil, wet leather

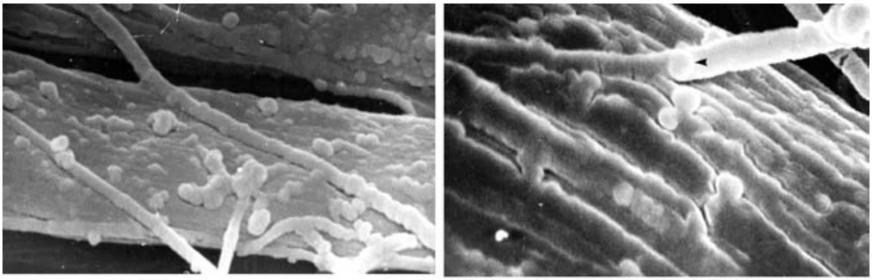


Sulfated oil, dry leather

Nonionic surfactant and neutral oil, dry leather

Figure 17.6 Leathers treated with sulfated synthetic oil fatliquor and with neutral synthetic oil emulsified with non-ionic surfactant (from Table 17.1).

get both surface and internal lubrication. But there is another consequence of the lower affinity of sulfited oil for the fibre surface: the sulfo fraction remains available to interact with oil deposited on the leather surface. This is illustrated in Figure 17.7, where it is apparent that the neutral oil is deposited in a globular



globular sulfated oil

globular and smeared sulfited oil

Figure 17.7 Effect of sulfation or sulfonation on the mode of deposition of neutral oil on leather.

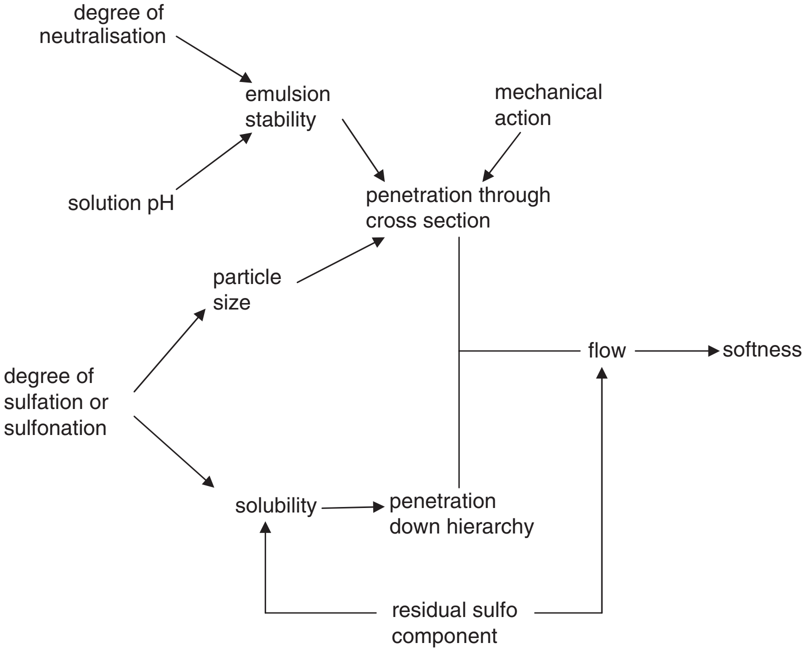


Figure 17.8 Model of the fatliquoring mechanism.

manner by sulfated emulsifier, but in both a globular and a smeared manner by the sulfited emulsifier.

The mechanism of fatliquoring can be summarised by the interaction of the contributing parameters (Figure 17.8).[1]

The development of softness in leather is intimately associated with mechanical action, because the process of drying causes adhesions to occur, weak adhesion in the case of well fatliquored leather, which must be broken to soften the leather. This is achieved by the process of staking, in which the

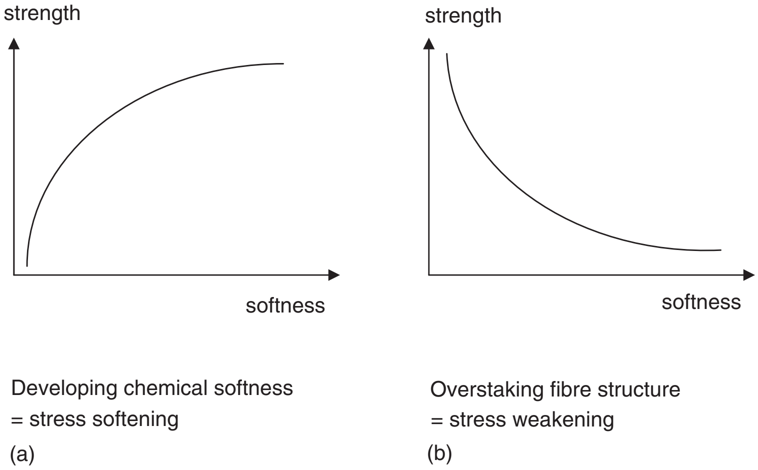


Figure 17.9 (*a*) Chemical softness; (*b*) stress softness.

leather is mechanically stressed: in industry the process used to involve bending the leather by hand through an acute angle over a blunt blade, but now machines pummel the leather automatically and with precisely controlled force. A crucial feature of the staking process is the water content of the leather: more than equilibrium moisture content is required, 15–20%, to provide additional lubrication of the fibre structure.

Figure 17.9 demonstrates the relationship between softness and strength.[5] In Figure 17.9(a), there is positive correlation between softness and strength, indicating that higher strength is obtained from more effective fatliquoring. There will be a maximum value of the strength for any leather, which is dependent on the chemical processing up to the point of the fatliquoring: it is the fatliquoring process that determines whether the optimum strength is displayed or less. Figure 17.9(b) shows a negative correlation, demonstrating that as the stressing continues the fibre structure begins to break down. This can be achieved by too much mechanical action, either too much energy applied to the leather or lesser energy applied for too long, such as multiple passes through the staking machine. Alternatively and additionally, if the moisture content is too low, the fibre structure is less flexible, the components slip less easily, so the brittle structure tends to loosen and break, which is seen as increasing weakness.

17.2 ANIONIC FATLIQUORS

17.2.1 Sulfated Fatliquors

For sulfating, the oil must be unsaturated, with a minimum iodine value of 70: the iodine value is the defined as the number of grams of iodine absorbed by 100 grams of oil or fat. Oils that have been used in this regard are castor, neatsfoot, soya, groundnut, cod. Note, after 1980, sperm whale oil was voluntarily abandoned by the global leather industry.

The chemistry of the preparation of a sulfated oil is in three steps:

1. Preparation: 10–20% Concentrated sulfuric acid on the weight of the oil is added slowly to the oil, with constant stirring. The temperature of the exothermic reaction must be controlled to $<28\,^{\circ}\mathrm{C}$, otherwise the oil can char, causing darkening, and the triglyceride oil may be hydrolysed to release free fatty acids. This latter effect can give rise to the problem of 'spue', when the longer chain carboxylic acids can migrate from the internal structure of the leather to the grain surface, visible as a white efflorescence. Diagnosis is confirmed when the efflorescence melts by the effect of a match. Problems associated by overheating can be catalysed by the presence of iron salts. An alternative is to use a mixture of sulfuric and phosphoric acids (usually in the ratio 0.8 : 1.0). This removes the effect of iron (by reaction with the phosphoric acid), the reaction is less exothermic, so the acid mixture can be added faster. The process is more expensive and results in a mixture of sulfated and phosphated oils.
2. Brine wash: Excess free acid is removed by washing the partially sulfate oil with brine, which also separates the oil fraction from the aqueous fraction. Brine is used to avoid creating an emulsion, which would happen if water alone were to be used. Alternatively, sodium sulfate, ammonium chloride or sulfate could be used. Some hydrolysis of bound sulfate may take place. Additionally, there may be lactonisation of adjacent hydroxyl groups with carboxyl groups (Figure 17.10).
3. Neutralisation: bound and free acid groups are neutralised with alkali:

$$\text{-OSO}_3\text{H} \rightarrow \text{-OSO}_3^-\text{Na}^+ \text{ or } \text{NH}_4^+, \textit{ etc.}$$

$$\text{-COOH(free fatty acid)} \rightarrow \text{-COO}^-\text{Na}^+ \text{ or } \text{NH}_4^+ \textit{ etc.} \text{ (water soluble soap)}$$

   Also, free sulfuric acid is converted into salts: $2\text{Na}^+\text{SO}_4{}^{2-}$ or $2\text{NH}_4{}^+\text{SO}_4{}^{2-}$, *etc.* Any lactones will be hydrolysed.

Bound SO_3 may range from 2%, considered a low level, to 3–4%, considered medium level, to 6–8%, considered to be high level: fatliquors may therefore be designated low, medium or high sulfated. Figure 17.11 shows some sulfating reactions.

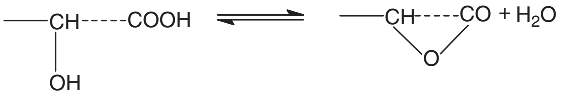
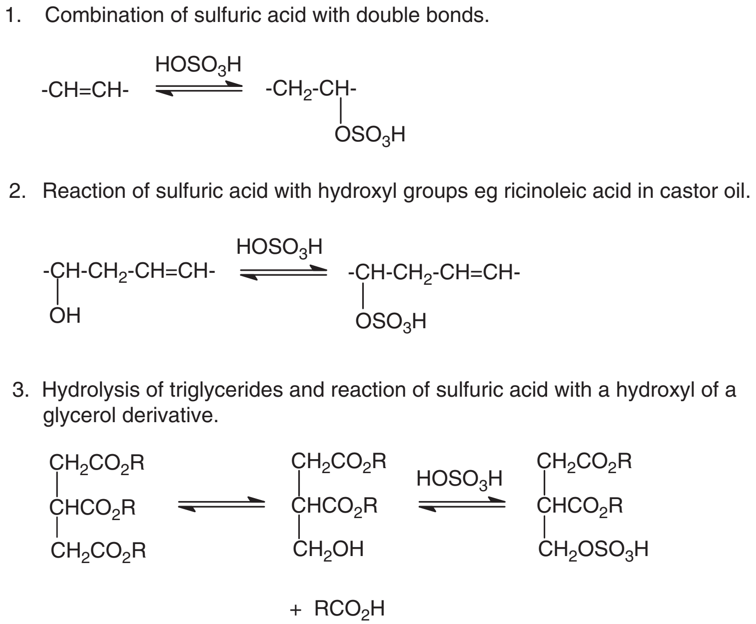


Figure 17.10 Lactonisation.



1. Combination of sulfuric acid with double bonds.

$$\text{-CH=CH-} \xrightleftharpoons{HOSO_3H} \text{-CH}_2\text{-}\underset{\displaystyle OSO_3H}{\underset{|}{\text{CH}}}\text{-}$$

2. Reaction of sulfuric acid with hydroxyl groups eg ricinoleic acid in castor oil.

$$\text{-}\underset{\displaystyle OH}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-CH=CH-} \xrightleftharpoons{HOSO_3H} \text{-}\underset{\displaystyle OSO_3H}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-CH=CH-}$$

3. Hydrolysis of triglycerides and reaction of sulfuric acid with a hydroxyl of a glycerol derivative.

$$\begin{array}{l} CH_2CO_2R \\ | \\ CHCO_2R \\ | \\ CH_2CO_2R \end{array} \rightleftharpoons \begin{array}{l} CH_2CO_2R \\ | \\ CHCO_2R \\ | \\ CH_2OH \end{array} \xrightleftharpoons{HOSO_3H} \begin{array}{l} CH_2CO_2R \\ | \\ CHCO_2R \\ | \\ CH_2OSO_3H \end{array}$$

$$+ \ RCO_2H$$

Figure 17.11 Sulfating reactions.

As the level of sulfation increases:

- anionic charge increases, hence greater affinity for cationic leather;
- lubricating effect decreases, due to the lower concentration of neutral oil;
- emulsion particle size decreases, ultimately to the point of forming a microemulsion (<5 nm) or even actually dissolving in water;
- stability of the emulsion to coagulation by acid or metal salts increases;
- at high levels, the oil functions more like a wetting agent than a lubricant, hence the leather becomes more hydrophilic;
- the leather becomes looser, in terms of break, possibly due to the damaging effect of the sulfate species on collagen;
- the likelihood of hydrolysing the oil to create free fatty acids increases, thereby creating the possibility of chrome soaps, fatty acid spue, poor wetting back, uneven dyeing and poor finish adhesion.

Sulfated oils are used as follows:

- Low level of sulfation: Low stability of the emulsion to coagulating (cracking) by acids or metal salts. Typically used to lubricate the outer surfaces, particularly the grain. May be used for drum oiling of vegetable tanned leather.

- Medium level of sulfation: More stable to coagulation, therefore greater potential for penetration. Used for surface neutralised chrome leather.
- High level of sulfation: used for complete penetration, *e.g.* through neutralised chrome leather for gloving, clothing, softee leathers.

17.2.2 Sulfited Oils

The requirement for the oil is unsaturation, as for sulfating. Options include cod oil, neatsfoot oil, *etc*. Preparation is conducted in two steps:

1. Sulfitation/oxidation: Using the example of cod oil, air is blown through a mixture of 100 parts of oil and 50 parts of 40° Baume sodium bisulfite solution, with stirring at 60–80 °C. Alternatively, hydrogen peroxide may be used instead of air. Figure 17.12 illustrates the chemistry involved.
2. Brine wash: washing with brine removes excess sodium bisulfite.

Note, there is no pH adjustment required, due to the use of bisulfite rather than sulfur dioxide or sulfurous acid.

Compared with sulfated oils, sulfited oils exhibit the following properties:

- no charring or darkening;
- higher emulsion stability to acids, hard water salts, metal ions, *e.g.* Al(III), Cr(III), due to the presence of sulfonate and hydroxysulfonate groups and the low level of free fatty acids or soaps, because there is little hydrolysis of triglyceride during synthesis.

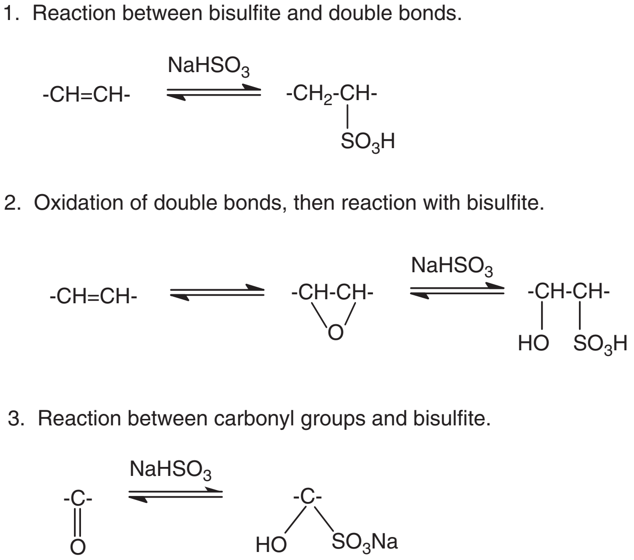


Figure 17.12 Sulfitation and oxidation.

The fatliquor may be formulated with non-ionic detergent, to increase emulsion stability, to promote better penetration, to make the leather softer and fuller. There is a danger of giving the leather loose break.

Sulfited oils are used as follows:

- softness and strength (see below) for all leathers by deep penetration;
- woolskins and furskins in mineral tanning baths;
- in shrunken grain production, to minimise loss of tensile strength in the acidic tanning bath.

17.3 SOAP FATLIQUORS

Raw oil, *e.g.* neatsfoot (100 parts), is emulsified with soft soap, *e.g.* potassium oleate (30 parts). Note, stearate is likely to cause fatty acid spue. The emulsions have a large particle size, due to their tendency to have low stability to water hardness and acid. The formulation typically has pH ~ 8. At pH <6, the soap is increasingly converted into free fatty acid (Figure 17.13), which does not act as an emulsifier, and so the emulsion coagulates.

The uses of soap fatliquors are limited, due to the low emulsion stability. They have traditionally been used for surface fatliquoring calfskins for shoe uppers and formaldehyde tanned sheepskin for gloving leather. There is an American practice of improving the emulsion stability by formulating a soap fatliquor with a small amount of low sulfated oil (up to 0.5% SO_3 on moisture free basis), together with a stabilising colloid, *e.g.* starch or natural gum.

17.4 CATIONIC FATLIQUORS

Raw oil is emulsified with a cationic agent, exemplified by the structures in Figure 17.14, where the hydrophilic group is typically straight chain, aliphatic C_{10} to C_{18}. The following points apply to such fatliquors:

- low affinity for cationic charged leathers, *e.g.* chrome tanned;
- high affinity for anionic charged leathers, *e.g.* vegetable tanned, for lubricating the outer layers;
- incompatible with anionic reagents, *e.g.* anionic dyes, fatliquors, retans;
- high stability to acid, but unstable to alkali;

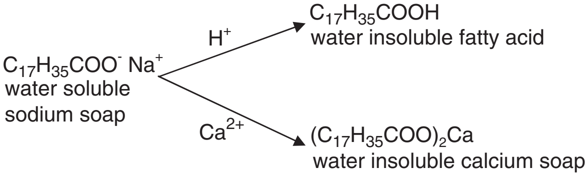


Figure 17.13 Soap reactions.

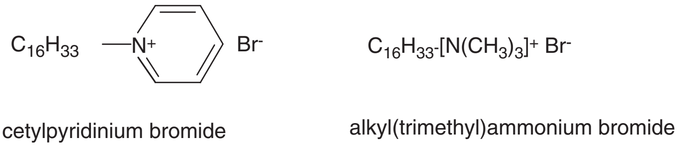


Figure 17.14 Examples of cationic emulsifying agents.

- good stability to metal ions and salts;
- may have poor shelf-life;
- emulsion stability can be improved by formulating with non-ionic detergents, *e.g.* alkyl ethylene oxide condensates;
- as a second fatliquor after anionic fatliquor (*cf.* 'sandwich dyeing').

It is well known in the detergent industry that a combination of anionic and cationic surfactants that creates a total carbon chain length of >24 will produce a water-insoluble precipitate. This can be easily observed by mixing any domestic anionic liquid detergent with any domestic cationic fabric softener:

- on chrome retanned leather to increase surface oil and aid paste drying;
- on vegetable tanned leather for bags or cases, to lubricate the grain layer and it make it more pliable;
- for oiling vegetable tanned leather;
- in combination with basic aluminium(III) chloride, for retanning chrome leather for suede; this will increase the cationic charge, which gives higher affinity for anionic dyestuff and produces a greasy nap;
- for woolskins in the mineral tanning bath;
- for white gloving leather, which might be made with a combination of aluminium(III) and sulfonyl chloride.

17.5 NONIONIC FATLIQUORS

17.5.1 Alkyl Ethylene Oxide Condensates

These fatliquors are emulsified with compounds made by condensing ethylene oxide in the presence of an aliphatic alcohol:

$$C_nH_{2n+1}\text{-}(OCH_2CH_2)_xOH$$

The properties of the emulsifying agent depend on the value of n, the aliphatic carbon chain length and the value of x, the degree of polymerisation of ethylene oxide. These compounds are not very good emulsifying agents because the hydrophilic end, the ethylene oxide chain, does not have a high affinity for water, relying only on hydrogen bonding *via* the ether oxygens.

The following points apply to these fatliquors:

- high stability to metal ions, salts, hard water and wide pH tolerance;
- miscible with cationic and anionic reagents;
- little or no affinity for anionic or cationic charged leathers;
- the non-ionic emulsifier increases the hydrophilicity of leather;
- used for fatliquoring zirconium(IV) or aluminium(III) tanned leathers, which are highly cationic charged;
- as a crusting fatliquor for suede splits, *i.e.* merely to prevent fibre resticking on drying, to aid rewetting;
- may be formulated with anionic or cationic fatliquors, to improve stability.

17.5.2 Protein Emulsifiers

Uncharged proteins, at their isoelectric point, can act as emulsifiers. Globulin proteins, *e.g.* albumin, produce a 'mayonnaise' type of fatliquor. These products are limited to a narrow pH range, close to the isoelectric point, otherwise they become significantly charged and function as anionic or cationic formulations.

17.6 MULTI-CHARGED FATLIQUORS

These fatliquors are formulations of non-ionic, anionic and cationic fatliquors, in which the presence of the non-ionic species prevents precipitation of the anionic and cationic species. They are more stable to a wider pH range than singly charged fatliquors and hence more stable to variations in leather charge. The proportions of the constituents can be varied, depending on the leather properties required, *i.e.* depth of penetration, surface lubrication and ease of removal from paste drying plates (where it would be an alternative to two-stage fatliquoring).

17.7 AMPHOTERIC FATLIQUORS

Raw oil is emulsified with an amphoteric reagent, *i.e.* one containing both acidic and basic groups, *e.g.* as shown in Figure 17.15.

The point of neutrality, the isoelectric point, depends on the numbers of acidic and basic groups, as discussed for proteins. A typical IEP for this type of structure is pH 5. At $\mathrm{pH} > 5$ the emulsifier is negatively charged, at $\mathrm{pH} < 5$ the emulsifier is positively charged. The choice of pH of the fatliquor depends on the charge of the leather and the requirement of surface reaction or penetration.

17.8 SOLVENT FATLIQUORS

These are typically anionic fatliquors, containing a high boiling point, polar petroleum solvent with minimum flash point 60 °C and preferably odourless.

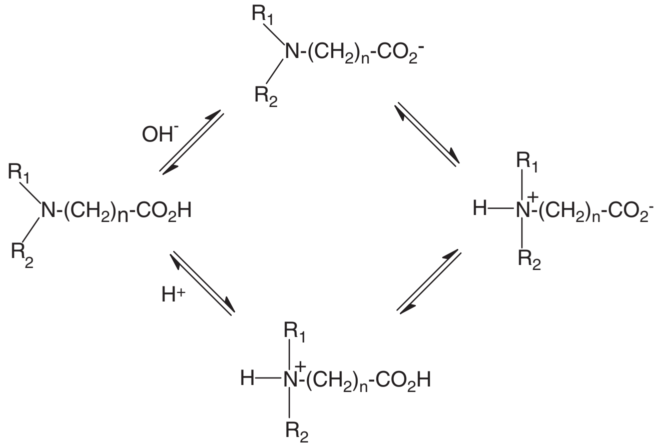


Figure 17.15 Amphoteric emulsifier.

The function of the solvent is to replace the water as it is removed during drying. With lesser affinity for the leather than the polar triglyceride oils, it can spread further and deeper. Therefore, these products are used for making soft leather. However, the current attitude to the use of solvents in leather making means that these products are used less now than in the past.

17.9 COMPLEXING FATLIQUORS/WATER RESISTANCE TREATMENTS

Water resistance is reviewed comprehensively below, discussing the chemistries of modern approaches. Before they were developed, a simpler approach to making leather hydrophobic was adopted, which was also part of the lubricating step in leather manufacture. There are two traditional forms of these reagents, designed to be applied to chrome tanned leather:

1. An old option was to use a long-chain fatty acid dimer, *e.g.* oleic acid dimer, applied as a soap at pH 8.[6,7] These were used as a method of introducing water resistance, when the carboxylic groups are complexed with bound chromium(III), leaving the hydrophobic moieties exposed over the fibre structure. More often than not, the technology did not work in industrial practice.
2. Another traditional option was to use a dibasic or tribasic acid esters, such as succinic, phthalic, citric or phosphoric acid, bound to an aliphatic chain with 15–24 carbon atoms (Figure 17.16). These too were unreliable reagents for making water resistant leather.

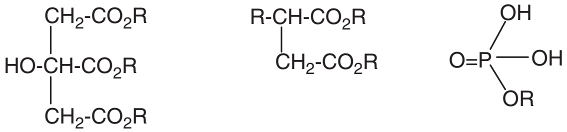


Figure 17.16 Complexing lubricants.

17.10 WATER RESISTANCE

17.10.1 Introduction

The general function of post tanning operations is to confer specific performance properties to the leather. One of the important features of that part of leather making is to make the leather water resistant. This is typically applied only to shoes and boots, with the possible inclusion of clothing leathers. Such processes are usually applied to chrome tanned leather, since other methods of tanning make the leather too hydrophilic to allow high levels of water resistance to be conferred.

It is common to refer to treatments for leather with hydrophobic reagents as waterproofing. This implies that water is completely excluded from the cross section of the leather, so that no transmission of moisture occurs. In practice, the traditional methods of achieving this were to fill the structure with grease, so-called ‘stuffing’, or to apply a water impermeable finish coating. In the first case, the treatment is not actually completely effective, since moisture can still find its way through the fibre structure. In the second case, the product is more like plastic than leather. The role of finishing in creating water resistance is recognised in the Official Methods of testing, where a requirement is to remove the finish by buffing prior to testing. It is important to recognise that leather is expected to ‘breathe’, *i.e.* its water vapour permeability must not be significantly reduced by some treatments. Therefore, some of the techniques used hitherto fail by this criterion. It is also useful to bear in mind that the success of the possible treatments is relative, ranging from small to large effect; hence the application of hydrophobing treatments is preferably referred to as conferring water resistance: the term waterproof is typically not used in a leather context.

In considering ways to confer water resistance, it is useful to consider how a leather can fail a water resistance test or fail in use. There are three mechanisms:

1. Water may flow through the fibre structure, because of the voids in the material.
2. Water may wet the surfaces of the fibre structure and flow across the solid surface.
3. Water may travel through the fibre structure, in the way wax flows through a wick in a candle: this mechanism is referred to as ‘wicking’.

The first mechanism is resisted by the barrier approaches. The second mechanism is resisted by making the fibres less wettable. The third mechanism is a special example of the second mechanism, since wicking depends on the inner elements of the fibre structure being unaffected by the water resistance treatment. Therefore, the second mechanism is addressed by a relatively unsophisticated hydrophobing treatment, which is required to penetrate through the cross section, but may not penetrate down the hierarchy of structure. The third mechanism can only be countered if the treatment penetrates down the hierarchy of structure: it is relatively easy to reach to the level of the fibril bundles, since that is achievable in well conducted fatliquoring, so this may confer a good degree of water resistance. Consequently, it may be assumed that the highest degree of water resistance is conferred by treating the fibre structure at the level of the fibrils. From fatliquoring science, it is known that penetration to this level requires the reagent to be solubilised or, at the limit, to be in the form of micro-emulsions.

The water resistance of a material like leather depends on the way in which water (or any other solvent) interacts with the surface. In the case of leather, this means not only the actual surfaces, but also the surface of the fibres within the fibre structure and lower down the hierarchy. This is illustrated in Figure 17.17.

The surface tension of the solvent and the surface determine the wetting of the surface by the solvent. Table 17.2 presents some values.

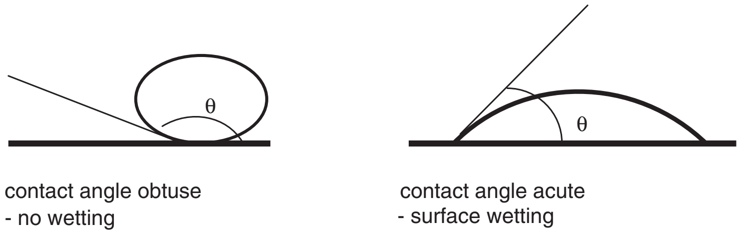


Figure 17.17 Interaction between a liquid and a surface: the contact angle (θ).

Table 17.2 Surface tension (γ) of some liquids and the critical surface tension (γ_c) of some solid surfaces.

Surface/liquid	*Chemistry*	*Surface tension, γ or γ_c ($mN\,m^{-1}$)*
Water	H_2O	74
Ethanol	CH_3CH_2OH	23
Acetone	CH_3COCH_3	24
n-Octane (liquid)	C_8H_{18}	22
Leather	Collagen	>70
Polyurethane	$[\text{-}CO_2(CH_2)_x\text{-}NH\text{-}CO_2\text{-}(CH_2)_y\text{-}O\text{-}]_n$	33
Silicone polymer	$[(CH_3)SiHO]_n$	24
Fluorinated polyacrylate	$[CH_2CH(CO_2C_nF_{2n+1})]_m$	11

The critical surface tension of a solid, γ_c, is equivalent to the surface tension of a liquid, γ, if the contact angle is zero. Liquids that have γ values greater than γ_c will not wet the surface, but if $\gamma < \gamma_c$ the surface will be wetted. The purpose of modern water resistance treatments is to change the critical surface tension of the available fibre surface sufficiently to prevent water wetting it. Note, the presence of neutral electrolyte in aqueous solution does not change the surface tension markedly.

17.10.2 Principles of Conferring Water Resistance

The ability of a material such as leather to resist the absorption and transmission of water can be expressed in terms of weak resistance and strong resistance. Weak resistance can be regarded in clothing terms as 'shower resistance': this means a garment does not immediately absorb rain water, but prolonged exposure will result in both rapid absorption of water and its transmission through the cross section. This applies to both clothing and shoes: in the case of the latter, almost any wet circumstances will result in wet feet. Shower resistance may be enough to prevent water spotting of double face or suede clothing leathers: this is the effect of wetting causing the surface fibres to stick, giving rise to a visible non-uniformity, typically in the form of spots from the raindrops. Strong resistance means that there is a significant delay between exposure to water and its transmission across the cross section: the accompanying amount of water absorption reflects the movement of water within the material, although the relationship between wetting and transmission depends on the nature of the material, including methods of leather processing. Whilst the resistance of leather to wetting can be high, notably it cannot strictly be called 'waterproof', because that term must be reserved for materials that constitute a continuous and complete barrier to water, *e.g.* a plastic sheet. The importance of water resistance was demonstrated when the American Leather Chemists Association (ALCA) held a symposium in 1995, when it was the only topic.[8,9]

The water resistance specifications for defence leathers vary from country to country, but in no case might the requirement be regarded as 'high performance': *e.g.* in the UK, resistance to water penetration in the Bally Penetrometer test (IUP 10[10]) (Figure 17.18) is required to be only 3 hours.[11] For the modern soldier in the field, in a war theatre for periods of 24 hours or more, such performance is unsatisfactory. However, it is possible to raise the water resistance to over 120 hours on the Bally Penetrometer or $>500\,000$ flexes on the more stringent, but similar Maeser tester. It is likely that lack of failure after a week on these tests means that the leather is unlikely to fail the test at all, although the fibre structure may fail. See below for technologies to exceed that specification.

There are many types of treatment traditionally offered to the leather industry and some more modern (see below). However, it has been a feature of water resistance treatments that there are two shortcomings, which for many

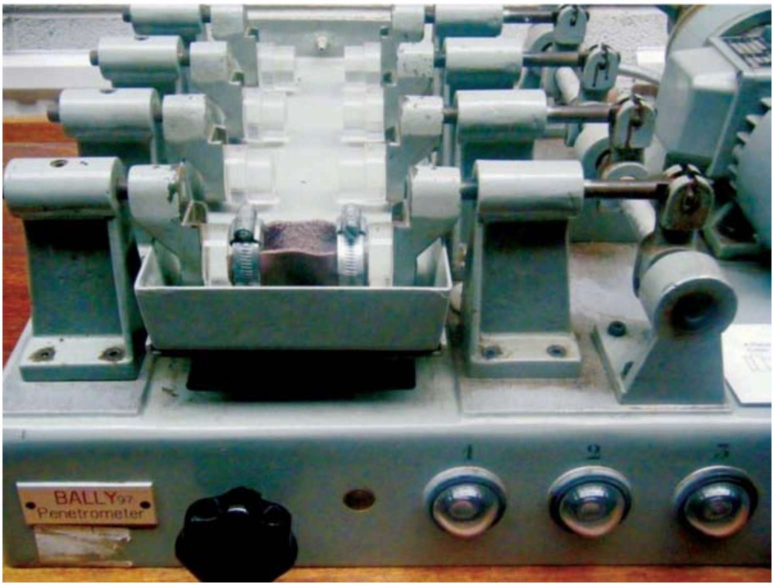


Figure 17.18 Bally Penetrometer for measuring water resistance: bent leather is flexed in a bath of water until penetration through the cross section occurs.

years resulted in the technologies being kept a closely guarded secret in each tannery making such leather:

- The effects were often moderate, conferring relatively poor water resistance.
- The effects were often inconsistent, sometimes working, sometimes not.

In the modern leather industry, such inconsistency and poor performance are easily overcome, if the tanner is aware of the factors that contribute to the outcome of modern treatments. Very high degrees of water resistance can be achieved by careful control of appropriate chemical treatments, even those not known for conferring high performance do have the potential to work better than might be expected. The chemistries are specifically designed to retain the ability of the leather to allow transmission of water vapour, the ‘breathability’ property. Although the treatments are technically feasible and relatively simple, the outcome of the treatments depends on many factors that can either prevent the developing of water resistance or contribute to its creation.

Some workers have addressed the factors that influence water resistance:[12] for any chemical treatment, the factors that influence the developing of water resistance can be listed and rationalised as follows.

17.10.2.1 Opening Up. The opening up is critical, to allow the reagent to penetrate deeply down the hierarchy of structure. Here, the important effect is to split the fibre structure finely, separating the fibres at the fibril bundle level, to allow the penetration of reagents. In the case of reagents that must be presented in the form of an emulsion, the particle size requirement may mean taking particular steps to solubilise materials that would ordinarily be applied as an emulsion, thereby contributing to the performance of the reagent. This may be accomplished simply, depending on the chemistry of the reagent, *e.g.* adjusting the pH to a higher value than specified or as supplied. Alternatively, if the hydrophobic agent can only be solubilised by means of detergents, this is clearly counter-productive (see below).

The degree of opening up is important, because unsplit fibres can act as a wick, to transport water through the leather cross section. The more finely split the fibres are, the less easily it can be wetted and the wicking mechanism is reduced. Clearly, if the reagent penetrates to the level of the fibril surfaces, this is the best treatment that may be achieved.

17.10.2.2 Looseness. If opening up goes too far or too much mechanical action is applied, particularly in the alkaline swollen condition, the corium structure will become loosened. The open structure will facilitate water transmission, because it can occur without wetting the fibres. Similarly, it is more difficult to confer high water resistance to leathers with a naturally open structure, *e.g.* sheepskin.

17.10.2.3 Substrate. The primary tanning chemistry can influence the ability of the leather to achieve high water resistance: in essence, there are two practical possibilities in this regard:

1. Chrome tannage: The hydrophilicity/hydrophobicity of chrome tanned leather can be controlled by the way in which the tannage is conducted. In this case the parameters can be set to obtain the maximum hydrophobic nature, *i.e.* slowest rate of change of pH and temperature, within the constraints of the processing time.
2. Hydrophilic tannage: The use of vegetable tannins (plant polyphenols), resins or syntans, either for low stability tannage or in combination for high hydrothermal stability tannage, depends on the formation of hydrogen bonds between the tanning agent and the collagen. This reaction necessarily produces hydrophilic leather – in the case of vegetable tannins, hydrolysable tannins are worse than condensed tannins in this regard. These tannages make it more difficult to make water resistant leather: this is mostly due to the hydrophilicity, but also relates to the lack of metal species in the leather, which is essential for some powerful water resistance treatments.

17.10.2.4 Reagent Chemistry. There are many strategies for incorporating hydrophobic groups into the leather structure (see below). These range from the so-called hydrophobic fatliquors through to specific agents. Modern high-performance agents are based on partial esters of acrylate polymers: these can react covalently with bound chromium(III) in chrome tanned leather. If there is no metal 'mordant' for this function, other reagents may have to be used, *e.g.* metal complexes of fluorochemicals or siloxane derivatives.

17.10.2.5 Reagent Offer. The degree of water resistance conferred typically correlates with the amount of the reagent used, although there is an effective upper limit to the amount that is necessary to achieve high performance. This can be understood in terms of the extent of the treatment over the available fibre structure surface. If the whole surface is inadequately treated, there is a mechanism for water to pass through the wetted regions.

17.10.2.6 Neutralisation. Most modern high-performance, water resistance reagents are anionic compounds and hence rely for their effect on penetration into the fibre structure, which in turn depends on the degree of neutralisation of the leather. There are three components to this step that must be considered:

1. The isoelectric point of the leather determines the nature and magnitude of the charge on the leather at any point on the pH scale. In the case of acrylate reagents with $pK_a \sim 4$, the leather must be neutral or anionic at pH 6. Any processing that raises the IEP significantly above pH 6 would be counter-productive in this regard: this therefore rules out tannages that target the basic amino sidechains.
2. The pH must be high enough to ensure that there is minimum interaction between the anionic reagent and the leather, *i.e.* cationic centres: these include both protonated basic groups and residual cationic character in the bound metal ions. In the case of applying a cationic agent, such as a fluorocarbon complex of chromium(III), the pH must lie below the isoelectric point.
3. The process must be prolonged, to allow neutralisation to take place down the hierarchy of fibre structure. The conventional neutralising period is relatively short, because for most post tanning processes neutralisation is less critical in this regard.

17.10.2.7 Temperature. The temperature at which the reagent is prepared can be important, whether the condition refers to emulsification or solubilisation. When making emulsions, it is critical that the solvent and the product should be heated, to reduce the viscosity of the hydrophobic compound, so it can break up into as small particles as the chemistry allows. It is not possible to define an optimum temperature for this operation. This is because high temperature is an effective way of destabilising emulsions, so there is a practical upper limit to the temperature used, usually 60–70 °C. Destabilisation occurs when the temperature is high enough to make the particles collide with sufficient energy to overcome the charge repulsion and hence they coalesce. Also, elevated temperature can help the reagent to penetrate and, depending on its chemistry, to fix.

17.10.2.8 Neutral Electrolyte. The wettability of a leather is the starting point for water resistance: the easier it is to wet the fibres, the easier it is for water to be transmitted through the leather. The presence of neutral electrolyte makes the fibres easier to wet, because ions attract water into their solvation shell, providing nuclei for additional water fixation: the more water soluble the salt is, the worse the effect on water resistance. Therefore, it is important to minimise the amount of salts in the leather, first by ensuring there is minimum neutral salt in all post tanning processing and then by washing prior to applying the water resistance treatment and washing afterwards, before drying the leather.

17.10.2.9 Surfactants. It is common to include surfactants of various types in leather making processes, particularly in the earlier steps of beamhouse processing. Since their function is to facilitate wetting, their presence in leather is incompatible with water resistance. Cationic detergents are unusual and typically not used in the leather industry. Anionic detergents are the most common industrial and domestic agents, because they are the most effective wetting and cleaning agents. It is particularly important to exclude these agents from processing if water resistant leather is the required product. Sulfates and sulfonates have high affinity for leather and they can remain within the structure long after they have been applied. If a wetting agent is needed in the beamhouse, non-ionic surfactants should be used. Although they are less effective at wetting and cleaning, they have little affinity for collagen and therefore do not persist in the leather.

17.10.2.10 Post Tanning. It is usual to apply a water resistance treatment at the end of the post tanning sequence of operations, because of the likely interference it would have on other processes if the fibre structure becomes hydrophobic. So it is important to recognise the influence of the other post tanning reagents on the final performance of the leather as a water resistant material:

- Retanning: just as the primary tanning chemistry can influence water resistance, the retanning can control it. If a hydrophilic retanning agent is used, it will confer wettability to the leather. A less hydrophilic retannage, such as chromium(III) is more compatible with water resistance and this may be further controlled by appropriate masking.
- Dyeing: the choice of dyes can influence the wettability of leather, because their chemistries can vary, even within a group of the same or similar colour. Indeed, the concept of hydrophilic/hydrophobic balance (HHB) as

a quantifiable parameter is already established for dyestuffs and used to control the degree of surface reaction or penetration. The presence of hydrophilic dyes in the leather will act as a wetting agent, allowing water to be transmitted through the leather.

- Fatliquoring: the extent of reliance upon lubricants other than the water resistance agent depends on the nature of the water resistance agent, since some can operate effectively as the lubricant. For others it is necessary to include some conventional fatliquoring agents. Fatliquor formulations typically contain partially sulfated or sulfited (sulfonated) oil, as the emulsifying agent for the neutral oil. Therefore, they act like surfactants, possessing hydrophilic and hydrophobic functionality; consequently, they also have the ability to wet surfaces. So, despite the oily nature of the fatliquor, it can have the same effect as an anionic detergent treatment.

  The choice of fatliquor should be confined to the so-called 'water resistant fatliquors': they typically have a weak effect on water resistance, but will offer the least adverse effect on a more powerful water resistance treatment.

17.10.2.11 Capping. The acrylic based water resistance treatments include a final step called 'capping', in which the residual anionic character of the leather is neutralised by applying a cationic agent. If this step is omitted, the water resistance treatment will merely confer a weak effect, *e.g.* resistance to water penetration for a few minutes or an hour on the Bally Penetrometer. Effective capping can extend the period of resistance to many hours. It is possible to use various cationic agents. Those that merely interact electrostatically, such as quaternary ammonium compounds, are not very effective. Similarly, metals that react electrostatically with the carboxyl groups of the acrylic polymer, *e.g.* Al(III), Ti(IV) and Zr(IV), are not optimally effective. The preferred reagent is chromium(III), which forms covalent complexes: this has less charge separation in the bonding and, thereby, does not exhibit the equivalent effect of the presence of neutral electrolyte.

17.10.2.12 Solvent. Water resistance agents may be formulated with non-aqueous solvent, such as cellusolve, as part of the manufacturing process or as an aid to emulsification. Its presence in leather can also facilitate wetting, since such solvents are water miscible, and the consequence may be observed as time dependent water resistance following crusting. That is, if the leather is tested immediately after crusting and conditioning, it may exhibit poor water resistance because the solvent remains in the leather. However, if the leather is stored for several days, *e.g.* in the conditioning room, further testing would show an improvement in water resistance, because the storage period allows residual solvent to evaporate.

17.10.3 Chemistries of Water Resistance Treatments

In the time when leather was made predominantly from vegetable tanning, it was difficult to confer a high degree of water resistance. However, filling the fibre structure of the leather with hydrophobic, greasy material was the only traditional option in this regard. For example, Tim Severin's successful experiment to reproduce the transatlantic voyage of St Brendan from Ireland to America in a leather boat was achieved by constructing the boat from oak tanned hides, stuffed for water resistance with wool grease.[13] However, clearly, this approach to creating water resistance from a hydrophilic substrate offers limited wider applications.

17.10.4 Chrome Tanned Leather

Chrome leather is naturally relatively hydrophobic, at least in comparison with untanned collagen. Hence, it provides a good start for making water resistant leather.

Compared to the simplistic barrier approaches to water resistance of the past, what is needed in the modern industry is chemical treatments that do not adversely affect the handle and 'breathability' properties of the leather. Figures 17.19 and 17.20 briefly present some such treatments, where is can be seen that they tend to rely on the presence of bound chromium(III) species, acting as a type of mordant for the hydrophobic agent.

The silicone reaction is readily understood: the chain of Si–O moieties provides many oxygen atoms that can interact electrostatically with collagen or

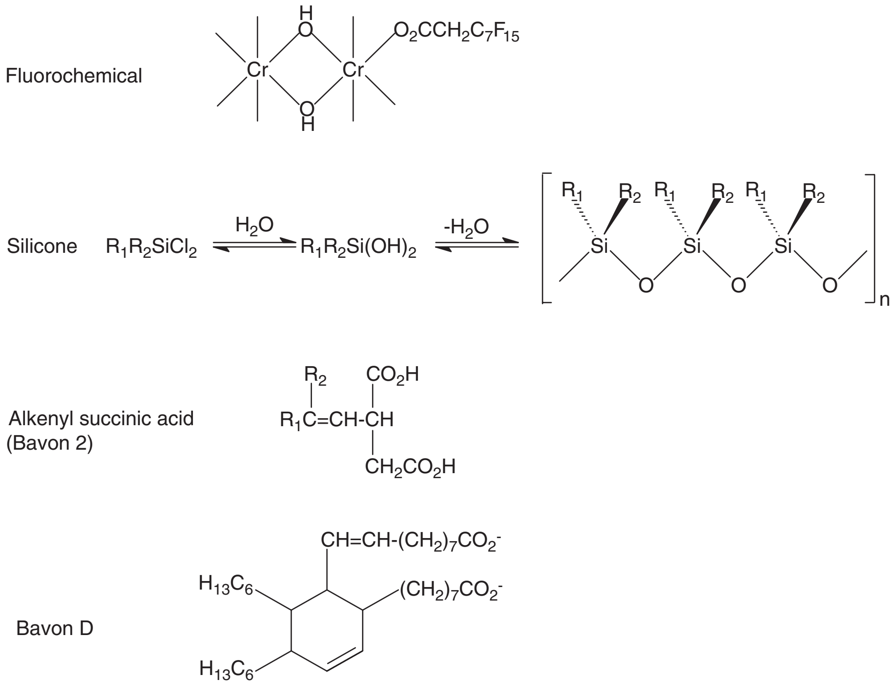


Figure 17.19 Chemistries of some water resistance treatments.

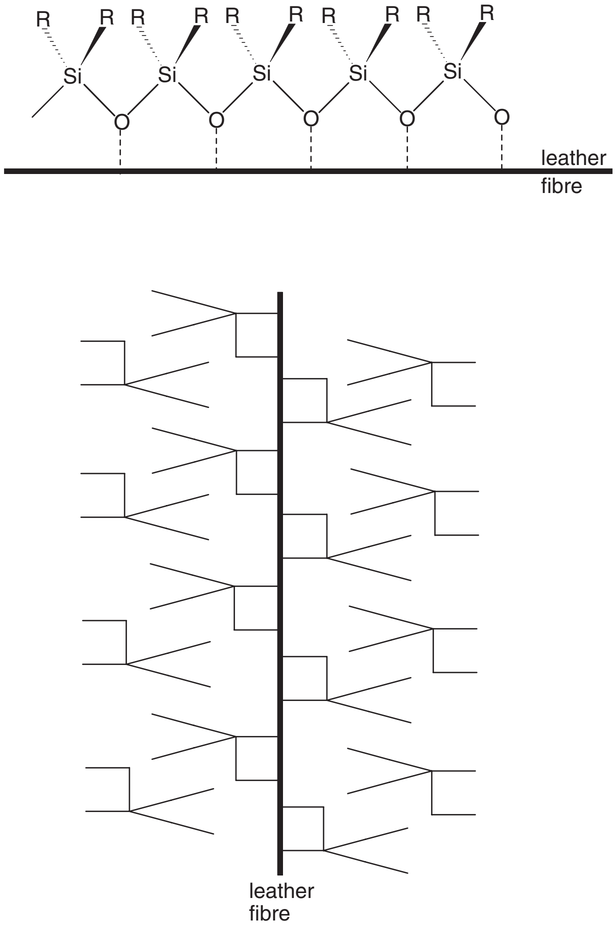


Figure 17.20 Modes of action of silicone and the Bavon processes.

leather. In this way, the fibre structure becomes coated with a surface of water repellent alkyl groups. This is an effective type of treatment, although it is more commonly used in conjunction with other chemistries, which facilitate the delivery of the silicone.

The Bavon process was used commercially for some time, but is the archetypal inconsistent process. The principle lies in a stepwise mechanism:

1. Reaction between the alkyl succinyl dicarboxylate and bound chromium(III);
2. Creation of a second layer of the reagent, when the alkyl groups interact in a hydrophobic bonding arrangement;
3. When the dry leather is wetted, a water-in-oil emulsion structure is formed at the carboxylate surface, preventing the passage of water through to the fibre surface.

Table 17.3 Glass transition temperatures (T_g) of some polymers.

Polymer	*T_g (°C)*
Polydimethylsiloxane	−127
Polyethylene	−125
Polythiofluoromethylene	−118
Polytetrafluoroethylene	−113
Polyisobutylene	−73

At least, that is the theory! Sometimes it worked, but success could never be guaranteed. Hence, for many years, tanners closely guarded the details of processing for water resistant leather.

The current industry standard for making water resistant leather from chrome tanned stock is partially esterified acrylic polymers, exemplified by the Lubritan series of agents from Rohm and Haas Co. The process is simple, if the conditions set out above are adhered to. Here the mechanism involves complexing available carboxyl group in the polymer with bound chromium(III), therefore presenting the surface of the fibre structure as covered with alkyl groups. These groups also act as spacers within the fibre structure, functioning like a lubricant. In this way, processing is made more compact (see below).

The role of silicones in this context is interesting, because there is added versatility due to the potential for introducing additional functionality into the molecule, such as amine, amide, carboxyl and epoxide groups, which can enhance the use of these reagents in retanning.[14] The reactivity of silicones is assisted by the unusually flexible nature of the molecule: the rotational energy for the Si–O bond is close to zero, compared to 14 and 20 kJ mol^{-1} for polyethylene and polytetrafluoroethylene, respectively. In addition, polydimethylsiloxane exhibits the lowest known glass transition temperature (Table 17.3), making it the most flexible polymer known.

17.10.5 Non-chrome Tanned Leather

The alternative substrate for water resistance is leather tanned with reagents other than chromium(III): this means all those organic tannages, such as aldehyde, syntan and vegetable. These tannages have the common feature of making the leather highly hydrophilic. This makes the task of introducing water resistance much more difficult than for chrome leather. The options available are:

- Silicones, which can bind to the hydrophilic groups, but are not very effective as solo agents.
- Fluorocarboxylate complexes of chromium(III). The 3M company offers such a product. However, if the purpose of the tannage is to make mineral-free, specifically chrome-free, leather this is counter-productive.

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