



The manufacture and control of water-resistant leather



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Many factors must be taken into account when manufacturing water-resistant leathers. This includes both the raw materials selection, and the processing to the finished state. Care must be taken to ensure that the achievements gained by careful materials procurement and leather manufacturing techniques are not diminished by inappropriate works practices.

For thousands of years leather has proven itself as one of the most versatile substrates known to man. Its use is documented throughout history in articles of clothing, footwear, weaponry, household goods and industry.

The use of hydrophobic leather is also not new, with leather being widely used in drinking vessels and water carriers in medieval times. Perhaps one of the most interesting uses of water resistant leather is documented in the ninth century Latin text "Navigatio Santi Brendani Abatis". This refers to the voyage of Brendan, an Irish monk who lived from about 484 A.D. until 577 A.D., and is reported to have undertaken a voyage of discovery from the west coast of Ireland to Newfoundland in a leather boat. This was made from oak bark tanned ox hides, made water resistant by treating with wool grease and tallow.^[Legend 1]

Over the past 150 years our understanding of leather manufacturing has moved from craft status to a more scientific basis. Many 'new' developments have been adopted in the leather industry including the tanning drum and chrome tanning. Rapid development in chemical synthesis has also played a major role in allowing a much wider spectrum of chemicals to be utilised in leather processing.

Achieving water-repellent and hydrophobic effects on leather

The requirements of modern water-resistant leathers can be summarised as follows:

- Even and well distributed water-resistant properties throughout the leather cross section.
- The waterproofing effect should be permanent throughout the life span of the leather.
- The character of the leather in terms of handle and feel should be maintained.
- The dyeability and finishing properties should not be adversely affected.
- The water vapour permeability must be sufficient to allow the leather to 'breathe'.

Over the years many products have been utilised to achieve these properties including:

Definition



Water-repellent leathers: Mainly surface treatments which allow water to be shed from the leather surface.

Water-resistant or Hydrophobic leathers: Exhibit resistance to water penetration throughout the cross section when subjected to dynamic stress caused by flexing.

IMPREGNATION AND SURFACE TREATMENTS

- Drum stuffing or dipping with oils or waxes to coat the leather fibres and fill interfibrillary spaces to form an impermeable water barrier.
- Impregnation with solvent-based silicone oils or fluorinated resins, by curtain coating, spraying or drum application.

Drum stuffing techniques tend to be limited to the production of heavy vegetable tanned leathers. Fluorinated resins produce excellent surface repellency against water and staining but do not allow the leather to be finished or re-dyed. In addition, such products tend to be expensive.



CLASSIC HYDROPHOBING FATLIQUORS⁽¹⁾

Such products are generally based on saponification adducts of fatty acids, often coupled together with wax and/or oil based hydrophobing agents. With these products, drum application is possible, allowing good softening and moderate hydrophobing properties to be achieved at a reasonable cost.

However, the products often exhibited poor emulsion stability to hard water, electrolytes and low pH that could lead to irregular results in terms of water resistance and fatliquoring properties.

In addition many such products were often associated with causing loose leather due to the high pH of their application range required to promote penetration.

The expansion of production and increased economical viability of certain types of phosphoric acid esters widely used in the cosmetic industry facilitated their use in classic hydrophobic fatliquors. This allowed products to be manufactured with improved water resistance properties along with much wider application tolerance levels.

HYDROPHOBING POLYMERS

Towards the end of the last century a range of softening hydrophobic polymers were introduced to the leather-making world^(Legend 2). These high molecular weight polymers allowed water-resistant and washable leathers to be produced with outstanding dynamic water resistance and low extractability. However, they tended to impart to the leather a rubbery feel with a certain degree of area loss if not used carefully.

COMBINATION SYSTEMS⁽²⁾

Further development in the field of hydrophobic leather chemicals followed with the introduction of combination systems. These were based on water emulsifiable hydrophobing polymer/fatliquor blends that could be combined with water insoluble silicones. A ratio of approximately 10 parts polymer/fatliquor to 1 part silicone can be taken as a general guideline.

Such combination products facilitated a high flexibility of use and provided excellent hydrophobing and fatliquoring properties. But, if too much silicone oil was used, there exists the danger of a greasy surface feel.

In addition, a minimum quantity of the products were required to attain high specification dynamic water resistance which, depending upon the degree of retanning materials utilised, could lead to over softening of the leather.

DESIGNER PRODUCTS⁽³⁾

The so-called “designer water proofing products” was a natural progression from the “combination systems”. These single product water-proof compounds were specifically formulated to incorporate the benefits of polymeric and classical hydrophobic materials along with functional polysiloxanes and synergistic stabilisers. Their introduction marked a major breakthrough in the field of water resistant leather manufacture by allowing the tanner a flexibility of use previously thought not possible.

These products are readily water emulsifiable and extremely stable to low pH conditions as well as high concentrations of electrolytes. This allows their use at various stages of the leather making process, including neutralisation, retanning and dyeing.

The functionality exhibited by the product allows co - valent bonding with the chrome tanned substrate. Leathers with extremely high Maeser values can be easily - and more importantly consistently - achieved whilst maintaining the

aesthetic properties and handle of natural feeling leather.

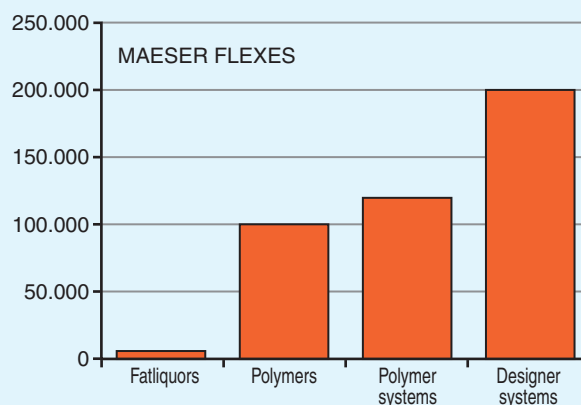
Water resistance

The provision of water resistance to leather has made considerable advances in a relatively short period of time. Improvements in terms of performance of the systems that have been developed are illustrated in *Panel 1*:

There are, however, several ways of measuring water

Panel 1:

Advances in hydrophobing



resistance, and these include:

- Spot tests using water/isopropanol.
- Static water uptake.
- The Bally penetrometer.
- The Maeser test.

In addition, customers may have specific requirements, which will influence the test method used. For example, the following details may need to be established:

- Is the leather tested in the finished, finished and abraded, or unfinished states?
- What are the time limits set for the water penetration and uptake in the Bally test method?
- How many flexes are required in the Maeser test method?
- Is the penetration of water through the sample based on visual or electrical assessment?

An overview of the requirements for several different types of leather in various countries is given as *Panel 2*:

Panel 2: Water resistance specifications

Country	Leather type	Method	Specification	Uptake
USA	Army boots	Maeser	15,000 - 20,000	< 30%
Germany	Army boots	Bally abraided	minimum 360 min	Max 20%
	Army shoes	Bally abraided	minimum 60 min	
	Army gloves	Bally abraided	minimum 180 min	
Britain	Min Defence shoes	Bally	minimum 360 min	
	Min Defence gloves	Pressure test		



The manufacture of water-resistant leathers

Although great strides have been made in the chemistry and technology of waterproofing compounds over the past 30 years there are still numerous factors that must be taken into account when manufacturing water-resistant leathers.

RAW MATERIAL SELECTION

The tanner is faced with various choices depending upon his circumstances and the ability to control his own supply of raw material, amongst which are the following:

- Raw hides or skins converted in-house to the wet blue condition.
- Wet blue purchased or contract tanned from a single supplier.
- Wet blue from various suppliers.

The successful manufacture of water-resistant leather is only possible where the wet blue process is carefully controlled to meet certain parameters. The consistent manufacture of water-resistant leathers to a high standard will lead to great difficulties when the wet blue production is variable.

PROCESSING TO WET BLUE

As with all water-resistant leathers several factors should be observed in the beamhouse in order to negate subsequent inconsistencies and problems:

- A thorough soaking of the hides is advantageous.
- Avoid, if possible, the use of large amounts of surfactants (particularly nonionics) in soaking and liming.
- Obtain a well-opened fibre structure in the liming stage.
- Delime to remove residual calcium, and avoid the use of excessive surfactants.
- Use a combination pickle using formic/sulphuric acid. Masking salts can be used.
- Avoid the use of pickle stable fatliquors.
- An even distribution of chrome throughout the cross section of the leather will prove beneficial in obtaining consistently high water resistance properties.

POST-TANNING OPERATIONS

- The wet blue should be initially well washed to remove hygroscopic salts.
- The wet blue should be thoroughly wet back prior to re-chroming or neutralisation.
- Re-chroming will help to refresh old wet blue stock.
- Care should be taken to ensure good fixation so that there is as little as possible free chrome in the bath.
- The neutralisation process is critical in obtaining an evenly distributed retannage and subsequent fatliquoring.
- Neutralisation pH can vary between pH 4.5 and 7.5 depending upon the type of leather required.

RETANNAGE

- A careful screening of products is highly recommended, particularly when utilising resin retanning agents based on polymers.
- Phenolic syntans and naphthalene sulfonic acid based auxiliaries can, as a rule, be used without a negative influence on water resistance.
- Sulfited vegetable extracts may adversely affect water resistance.

- The use of preselected and tested retanning materials will greatly assist in achieving good water resistance.⁽⁴⁾

DYEING

- Avoid penetrators and levelling agents based on ethoxylated fatty amides or other surfactants.
- Choose dyes with good compatibility in terms of their dyeing properties and solubilities.
- Liquid dyes which may contain solvents or tensides as stabilisers should be avoided.
- The quantity and type of dyestuff may have a marked effect upon the stability of certain waterproofing compounds due to bringing high salt loadings (dilutents based on sodium sulphate) into the process.

FATLIQUORING OF HYDROPHOBIC LEATHER

The fatliquoring process in the production of water-resistant leathers is two-fold.

- To lubricate, soften and provide handle properties to the leather.
- To impart water resistance.

General Process Control

Having said a little about the individual process stages in the leather-making cycle it is perhaps pertinent at this point to highlight some further details which should be taken into consideration in the processing of water-resistant leathers if consistently high values are to be achieved.

- Carefully control all the washing stages to ensure removal of loosely bound surfactants and hygroscopic salts.
- Control the degree and level of neutralisation by checking the cut edge of the leather in various sampling positions i.e. neck, belly, and butt, with suitable indicators:

e.g. Bromo Cresol Green pH 3.8 - 5.5 (yellow -blue)
Bromo Cresol Purple pH 5.2 - 6.8 (yellow-purple)
Bromo Thymol Blue pH 6.0 - 7.6 (yellow-blue)

- The quantity and type of retannage will have a direct influence not only on the water resistance properties, but also the softness fullness and handle of the leather.
- The quantity, type and emulsion stability of the waterproofing fatliquor or compound must be carefully established in relation to other processing factors if problems are to be avoided.
- The temperature, time and mechanical action in processing should be carefully controlled and standardised, once processing parameters have been established.

FIXATION

Careful attention is also needed in the following stages:

- Close control of fatliquor exhaustion and rate of uptake.
- Close control of fixation using formic acid (no sudden pH jumps).
- Washing in the form of batch washes.
- Fixation or capping with mineral tanning salts together with selected auxiliaries⁽⁵⁾.
- Control of the float length in mineral capping to 200% minimum.



- Control of the float temperature in mineral capping to 35°C maximum.
- Control of the running time to 60 minutes minimum.

The use of selected auxiliaries⁽⁵⁾ during the capping stage greatly assists in gently increasing the final pH of the bath to approximately pH 4.0, thus ensuring maximum uptake of the mineral tanning salt and optimum waterproofing effects.

The quantity and temperature of the water used in the capping stage is also critical in ensuring that the reaction rate between the mineral tanning salt and the waterproofing compound is not too fast. This is to avoid a pebbling effect and subsequent area loss often seen during this stage of processing.

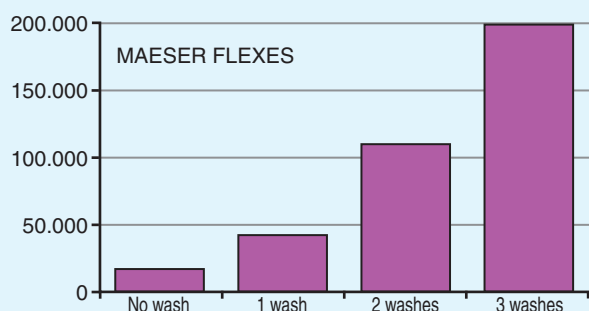
POST-FIXATION

Attention should also be given to the following processing steps in order to ensure that the achievements gained in the earlier stages are not diminished by careless work practices.

- In order to obtain optimum waterproofing performance the build up of hygroscopic salts in the leather resulting from earlier process steps must be removed. This is best achieved by batch washing the leather in a closed drum with three times 200% water at 40°C for 3 periods of 10 minutes. The effects of washing are shown in *Panel 3*.

Panel 3:

Improvement of water resistance by washing



- In order to allow a certain degree of equilibrium to take place in the leather it is advisable whenever possible to horse up over night.
- The samming and setting operations are often overlooked in the production of water-resistant leathers. These operations may lead to poor results due to contaminated felts or pre-dipping the leather in water containing leached out surfactants or anionic fatliquors from other leather types.

Testing Methods and Practice

- Storing the leather for long periods of time will almost certainly lead to improved dynamic water resistance. This fact should be borne in mind when testing the leather and if subsequent problems are to be avoided in finishing.
- Sampling positions should be taken in to consideration when testing for dynamic water resistance due to the actual fibre density and structure of the hide. It is common practice in many tanneries to make tests on samples taken from the butt, belly and neck areas.

Panel 4: Maeser Penetration Test



The steel balls placed in the folded leather ensure good electrical contact at the time of water penetration.

- When testing leathers by either the Maeser or Bally methods it is extremely important to ensure that the equipment is kept clean and that fresh solutions are made up for each new test series.

Summary

During the past 30 years or so considerable advances have been made in the manufacture of water-resistant leathers. The technology has evolved on the basis of novel types of hydrophobic fatliquoring products developed specifically for this purpose. Nevertheless, these products can only achieve high quality and consistent results if particular care and attention to detail is taken throughout the whole manufacturing sequence. Small variations or inappropriate processing in many of the stages of manufacture can cause a significant loss in performance within the final leather. However, with good attention and control throughout the manufacturing sequence and careful screening and selection of products high performance results can be assured. 🌐

Legend

- 1) *The Brendan Vogage* was replicated in 1976, by Tim Severin, utilising a leather boat made by the same traditional methods described. See: "The voyage of Saint Brendan", *World Leather* June/July 2001, p40-41
- 2) *Lubritan products* (Rohm & Haas)

References

Products by Trumpler International:

- 1) *Truposist WRM*
- 2) *Truposist A & C System*
- 3) *Truposist D & F (Patented products)*
- 4) *Trupotan GD, Trupotan WRT, Trupotan RKM, Trupotan DAR*
- 5) *Trupofix WP*