



The hydrophobing of chrome-free leather

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Nowadays, hydrophobic qualities in high quality leather are demanded for many fields of application. These properties range from the so-called 'pearl' effect through to 'waterproofness', as given by classical impregnation.

However, requirements for good waterproofing include water resistance throughout the whole leather cross-section and reduced water uptake. These characteristics have to remain durable under static and dynamic conditions whilst at the same time the leathers should show reasonable water vapour permeability. This is to ensure a high wearing comfort for shoe upper leathers and sitting comfort for upholstery leather.

Basically, two different modes of hydrophobing can be distinguished:

- 'closed hydrophobing' where, in principle, all of the fibre interstices are filled with water repellent substances.
- 'open hydrophobing' where the fibres are wrapped with a hydrophobic 'net', without the fibre gaps being filled.

By embedding water-in-oil-emulsifiers (*certain dicarboxylic acid derivatives*), any water that penetrates the fibre interstices is bound in a water-in-oil emulsion. This consequently generates a barrier against further water penetration⁽¹⁾. During subsequent drying, the water evaporates and is replaced with air and water vapour.

The effect of such derivatives relies on the mode by which they are bound to the chrome tanned leather matrix. The carboxyl groups form a chelate complex with the chromium, while the hydrophobic alkyl chains are repelled from the fibre, thus protecting it.

A similar mechanism occurs⁽²⁾ with other carboxyl-groups containing hydrophobing agents (*e.g. chromium and aluminium soaps of fatty acids, fluorinated carboxylic acids*), which enclose the leather fibre in a network of hydrophobic ends (*'open hydrophobing'*). In the case of polysiloxanes a bond to the fibre via oxygen is possible, with the hydrophobic alkyl-silyl-end orientated towards the water.

In contrast, the water-repellent effect of fluorochemicals can be attributed to the special inter-face properties of these substances. By generating a negative capillary pressure, the wetting and penetration of water are impeded. Using products on the basis of so-called 'fluorotelomers', even supplemental oil repellence can be achieved⁽³⁾.

Factors influencing hydrophobing

According to the studies available, the quality of hydrophobing obtained within manufacture depends on a series of factors:

- The selection of raw material (*hides*), and the selection of beamhouse and tanning processes to produce a densely structured hide material⁽⁴⁾.

- The minimisation of chemicals with hydrophilic effects on leather (*salts, wetting agents*)⁽⁵⁾
- Intensive washing in order to remove salts from the leather⁽⁶⁾
- Neutralisation throughout the hide cross-section to ensure good penetration of hydrophobing chemicals⁽⁷⁾
- Higher process temperatures to produce better penetration of emulsions.

A series of hydrophobing agents and systems are available to support the production of waterproof leathers. The so-called reactive hydrophobing agents, based on polymers, bind to the chromium-collagen-complex by means of a polar chrome-affine structure unit. This makes the subsequent fixation with chromium salt unnecessary⁽⁸⁾. The positive influence of such products, also called polymeric fattening agents, has been described by other authors⁽⁹⁾ too.

Modern polymeric hydrophobing systems are typically composed of co-polymers made up of acrylic acid, methacrylic acid and maleinic acid containing longer hydrophobic side chains that provide a lubricating action⁽¹⁰⁾. Likewise, combined systems consisting of poly-acrylates and polysiloxanes have been successfully employed⁽¹¹⁾.

In more recent developments, a two-component system based on a special polyacrylate and an anionic polysiloxane has been successfully used. This can be fixed to the leather fibre by using formic acid alone, thus making metal salt fixation unnecessary⁽¹²⁾.

In the case of chrome-tanned leathers, which account for some 80% to 85% of the leather produced worldwide, hydrophobing does not usually present difficulties, and the market requirements are met through various state-of-the-art systems which have been developed by the chemical industry.

Nevertheless, there is an increasing interest in using chrome-free leathers, particularly in the automotive industry where, in the case of leathers used for lamination, high requirements regarding shrinkage stability have to be fulfilled. At present, this is best achieved by using leather based on wet white, and produced using combined vegetable/synthetic tannage/retannage procedures. The demand for chrome-free leathers in the area of shoe upper manufacture has also increased, mainly as a result of an increased demand for environmentally-friendly products.

When compared with chrome tanned leather, the possibilities for waterproofing chrome-free leather are extremely limited. Due to the tanning technique, the preferred bonding locations do not exist. Additionally, in producing 'free of chrome' leather the use of chrome salts for fixation is unacceptable.

The investigation

Attempts were made to produce hydrophobic chrome-free shoe uppers with a 1.6 mm thickness using south German raw hides. An open hydrophobing was needed to maintain the ➤



THE HYDROPHOBING OF CHROME-FREE LEATHER

Panel 1:

The effect of different unhairing/liming systems on waterproofing

Test procedure	Liming variant		
	Calcium hydroxide/ sodium sulfide	Sulfide-free, reduced swelling	Waterglass, reduced pH
Static water uptake			
(%) after 30 mins	23.1	23.8	25.7
(%) after 2hrs	40.5	33.7	43.2
Penetrometer (Bally)			
Water penetration (mins)	> 480	173	253
Water uptake % in 2hrs	7.3	7.7	7.4
Colour fastness to water spotting, modified	150 µl	150 µl	150 µl
Wetting time (secs)	20	20	20
Penetration time (min)	378	394	393
Assessment: immediately	dark spot	dark spot	dark spot, swelling
after 16hrs	no changes	white borders	white borders

water vapour permeability at an acceptable level. A wet white procedure was used, and the influence of each particular process on the hydrophobic properties of the leather—excluding finishing—was studied.

An evaluation of the hydrophobic properties of the test leathers was made on the basis of the following physical test methods:

- Determination of the static absorption of water (*EN ISO 2417*)
- Determination of water resistance of flexible leathers (*EN ISO 5403*)
- Dynamic water resistance of the shoe upper leather by the Maeser water penetration tester (*ASTM D2099*)
- Colour fastness to water spotting (*EN ISO 15700, modified*)

Panel 2:

Different pretanning procedures after calcium hydroxide / Na-sulfide liming

Test procedure	Pretannage			
	1	2	3	4
Static water uptake				
(%) after 30 mins	23.1	17.0	19.0	18.9
(%) after 2hrs	40.5	29.3	33.4	35.9
Penetrometer (Bally)				
Water penetration (mins)	> 480	> 480	53	107
Water uptake % in 2hrs	7.3	5.9		8.7
C. f. to water spotting, m.	150 µl	150 µl	150 µl	150 µl
Wetting time (mins)	20 s	130	180	not observable
Penetration time (mins)	378	>480	>480	>480
Assessment: immediately	dark spot	dark spot	dark spot	dark spot
after 16hrs	no changes	no changes	no changes	no changes

In order to assess the influence of hydrophobing on other relevant leather properties, some leathers were submitted to the following supplementary tests:

- Determination of water vapour permeability (*EN ISO 14268*)
- Determination of water vapour uptake (*EN 420*)
- Determination of oleophobic properties (*AATCC 118*)
- Determination of pH (*EN ISO 4045*)

Samples were taken, as far as possible in accordance with *EN ISO 2418*, and all of the tests were performed on conditioned specimens (*EN ISO 2419*, 23°C / 50% *rel. humidity*). In addition, the visual appearance and feel of the leathers were assessed.

The effects of different unhairing/liming systems

The investigation focused on the following options:

- Hair-destroying (*calcium hydroxide/sodium sulfide*) liming, then deliming with inorganic and organic acids
- Sulfide-free liming with reduced swelling
- Liming system on the basis of waterglass (*sodium silicate*)

The subsequent processes were the same for all three unhairing/liming systems:

- Pickling with sodium chloride/formic acid/sulfuric acid
- Pretannage using modified glutaraldehyde/syntan
- Retannage based on a polymeric product
- Hydrophobing systems included products based on polyorganosiloxanes and other polymeric compounds (*oleylsarcosides*), with specific auxiliaries to improve the penetration
- Fixation of the hydrophobic agents with a metal salt (*Al*)
- Two washing steps at the end of the process
- Drying using a vacuum dryer
- Conditioned and tested after storage for two weeks

The resulting leathers showed no variation in visual appearance and feel. Regarding both static and dynamic water uptake, and the penetration time of a water droplet, no significant differences could be observed. However, there was a distinction in the amount of time taken for water penetration between the experiments as given in *Panel 1*.

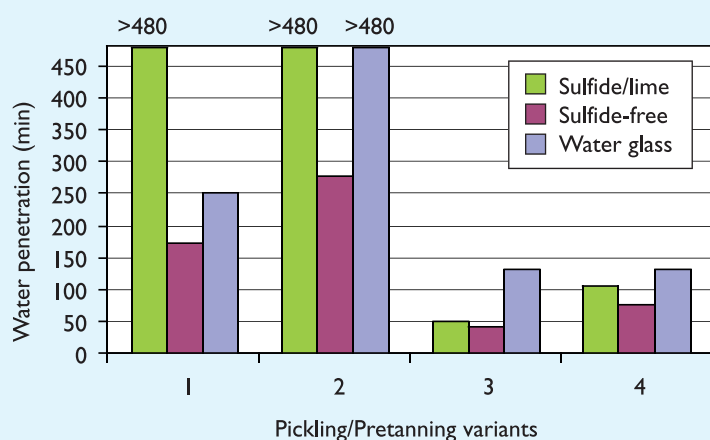
The effects of variation within pretanning systems

The three different liming systems were each combined with four different pretanning variants:

1. Sodium chloride / formic acid / sulfuric acid pickling + pretannage with modified glu-taraldehyde and syntan
2. Salt-free pickling + pretannage with modified glutaraldehyde and syntan
3. Sodium chloride / formic acid / sulfuric acid pickling + pretannage with syntan
4. Fibre stabilisation with sodium silicate (*water glass*) ➤

**Panel 3:**

Dynamic water resistance
Comparison of different pretanning variants on
three different unhairing/liming systems

**Panel 4:**

Comparison of different fixation options

Test procedure	Hydrophobing system H1 Fixation mode			Hydrophobing system H2 Fixation mode		
	Acid	Al-Salt	Zr-Salt	Acid	Al-Salt	Zr-Salt
Static water uptake						
(%) after 30 mins	127.4	28.3	44.7	117.2	56.8	69.0
(%) after 2hrs	129.7	70.5	72.3	121.8	135.0	86.2
Penetrometer (Bally)						
Water penetration (mins)	5	46	> 480	33	86	>480
Water uptake % in 1hrs	89.8	21.2	5.9	86.0	24.3	11.0
Water uptake % in 2hrs			8.2		54.0	16.7

In the test—based on sulfide-containing liming—variants (1) and (2) showed relatively good hydrophobic properties, together with suitable feel and visual appearance. However, variants (3) and (4) showed a considerable decrease in water resistance. These findings are shown in *Panel 2*.

The variants with the conventional salt/acid pickle were subsequently compared with salt-free pickling using the Maeser test. This resulted in significantly better Maeser values for the salt-free pickling system (2) at 11,300 flexes at water penetration, compared with 4,600 flexes for the acid pickle (1).

It was noted that the relatively long penetration times of water droplets in case of variants (3) and (4) were caused by the distribution of fatting and hydrophobing agents in the leather. These are mostly located on the surface, and are confirmed by the greasy feel of the corresponding leathers. This applied to the leathers produced according to the pretanning variants (3) and (4) but starting with sulfide-free liming and liming using water glass as well.

The water penetration times using the Bally Penetrometer for all the experimental variants are illustrated in *Panel 3*.

The effects of different hydrophobic systems and their fixation

Different waterproofing systems were investigated, and the

crux of the process proved to be the fixation of the hydrophobic system to the leather substrate. As the preferred bonding locations do not exist on chrome-free leathers, several attempts were made to improve the attachment of the hydrophobing chemicals. This involved the application of many amphoteric, cationic auxiliaries and retanning agents, but these products proved to be completely inadequate for this purpose.

Based on the waterproofing systems available at the time, it appeared that the use of metal salts was unavoidable. Fixation through the use of zirconium salt achieved the best results when compared with aluminium salts. These findings are shown in *Panel 4*.

- H1 - polyorganosiloxanes and polyacrylates
- H2 - polyorganosiloxanes and amides of higher fatty acids
- It is noted that the waterproofing system H2, when fixed with zirconium salt provided 15,000 Maeser flexes before water penetration.

Nevertheless, fixation with Zr-salt presents a number of drawbacks as the leathers showed low pH-values in the aqueous extract together with a high difference figure^(Legend 1). When the amount of Zr-salt was reduced, the effectiveness for waterproofing was limited without solving the problem of the difference figure. Neutralising with sodium formate was helpful, but significantly increased the running time of the process.

INVESTIGATIONS FOR IMPROVEMENT USING FLUOROCARBON RESINS

Several experiments with fluorocarbon resins resulted in good hydrophobic effects, especially when no metal-salt-fixation occurred. In this context, a positive influence on the wetting behaviour was observed. However, when an adequate hydrophobing system fixed with metal salts was used, then no further improvement in water resistance was observed.

INVESTIGATIONS INTO ALUMINIUM FIXATION

Taking into account the drawbacks of Zr-salt-fixation, attempts then concentrated on improving the Al-salt alternative. Using a recipe based on a glutardaldehyde/synton tanning

Panel 5:

The effect of change in the application point
of hydrophobing agents

Test procedure	Reference recipe	Hydrophobing prior to retanning	
		partly	completely
Static water uptake			
(%) after 30 mins	23.2	31.1	31.6
(%) after 2hrs	33.2	38.6	39.9
Penetrometer (Bally)			
Water penetration (mins)	115 >480	> 480	> 480
Water uptake % in 1hrs	5.1	5.8	6.0
Water uptake % in 2hrs	7.2	7.7	7.7



Panel 6:
Uniformity of hydrophobing over the area of a hide
(Al-salt-fixation)

Test procedure	Al-salt-fixation			
	Standard sample area	Shoulder	Upper butt	Belly
Static water uptake				
(%) after 30 mins	16.9	23.7	25.6	23.5
(%) after 2hrs	30.8	33.6	40.5	37.2
Penetrometer (Bally)				
Water penetration (mins)	>480 137	68	212	146
Water uptake % in 1hrs	4.7	5.8	5.8	7.7
Maeser				
Water penetration (flexes)	1,150	760	1,800	900
Water uptake % (5,700 fl.)	6.4	5.1	4.4	5.7

Panel 7:
Uniformity of hydrophobing over the area of a hide
(Zr-salt-fixation)

Test procedure	Zr-salt-fixation			
	Standard sample area	Shoulder	Upper butt	Belly
Static water uptake				
(%) after 30 mins	19.9	17.1	17.7	19.7
(%) after 2hrs	30.9	32.4	31.9	41.4
Penetrometer (Bally)				
Water penetration (min)	>480	>480	>480	>480
Water uptake % in 2hrs	5.8	6.4	6.7	6.6
Maeser				
Water penetration (flexes)	12,390	>45,600	>45,600	8,400
Water uptake % (11,400 fl.)	2.6	3.0	3.4	3.3

system and replacing one retanning agent (*polymeric compound*) with vegetable tannins, no significant changes in the water resistance of the resulting leathers were observed.

In these trials the point at which hydrophobing agents were employed in relation to the retannage was also investigated and the findings are given in *Panel 5*.

In this situation, no significant differences were found between the water penetration time even when the leathers were Maeser tested.

Cross-hide uniformity

The uniformity of hydrophobing constitutes a problem, even under optimised process conditions. Substantial differences are likely, both across the area of a hide and between hides of the same batch.

This fact is illustrated in *Panels 6* and *7*, which show the differences that sampling location can make, based on leathers produced using two

different process formulations. In these investigations, in addition to standard sampling positions test samples were taken from the following locations:

- Shoulder
- Upper part of the butt
- Belly

It was noted that when there was good waterproofing, the Bally-Penetrometer does not differentiate between the various leathers. Even an increase in the compression amplitude up to 15% can be inappropriate if tests can only run until the end of a working day (*8 hours*).

The effects of wetting/drying cycles

The hydrophobing effect was also investigated to see if it remained effective after repeated wetting/drying cycles. After the initial test, the specimens were gently dried, then reconditioned in a standard atmosphere (*23°C / 50% rel. humidity*), then tested again. This was then repeated for a second and third cycle.

For leathers manufactured using Al-salt-fixation, no significant changes were observed. The Maeser flexes to water penetration remained constantly low (ca. 1,000), while the water resistance measured with the Bally Penetrometer reached test periods >480 minutes. In the case of Zr-salt-fixed hydrophobing systems, variations could be observed, and these are given in *Panel 8*.

It was also observed that a longer time period had a positive effect on the hydrophobic properties of the leather. By testing leathers at well-defined time intervals a steady improvement was noticed. Leather made hydrophobic (*Al-salt-fixation*) resisted water penetration (*penetrometer*) for 99 minutes immediately after manufacturing, but eight weeks later 200 minutes could be realised, reaching >480 minutes after 12 weeks.

The influence of drying

Three different drying methods were used.

- Vacuum drying at 42°C
- Vacuum drying at 52°C
- Chamber toggle dryer

Drying acts on the hydrophobic properties of ►

Panel 8:

Hydrophobing properties as a result of
wetting/drying cycles
(Zr-salt-fixation)

Test procedure/	Hide B				Hide A		
	Initial	1	2	3	Initial	1	2
Penetrometer (Bally)							
Water penetration (mins)	>480	>480	>480	>480	>480	>480	>480
Water uptake % in 2hrs	5.8	6.0	6.6	6.5	6.1	7.0	6.8
Maeser-tester							
Water penetration (flexes)	12,390	15,200	8,390	7,300	22,200	13,070	38,800
					22,800	>45,600	>45,600
Water uptake % (11,400 fl.)	2.6	2.6	2.9	3.3	2.9	3.4	3.7



Panel 9:

Comparison between different drying techniques

Test procedure	Recipe A/H1 Acid fixation			Recipe B/H4 Al-Fixation			Recipe B/H6 Al-Fixation		
	V 55°C	V 42°C	Frame	V 55°C	V 42°C	Frame	V 55°C	V 42°C	Frame
WVP (mg/cm ² h)	8.81	9.89	11.36	7.64	8.04	9.13	7.76	8.05	8.90
WVU (mg/cm ² 8h)	7.4	6.8	14.5	8.8	9.9	8.8	9.0	10.3	9.0
Static water uptake									
(%) after 30 mins	90.3	112.4	142.1	19.7	22.1	28.2	24.0	18.3	23.1
(%) after 2hrs	93.7	118.6	148.8	36.9	39.9	36.4	34.7	31.3	35.5
Penetrometer (Bally)									
Water penetration (mins)	10	10	11	138	122	117	108	81	21
Water uptake % in 1hr	71.3	94.3	100.4	7.7	9.0	7.9	7.0	7.7	9.3

chrome-free leather in a similar way to waterproof chrome tanned leather, and these are already well-known. The effect of the leather structure on the hydrophobic characteristics, as well as on the water vapour permeability (WVP) and uptake (WVU) is illustrated in *Panel 9*.

As experienced with chrome-tanned leathers, the compactness of the fibre structure results in reduced water vapour permeability and water uptake, and in improved water resistance. This is irrespective of the recipe used.

Findings from the investigation

The investigation on hydrophobic chrome-free leather manufacture can be summarised as follows:

- Out of many combinations of liming and pickling systems, and a pretannage based on modified glutaraldehyde and syntan, the best results were obtained using:
 - calcium hydroxide/sodium sulfide, combined with a pickle based on sodium chloride/formic acid/sulfuric acid
 - calcium hydroxide/sodium sulfide, combined with a pickle based on 'non-swelling' sulfonic acids
- A metal-salt-fixation of hydrophobing agents is indispensable
- When using a zirconium-salt-fixation of the hydrophobing agent care has to be taken with the pH and the difference figure of the resulting leather
- The hydrophobic properties produced by metal-salt-fixation cannot be improved by additional treatment with fluorocarbon compounds
- In certain cases, the substitution of polymeric retanning agents with vegetable tanning agents can improve hydrophobing
- The effect of drying conditions on the degree of waterproofness was significant. This also affected the water vapour permeability of these leathers
- The hydrophobic effect was demonstrated as being durable to wetting/drying cycles
- The uniformity of water repellancy across the whole hide was not optimal
- Similar to chrome-tanned waterproof leathers, hydrophobing improves with time. 🌐

Legend

1. A high difference figure (0.7 - 1.0) indicates that strong acids (if pH < 4) or strong alkalis (if pH > 10) are present in the leather as opposed to weak acids or weak alkalis or a high buffering capacity. Method of determination: EN ISO4045|IUC11|FLC13.

Acknowledgements

The authors wish to acknowledge the financial support of the Forschungsgemeinschaft Leder e.V. and the Bundesministerium für Wirtschaft und Arbeit (AiF "Otto von Guericke" e.V.) through the project. Also recognised is the valuable input of all the colleagues at LGR involved in the project.

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