

Waterproofing innovation

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Introduction

The terms water repellency, water resistance and waterproof often have divergent meanings to different people in our leather industry so it is always a good idea to start with a definition of each “water repellency – the ability of a leather surface to resist wetting. Water resistance – the ability of a leather to resist absorption and transmission of water. Waterproof – leather will not transmit water through its cross-section under any circumstances”⁽¹⁾. Perfect waterproof leather could only truly be achievable if it was coated with a metal foil, but, however, this would render it impervious to water vapour and undesirable for the wearer of the usual final leather articles.

Generally speaking, the four major requirements for a waterproof leather are: (i) resistance to water penetration (ii) permanent effect, maintained throughout the serviceable life of the final article, (iii) leather meets the requirements of the end article (e.g., fashion) and (iv) wearer comfort factors such as water vapour permeability (WVP).

More specifically, with reference to technical specifications, waterproof is now a term commonly used in our industry for a leather that has high dynamic test performance (e.g., $\geq 100,000$ Maeser flexes and/or > 8 hours Bally @15% compression), low static water absorption (e.g., $< 30\%$ and zero millimetre wicking) with high water vapour permeability critical for wearer comfort. Nowadays the general population are being increasingly made aware of the health benefits of physical activity and especially outdoor exercise. Most of us can take part in activities such as hiking,

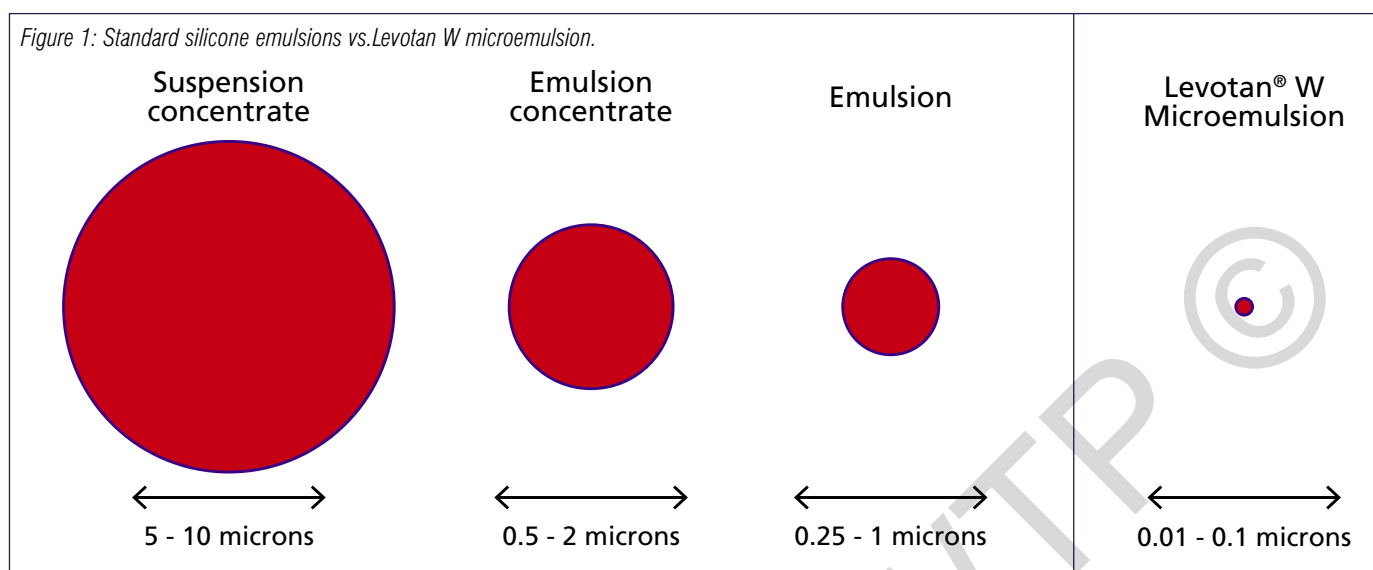
trekking or just simply walking and thus we have experienced the importance and value of “breathable” leather. However, without a proper leather waterproofing, just the presence of dew on grass is enough to prematurely end our exercise with uncomfortably wet feet. The advantages for example military applications are obvious and was a major factor in the establishment of committees to investigate poor waterproofing⁽²⁾.

The approaches

Stuffing the leather with various fats and oils was the earliest form of protecting leather from static water exposure, but on flexing these demonstrate poor resistance as they do not fix and they also reduce water vapour permeability. It is commonly known that more recently work was initiated with metal complexes (with stearic acid or fluorinated coordinating groups), then elastomeric and resinous systems, followed by silicones. Later came adducts of succinic acid, for example, alkenyl succinic anhydrides. However, any system that involves the blocking of the leather matrix to prevent transmission of water as originally with fats and oils, the so called “closed” system, adversely affects water vapour permeability and thus is not viable. “Open” breathable systems are a necessity so those which function by giving the leather fibres and fibrils themselves a hydrophobic character, where the contact angle between coated fibre and fibrils and water is high, is imperative. This “open” system provides high water vapour permeability and absorption and better insulation.



Figure 1: Standard silicone emulsions vs. Levotan W microemulsion.



The challenge

Anyone who has tried rewetting pure full chrome tanned leather that has completely dried out realises that it should make an ideal base for waterproof leather. However, the challenge is to achieve the required leather article where we commonly have to apply numerous hydrophilic retanning, fatliquoring and dyeing products and yet maintain the inherent waterproof character.

Fluctuating test results often lead to tanners offering higher quantities of waterproofing chemicals than necessary to give a “margin of safety” above demanding specifications. Commonly, products used to produce water resistant leather have traditionally been based on fatliquors. Offering higher amounts of certain categories of these can lead to other problems like increasing leather weight, excessive softening, stronger smell and it can become more difficult to attain level dyeing. This increase in softness needs to be compensated, for example, by adding more retanning agents, which in turn can increase hydrophilic character, which then needs to be compensated for by adding more waterproofing agents, and so on. This makes it more challenging to attain the article required and ultimately this can adversely affect process robustness.

To make a leather waterproof non-water soluble products have to uniformly penetrate and distribute throughout the cross-section. Once in place this increases the interfacial tension between the leather fibres and fibrils and water thereby increasing the water resistance of the leather. One of the biggest hurdles is applying such products in a drum with water as the carrier. An “oil-in water” emulsion is the most common way today to transport such hydrophobic products into leather but these use hydrophilic emulsifiers which are, in this type of article, clearly counterproductive.

The innovation

The new patent filed polymer waterproofing product Levotan WRP is self-emulsifying and so no external emulsifier is needed nor any hydrophilic sulfonic acid groups. This together with the patented state-of-the-art functionalised silicone-containing microemulsion Levotan W (Figure 1) with its high penetration properties means that the leather industry now has a new, simple, synergistic system

available with a unique high performance profile. Both of these new innovative products are fatliquor-free and so in addition help meet the increasing demand for light weight, low density leather. We have demonstrated that increasing the offer of the polymer to attain higher values does not significantly soften the leather and dyeing levelness is not adversely affected.

Common waterproofing issues

We are regularly approached by tanners to help solve incredibly diverse technical problems, but, we often find they are interrelated. For example, inadequate penetration and/or fixation of chemicals, related to processing factors, is a common theme which can then be traced to certain root causes. It can be relatively easy to attain superficial water resistance but unless the entire cross-section is treated to the same degree then water will quickly penetrate.

Many tanners produce waterproof leather from wet blue where their influence on the prior processing of it is rather limited, but the quality can have a profound effect on waterproof performance. Adequately and freshly tanned wet blue is preferable and the tannage must be well distributed on the surface and stratigraphically, and well fixed. If not, the waterproofing chemicals are less likely to fix and so if the chrome content is not adequate and/or the wet blue is old re-chroming is highly recommended using a self-basifying, high fixation product^(a). Loose or unbound chrome in the float could cause premature activation of the waterproofing. This type of rechroming also minimises reactivity differences between wet blues from different tanning lots where chrome content might vary.

For those with at least some influence over the beamhouse, hyaluronic acid that fills the inter-fibrillary spaces and prevents the penetration of water and chemicals should be adequately removed. Furthermore, fibre splitting or “opening up” at fibril level is vital to ensure the penetration of all chemicals, including the waterproofing ones. A patented glucosidase, a carbohydrate splitting enzyme^{(b)(3)}, ensures removal of this acid, speeds up rehydration and starts opening up already in the soaking. Added benefits of this enzyme include reduced need for lime, residues of which are another common cause of subsequent chemical



penetration problems, with increasingly commoditised wet blue. (If working from wet blue, the best option to remove residual lime is to apply a dispersing agent based upon selected multiple organic acids^(c)). Traditional soaking inevitably leads to hydrolysis and some loss of collagen. This non-proteolytic enzyme ensures maximum leather fibres, fibrils and ultimately reactive groups are available for the fixation of waterproof chemicals. Furthermore, defects, damage, hair follicles and veins, which are all conduits for water, often blamed for premature dynamic testing failures, are not enlarged. The same argument applies to the application of a broad spectrum preserving agent^{(d)(4)} because any microbial activity during leather processing or storage will make these defects worse and thus adversely affect waterproofing performance.

We have also diagnosed penetration problems related to inadequate removal of the basement membrane, the lower part of the epidermis, which is a highly effective chemical barrier in life. A high selectivity enzyme which primarily targets the basement membrane by degrading the pre-kерatin^{(e)(5)} ensures efficient removal of the whole of the epidermis. It also loosens the hair root and with no chemical degradation of the hair itself it is, therefore, less brittle which together with the reduced alkaline swelling means they are more easily removed giving cleaner pelts for higher quality low finished or nubuck waterproof leather. This reduced swelling has the added bonus of less draw and has an “anti-wrinkle” effect on growth marks, both commonly highlighted problems in traditional waterproof leathers.

Wet blue contains varying amounts of residual natural fats. Higher amounts act as a barrier to penetration of chemicals, and lower amounts can still reduce penetration rates directly affecting waterproofing performance. Usually natural fats are irregularly distributed and thus can contribute to variation in waterproofing test results. Obviously the use of hydrophilic surfactants should be ideally avoided as any residues of these can destroy the waterproofing. A quality synthetically produced lipase enzyme^(f), that specifically targets and hydrolyses natural fat can partially or completely replace surfactants. This enzyme forms free fatty acids, monoglycerides and diglycerides converting the fat into an emulsifying system which is easier to disperse and/or remove, leading to better penetration and distribution of retanning chemicals and dyes together with excellent biodegradability.

Neutralisation is a particularly crucial step in waterproof leather production as inadequate neutralisation will directly reduce penetration of all subsequently added usual chemicals and waterproofing agents. A product that only adjusts the pH of the leather is not recommended. It is important to not only neutralise free and collagen bound acids but also adjust the isoelectric point (IEP) reducing the cationic charge^(g). This allows retanning at lower pH resulting in tighter waterproof leather. Such a product also reduces the need for alkaline salts, which are detrimental to waterproofing treatments generally.

Choice of dyestuff can directly affect the wettability of leather and levelness of dyeing which is important not only for the appearance crust but to have uniform test values across the hide or skin. It is important to understand relative affinity, shade coherence, molecular weight, hydrophobic hydrophilic balance (HHB) type, positioning and number of auxochromes/sulphonation, alkyl group substituents,



Figure 2: Clear microemulsion with Levotan W.

metallisation and homogeneity of the dyes selected to achieve maximum compatibility and uniform test results. In the case of HHB, for example, selecting highly hydrophobic dyes would seem logical for application on waterproof leather, but the low solubility leads to high aggregation which results in irregular dyeing. At the other end of the spectrum highly hydrophilic dyes with high solubility and low aggregation can also lead to irregular dyeing due to their susceptibility to pre-drying migration⁽⁶⁾. Therefore all factors have to be taken into consideration and not one in isolation for optimum waterproofing performance and a specific range of dyes has been selected for this^(h).

Vegetable tannins should be minimised and only applied if the article necessitates their use, the more sulfited the more hydrophilic they are. Selected poly-condensed sulfone (PCS) syntans⁽ⁱ⁾ have the added advantages of, for example, superior tanning ability so that on repeated exposure to water they remain fixed in the leather, whereas vegetable tannins with their weaker bonding continually leach out of the leather and can carry along with it other products. The first synthetic tanning agents to replace vegetable tannins, the so called “replacement tannins”, were the simple phenolic syntans. However, not only tanning ability but also fastness and filling effect of PCS syntans are also superior to these phenolic syntans. Residual monomers, for example, formaldehyde, is a topic of increasing concern and again it is the PCS syntans that have an advantage in this respect. Draw and emphasised growth marks can be a problem with waterproof leather. As vegetable tannins are relatively astringent, their replacement with PCS syntans will lead to reduced draw and accentuation of defects like growth marks all value adding to quality lightly finished or nubuck waterproof leather.

Salts tend to build up during leather processing, including in retanning. These can come from, for example, unavoidable by-products of synthesis of traditional retanning agents, or are present as standardising agents in dyestuffs. Salts directly increase hydrophilicity and are detrimental to waterproofing treatments. Excess salts also reduce reactivity, exhaustion and levelness of dyes and can form salt spews. The usual countermeasure is adequate washing with water, taking care with its quality. Tanneries using water directly from surface or underground sources have reported problems and fluctuations in waterproofing performance which can be linked to seasonal variations in waterborne

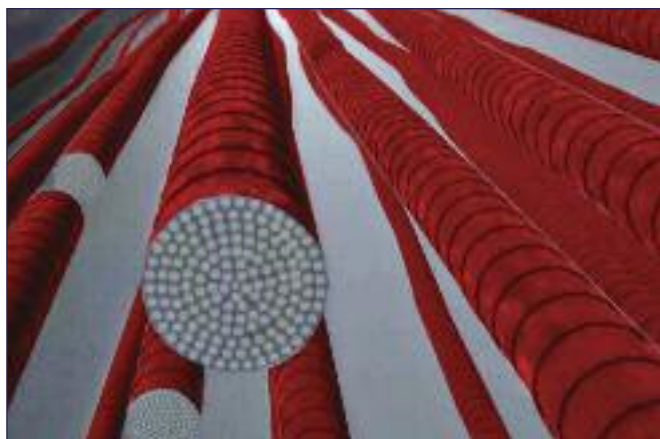


Figure 3: Leather at fibrillary level.

contaminants. Introducing into the recipe new generation retanning products^{(1)(7 & 8)}, which can be considered salt-free, reduce not only water consumption and thus effluent volume but also the contribution to total dissolved solids and chemical oxygen demand (COD).

For softy waterproof leather articles, hydrophilic products based fats and oils should be avoided. Selected self-emulsifying polymer softening products^{(k)(9)}, free of hydrophilic sulfonic acid groups and that possess some inherent hydrophobicity, can be used to soften leather further without disturbing the waterproofing treatment. Such polymers have high fixation, low migration and are thus ideal for leather that will have repeated exposure to water. As an added bonus such polymers being fat-free are lightweight, low bleaching, neutral or no smell and cannot form fat stains nor fatty acid spews.

Penetration/Fixation – the products themselves

In certain articles retanning penetration may be deliberately restricted and this makes it more challenging to penetrate and distribute evenly other subsequently added products including waterproofing agents. Typical particle size for suspensions and emulsions range from ca. 10-1 microns but a microemulsion can be as low as ca. 0.01 microns which means it can readily penetrate to fibrillary level and thus coat and protect individual fibrils (Figures 2 & 3). At the other extreme, some articles are heavily retanned throughout the entire cross-section. This not only dramatically reduces the available bonding sites for waterproofing chemicals but since virtually all traditional retanning agents are hydrophilic this can also be challenging to overcome. Here, for the waterproofing treatment, penetration is not the issue, but fixation is. The multi-component patented functionalised silicone-containing microemulsion (Levotan W) is designed to fix on different sites.

Varying degrees of premature precipitation of the waterproofing products themselves is another common cause of reduced penetration and fixation. Traditional products tend to have a relatively narrow application pH band but this inherent sensitivity and instability increases this risk of premature precipitation resulting in irregular dyeing and fatty stains. The polymer Levotan WRP and the microemulsion Levotan W together in a system has demonstrated greater stability than traditional systems to

lower pH, giving more than adequate time for full penetration and distribution and thus optimum results.

Metal salts are commonly used to fix waterproofing products, the so called “capping”. Water hardness, another type of electrolyte, can also contribute to the premature precipitation of waterproofing products. Auxiliaries have been offered to increase the stability of these products to water hardness and other electrolytes but this represents an additional expense and complication. A polymer and microemulsion in system has demonstrated together greater stability than traditional systems and thus eliminates the need for further auxiliaries.

Summary

Lanxess introduces an innovative patent filed self-emulsifying waterproofing polymer (Levotan WRP) which together with a functionalised silicone-containing microemulsion (Levotan W) forms a system which is used to produce top performing waterproof leather to keep you at the forefront of the market with demonstrable and sustainable advantages.

Whether working from raw or wet blue state-of-the-art beamhouse and/or patented retanning technologies supports the production of the optimum base material to give clear advantages for leather destined for waterproof production.

Comprehensive coverage of the challenges of each processing stage are addressed including general issues of penetration and fixation along with specifics such as natural fats, re-chroming, retanning and dyeing. ☺

- (a) Blancorol® RC.
- (b) Peltec® X-Zyme S*
- (c) Blancorol® CGA
- (d) Preventol® U-Tec G
- (e) Peltec® X-Zyme U*
- (f) Peltec® AL*
- (g) Tanigan® PAK
- (h) Baygenal® Range
- (i) e.g., Tanigan® FT
- (j) Levotan® X-Biomer range
- (k) Levotan® L / LB

*Novozymes A/S Denmark

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