Waterproof leather - requirements and technology

Dr. Wolfgang Herrmann
Münzing Chemie GmbH
Salzstrasse 174
D-74076 Heilbronn
Phone: +49/7131987-270
Fax: +49/7131987-125
e-Mail:
w.herrmann@munzing-chemie.com
Our homepage:
www.munzing-chemie.com

Introduction

The demand for waterproof leather might be lower than the demand for several other leather articles in terms of square feet. However, waterproof leathers are commercially of high interest because waterproof leathers are sold at a relative high price. This high price is justified because the tanning industry requires specialty products for making waterproof leather. In addition, special know-how is needed in production of waterproof leather. Very often producers of waterproof leathers and technicians get into this dilemma: chemicals and process steps to make the desired article object to the waterproof target, and waterproof agents and the methods of application prevent the production of the requested article.

When you look at old military boots in a historical museum and compare them with modern trekking shoes, you won't find many features in common. The differences are even more striking when you put the military boot on your right foot and the trekking boot on the left one and walk a few kilometres. The right foot and shoe will soon be soaked with sweat. This experience will be intensified if you walk through the water of a creek or pond. The military boot on your right foot will become wet and heavy. It will lose completely the ability to breathe. After a certain time your right leg will tire because of the heaviness of this old military boot. Probably your right foot will feel cold. This won't happen to your left foot on which you are wearing the trekking boot. After this experiment you will surely be happy to take off your right boot. For obvious reasons we stop this experiment now and we don't visualize further what will happen when you take off your right shoe. Your left foot will stay fresh during the whole experiment.

The obvious conclusion from this experiment follows: the real target of processing waterproof leather is producing leather which results in shoes or e. g. motorbike garment with high wearing comfort even under wet and cold conditions. Leather shall act as a second breathing skin. Obviously, waterproof leather stands literally for leather which water doesn't penetrate, however, the leather shall allow additionally high water vapour permeability and some reversible water up-take. The leather shall insulate against heat and cold and be lightweight.

Usage requirements	**Testing requirements**
No water penetration;	Water droplet test (IUP/420);
Controllable water up-take;	Kubelka water up-take (IUP/7);
High water vapour permeability;	Soaking-up test (Wicking-test);
Heat and cold insulation;	Bally penetrometer (IUP/10);
Lightweight;	Maeser (ASTM D 2099);
Wearing comfort;	Water vapour permeability (ISO 14268)
Second breathing skin	

Testing of the performance

The common testing procedure for waterproofness – the static tests life time of a water droplet, Kubelka water up-take and soaking up test as requested by Gore as well as the dynamic tests bally penetrometer and maeser value – are no end in itself, however, they have to be seen in combination with the use of this leather. For example, a high maeser value will be requested for an out-door walking shoe because the mechanical action during measurement simulates the mechanical action during walking in water. The situation turns out to be completely different for out-door shoes which bear a polymeric membrane. For it, excellent water vapour permeability is requested. Furthermore, the leather shall not soak up water neither from the grain side, nor from the flesh side, nor from the cut. But then, a static test will be enough. Likewise, the static water droplet test is sufficient for aniline upholstery leather, which is requested to be resistant against spilled liquids.

Mechanism of waterproofing

If we understand how the wetting of leather takes place, then we will understand more easily how we can slow down or completely prevent this process. The wetting of leather takes place in a 4-step process. The water spreads over and wets the leather surface. Then the water penetrates into the leather and fibre network and thereafter the water wets the fibre network, in other words, it wets the internal surface of the leather. Finally attractive interactions between water and leather network take place and the leather becomes wet. The collagen backbone but also tanning agents, dye molecules, salts etc., which are present in the leather network, might be involved into these interactions. This chain of process steps must be interrupted to prevent the wetting of leather. At least one process step must be stopped, which will be explained hereafter.

Covering the surface with closed waterproof film on the surface

A closed waterproof film can be applied in finishing. This prevents the penetration of water into the leather at least under static conditions. However, such films even with most modern technologies reduce drastically the water vapour permeability.

Filling the gaps within the fibre network

The gaps in the leather can be filled in two completely different ways: firstly, impregnation, and secondly, hydrophilic waterproofing. Firstly, impregnation is a treatment of leather by molten waxes. The filling of the gaps with wax prevents the penetration of the water into the fibre network. The disadvantage being that the leather is extremely heavy and prevents completely any air and water vapour permeability.

Secondly, hydrophilic waterproofing is achieved by application of certain surfactants. E. g. sulphosuccinates, which bind to the leather, make the leather absorb a certain quantity of water. The surfactants and the water form a water-in-oil emulsion, which fill the gaps in the fibre network. Additionally, these micelles are hydrophobic on their outer side and, therefore, the gaps are filled with a hydrophobic material. Shoes, which are made of this leather, might have an excellent wearing comfort directly after being put on because the leather is absorbing sweat. However, unfavourably, the leather weight increases drastically. In addition, the breathability of this leather will stop when water has been taken up. Afterwards the shoe will be dried and the water will be removed completely and the leather will get back its original state.

Covering of the internal surface with hydrophobic chemicals

The so-called open waterproofing is the smartest approach to make waterproof leather. The waterproof agent coats the leather fibres with a hydrophobic layer, which has a low surface tension. Water vapour can penetrate into the fibre network; however, the “hydrophilic water” droplets possess a high surface tension and cannot spread over the hydrophobic fibre surface and wet the internal surface. A binding interaction between fibre and waterproof agent is required and, therefore, this concept can be realised by of chrome stearates, so-called amphiphilic polymers[1] which consist of hydrophilic and of hydrophobic parts, hydrophobic esters[2] and silicone based products which have the highest waterproof effect. The use of chemically modified silicones materialized at the end of the last millennium. However, silicone free products might be preferable for some articles.

The latest developments contain mixtures of components and have a multiple working mechanism. Modified silicones are commercially available and widely used by the leather chemical industry. Our research has found a possibility to modify silicones differently and to produce them in an efficient way[3].

Here we report on the application of silicone based waterproof agents according to the process as shown.

Process principles

Wet-Blue, 1.8-2.0 mm, US Origin

Neutralisation PH, 5.0, wash well

Treatment with acrylic polymer[4]

Retannage and dying[5]

Addition silicone based waterproofing agent[3]

Fixation / hot water / acid / chrome

Leather, which is openly waterproof treated, acts like a membrane. Water can’t permeate. Water vapour penetrates always from the side with higher water vapour to the reverse side with lower water vapour concentration, from the side with higher temperature to the side with lower temperature.

Openly waterproof treated leathers are relaxed and lay flat out. Here, the waterproof treatment doesn’t cause an area loss, which takes place often when waterproof leathers are processed.

The open waterproof effect can be visualised by an example from nature. Water striders can walk and jump over water. Their tarsus is covered with hydrophobic hairs which can’t submerge into the water. Therefore, the water striders stay on water. If we put soap into this water, the surface tension of the water would decrease and water striders would sink into the water. Similarly, waterproof leather cannot be wetted. However, the presence of surfactants causes the leather to be wetted quickly and, therefore, should be strictly avoided.

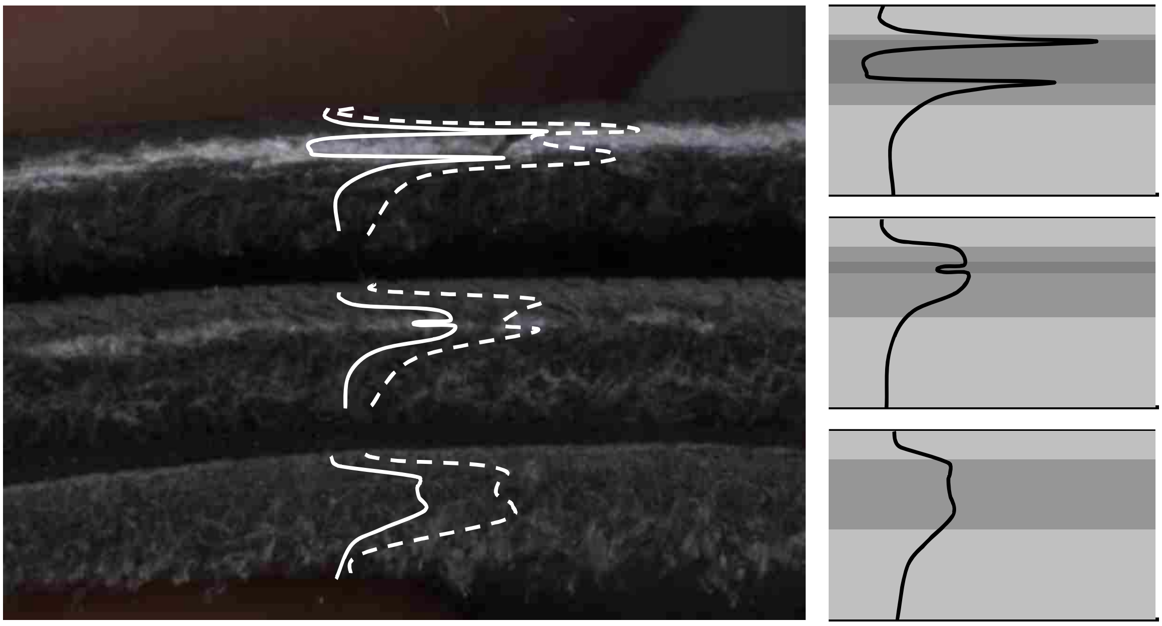
Influence of neutralisation and retannage

Actually, the presence of all kinds of hydrophilic substances within the leather negatively influences the waterproof values of this leather by varying degree. Salts originating from the neutralisation are hydrophilic and, therefore, their presence will increase the water absorption of the final leather article. During the processing of waterproof leather these salts might harm because they could cause the breaking of the emulsion of the waterproof agent and, therefore, prevent the even distribution through the cross-section. Therefore, waterproof leather should be washed well after neutralisation.

Likewise, retanning agents, which are huge and bulky molecules, might influence the waterproof values negatively. Therefore, vegetable tanning agents should be selected carefully; sweetened vegetable tanning agents have to be avoided strictly because they are even more hydrophilic. Normally synthetic retanning agents cause fewer problems. Urea containing aromatic syntans can be applied in small quantities. Other aromatic syntans and acrylates can be applied in normal quantities.

Despite their hydrophilicity, certain polymers[4] and syntans[5] support the waterproof effect as they promote the even distribution and penetration of the waterproof agent through the cross-section due to their dispersing effect.

The figure below shows the cross-section of three leathers. All leathers are dyed and waterproof treated. The curves show the distribution of the waterproof agent through the cross-section. The lower leather exhibits the best waterproof performance because the waterproof agent is evenly distributed through the cross-section; however, practitioners know that this leather – depending on the origin of the wet-blue - is likely to be loose. Therefore, some cationic charge and an uneven distribution of waterproofing agent in the middle of the cross-section is preferred, especially in the cross-section of heavy types and in the case of wet-blue which tends to grain looseness.



Cross-section of a strongly retanned waterproof leather (top line), cross-section of a medium retanned waterproof leather (middle line) and cross-section of a weakly retanned waterproof leather (bottom line). The grain side is always on the top. On the left side you see a photo of the cross-section showing the dye penetration. On the right side you see the cross-section of the leather. The dark grey background indicates a cationic zone. The light grey background indicates an anionic zone. The medium grey indicates the transition area. The white graph on the left side and the black graph on the right side are identical. Both show the distribution of the silicone based waterproof agent after a typical process as written before.
The dotted line shows the distribution of waterproof agent after a modified process.

Conclusion

The production of waterproof leathers showing excellent wearing comfort requires both appropriate products and application know-how. Both products and application process must be adapted to the requirements for the final article and to the processed wet-blue.

[1]OMBRELLON WD, [2]OMBRELLON WR, [3]OMBRELLON 072, OMBRELLON 073, OMBRELLON 2770, [4] METOLAT WP, [5] EDAPLIN