SmiTools - Waterproof

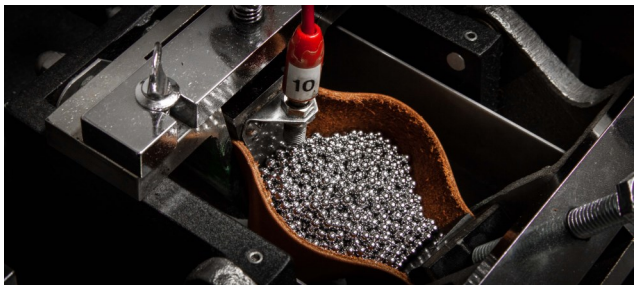
controlling the key waterproof parameters

In this SmiTools Smit & zoon is sharing a synopsis on the topic 'Waterproof'. Learn about the many different parameters that influence good waterproof leather. Making waterproof is much more than choosing the right fatliquor (this is actually the easiest part). The key is found in the right processes, e.g. running times, temperature control, washing and polyvalent metal fixing.

Introduction

The making of waterproof leather depends on a wide variety of factors that can influence its properties and performance. Many factors are negative factors: they reduce the performance. It is important to know what should not be done. Other factors can positively influence the performance of the waterproofing agents: what is best to do?

Before the development of a waterproof article we all face the same problem: where to start? It helps to realize that waterproof leathers are made the same way as other leathers with neutralizing, retanning and fatliquoring.



The differences

A few differences exist:

- A longer total running time
- No inclusion of washing agents in the floats
- More washes in-between and at the end of the process
- A modification of the fatliquor (fixation) with polyvalent metal salts

All other factors are more or less the same, much more than often thought.

The final leather has also a few specific properties:

- Waterproof
- A lower yield
- An increased tendency for grain shrinkage

Running time

To make a waterproofed leather takes longer than a standard leather. This is caused by the extra time needed for neutralization, more washing cycles and the necessity of chrome fixation.

Washing agents

Washing agents remain in the leather. It is not possible to wash them out completely. The only thing that can be done is not adding any extra quantities in those processes which can be controlled.

Non-ionic washing agents are adsorbed by the vegetable tanning agents used during retanning. In this way their negative effects on waterproofing are reduced so that they stop being a cause for unsatisfying water repellency.

Washing

Washing is important and every additional washing cycle helps. At the same time the time involved should be kept to a minimum and no washing other than those strictly necessary should be done. Every washing cycle means another refill of the drum and another total draining. Emptying and refilling take more time than the actual running time and it should therefore be tried to keep washing to a minimum. However, the influence of washing is apparent, both after neutralization and metal fixation. By reducing the washing cycles it becomes possible to shorten the total running time. When high Maeser flexes have been achieved, one could ask whether such extreme properties are required. The number of washing cycles could be reduced in accordance with the customer's requirements.

Polyvalent metal salts

Chrome is the most common chemical for reacting with the emulsifiers of the waterproofing agent. For the sake of the environment, as little as possible should be used. By ensuring a quick and even penetration more efficient use can be made of the fixing agent and its amount can be reduced accordingly.

Loading

Wetblue should always be folded open before throwing it into the retanning drum. It is known that very often this is not done, for whatever reasons. For waterproof leathers unfolding the hides is an important detail which should not be overlooked because the uniformity of the water repellency is influenced by it. Loading the right amount into the drum is also crucial. Neither overloading nor under-loading will generate the right properties.

Sensitivity

Waterproofing fatliquors are very sensitive to the influence of electrolytes and acids. The amount of electrolytes has a bigger influence on the behavior of the fatliquor than the amount of acid. Luckily the presence of electrolytes can easily be controlled by washing.

Dyeing

When making black leathers it is often difficult to exhaust the dye bath, often the dye bath is still very black when draining the water. In response more acid to fix the dyestuff is being added, very often this does not help much. It is therefore important to help the dyestuffs fix easily. One way of doing so is by raising the temperature to 35-40°C in the retanning and dye bath. In a properly set up process, no difficulties of dye penetration should be encountered. The amount of astringent retanning agents has to be carefully chosen because at higher temperatures they will cause more grain shrinkage.

Fatliquoring

Emulsification

Synthol EW 321 and Synthol DS 600 are perfectly pourable liquids that easily emulsify in water. In small-sized drums they can be added undissolved without any visible or measurable difference to the leather. This is due to the speedy distribution inside the drum. Such a quick distribution is not possible in large production vessels. It takes some time before the fatliquor has spread evenly. Undiluted addition of Synthol EW 321 would result in temporary high local concentrations. Eventually the differences disappear, but the initial unevenness can cause varying degrees of water repellency from hide to hide.

For this reason it is recommend to dilute these fatliquors in a ratio of 1:3 before adding.

Temperature

The recommended fatliquor temperature for waterproofing is 50-60°C, but lower temperatures can be chosen or even preferred, yet require careful monitoring. Our experience is that low temperatures do not affect water repellency.

Electrolytes: stability of fatliquor

Waterproofing fatliquors are used in a fresh bath. One washing cycle between the previous process and fatliquoring is advisable to reduce the electrolyte and acid content of the fatliquor bath. High amounts of auxiliary products, e.g. dispersing agents, which only form a loose bond with the leather are difficult to remove during washing. They are released in time and can have a destabilizing effect on the fatliquor bath.

This can be observed when after 15-30' the fatliquor starts to become unstable and eventually even separates. This is caused by the slow release of the mentioned products/electrolytes. Combined with the gradual decrease of the pH in the bath it causes the fatliquor to destabilize.

Amounts

When fatliquoring normal, non-waterproof, leathers the general rule applies: the thicker the leather, the smaller the amount of fatliquor applied. It is not necessary for thick leathers to be fully penetrated with fatliquor. They would become much too soft and loose. A more or less superficial deposit of the fatliquor gives the best results. To a large extent the amounts offered are based on the surface of the leather but calculations are always based on shaved weight. For this reason thick leathers have a different weight to surface ratio and the %-ages used have to change accordingly. This is the other reason why for thick leathers smaller amounts of fatliquor are used than for thin leathers.

A waterproof fatliquor serves a different purpose. Its lubricating power is far less important than its waterproofing properties and everything possible needs to be done for ensuring it penetrates and fixes evenly in all layers of the leather and not just on the surface. Superficial waterproofing will last for a while but the unprotected inside will act as a sponge and swell with water. This can be seen on the Maeser test when no signal is visible but water drops appear on the cutting edge of the leather.

A waterproofing fatliquor should be seen as a filling agent. And as with syntans, with increasing substance of the leather more product is needed.

Large amounts of fatliquor normally have a negative effect on grain tightness but on the other hand, using reduced amounts may not then again give sufficient water repellency.

It is recommend to use reasonable amounts of waterproofing agent, between 9 and 12%, to be sure that the right properties are achieved.

Pre-fatliquor in retannage

Fatliquoring with waterproofing agents should not take place in one bath. Spreading the fatliquor is beneficial for the final result: the leathers become fuller, tighter and more water repellent. A pre-fatliquor is normally added before the addition of acrylic resins and other retanning agents. Only when the resulting leathers need extra grain tightness, should the acrylic resin be added before the fatliquor. This increases grain tightness but it also makes dyeings less full.

Fixation of the fatliquor

Formic acid

Normally the fatliquor bath is fully exhausted by itself after 60' running time. The character of the fatliquor and the gradual decline of the pH in the fatliquor bath cause this.

Fixation therefore serves a different purpose. It starts to break down the emulsifier to an extent where superficial water repellency becomes visible. The main water repellency is then achieved by the fixation with polyvalent metal salts. In most cases this will be chrome.

Chrome is as sensitive to pH as a waterproofing agent is. It has to reach deep into the leather and react there with the product. When fixation has been insufficient and the bath has a too high pH, the chrome will be basified and fixes only on the outside. The fixation of the fatliquor should be seen as a preparation for the fixation with metal salts. Even when no fatliquor is visible in the bath anymore, running times should be long enough to guarantee a chrome-friendly pH inside the leather.

Metal salts

Only a subsequent treatment of the leathers with metal salts causes the full waterproofing properties to develop. These metals react with the emulsifier and take it away from the fat itself. In this way the previous emulsifyability of the product has been destroyed. This fixation is commonly done with chrome salts. For best effect the leather needs to be acidified sufficiently long (30 minutes or longer for leathers >2,0 mm) to a pH of 3,5-3,6. If the duration of the acidification is too short or the pH too high, chrome will not penetrate and activate the leather's water repellency. For good penetration of the fixing agent a longer float of 200% is beneficial. Shorter floats do not improve the penetration.

For white leathers chrome can not be used as it gives an undesired greenish and dirty shade to the color. The same applies for pastel shades. In certain countries environmental legislation prevents the use of chrome. Aluminum or zirconium are the only two other choices when chrome can not be used.

Aluminum has a too unstable nature to be able to penetrate evenly into the leathers. It's reacts superficially and can only be used when the leathers treated are not too thick, e.g. nappa's and some sport shoe leathers.

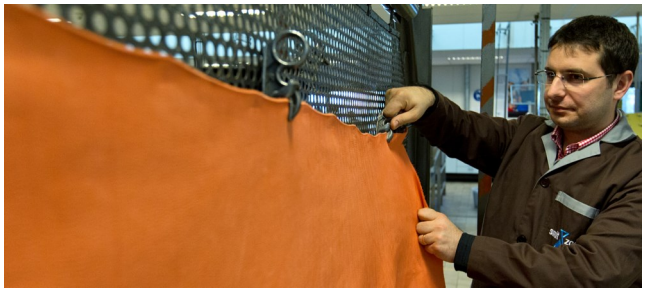
Zirconium is an acceptable replacement of chrome but its high price may be an obstacle. Chrome is still the best choice as its price is low and its stability is good enough to make it penetrate the leather.

Drying

The purpose of drying is the removal of water from the processed leather. In this water all chemical processes take place. As long as there is water in the leather there will be chemicals dissolved in it instead of being fixed to the leather. They only form bonds when the water is removed completely. Good drying is a condition for this. For complete water repellency the remaining chemical activity has to end.

For upper leathers vacuum drying is the first stage of the drying process. The desired appearance of the leather is more important for choosing the drying temperature and -time than the possible influence this may have on the water repellency. The second part of the drying process influences the latter much more.

Only hanging the leathers after vacuum drying can not guarantee the required removal of water from the fibers. Temperatures and humidity change during the seasons. Drying in a controlled environment is necessary. The drying temperatures do not have to be high to obtain a good result. A high drying temperature of 50°C has no beneficial effect compared to a temperature of 30°C. No increased water repellency is found and the appearance of the leathers is affected negatively by the high temperature. Only hang drying to a dry hand feel results in uneven water repellency and generally lower water repellency than controlled drying. The water content after drying should be fairly low: 8 -10%.



Conditioning

After drying the leathers can be conditioned in a normal way. The water will be absorbed slowly and sufficient resting time is necessary. The small amounts of water absorbed do not affect the water repellency.

Contact Smit & zoon for further information

The information given in this SmiTools is just a short synopsis on the topic. We would be glad to help you further in case of questions, the sharing of information or help with choosing the right wet-end products for your application. Please feel to contact our Leather Service Centre or your usual relation within Smit & zoon.