



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.

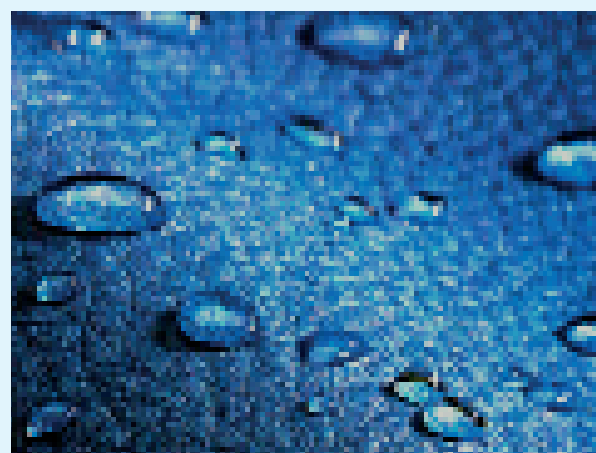
Achieving water-repellent and hydrophobic effects on leather

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.



THE MANUFACTURE AND CONTROL OF WATER-RESISTANT LEATHER

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.

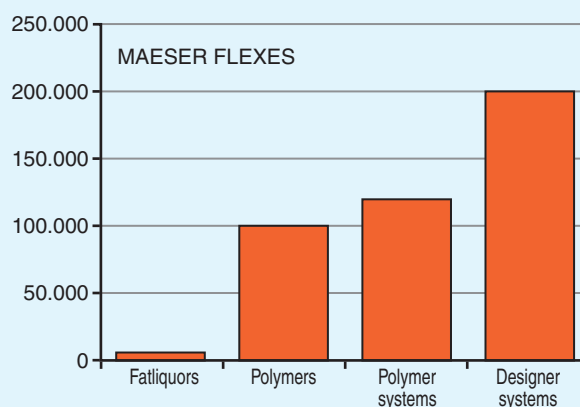
Water resistance

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%
	Army boots	Bally abraded	minimum 360 min	Max 20%
Germany	Army shoes	Bally abraded	minimum 60 min	
	Army gloves	Bally abraded	minimum 180 min	
Britain	Min Defence shoes	Bally	minimum 360 min	
	Min Defence gloves	Pressure test		