Investigations on the hydrophobing of chrome-free leather

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As compared with chrome tanned leather, the possibilities of waterproofing free-of-chrome leather are falling far short. Therefore it seemed to be necessary to investigate the influence of particular manufacturing processes on leather hydrophobing. In this context three different liming systems were compared for their effect on waterproofing. The liming variants were combined with several pretannage modes. In case of chrome-free tanned leather a metal-salt-fixation of hydrophobing agents is indispensable. A further improvement of an efficient waterproofing obtained by means of metal-salt-fixation could not be achieved by an additional treatment with fluorocarbon compounds. Trials to improve the possibilities for hydrophobing agents to attach to the leather fibre by means of different auxiliaries were unsuccessful. In certain cases the substitution of polymeric retanning agents by vegetable tanning agents can improve hydrophobing to some extent. As expected, the effect of drying conditions on the degree of waterproofness proved to be significant. With zirconium-salt-fixation of the hydrophobing chemicals problems arose with pH and difference figure of the resulting leather, but could be solved. The achieved hydrophobic effect showed to be durable, but the uniformity over the whole hide was not optimal. Analogous to chrome tanned waterproof leathers hydrophobing enhanced with time.

1. Introduction

Nowadays high quality leather for many fields of application should have certain hydrophobic qualities. The efficiency range of hydrophobing encompasses properties starting with the "pearl-off" effect up to "waterproofness", given by classical impregnation. However, requirements for good waterproofing include water resistance throughout the whole leather cross-section and a reduced water uptake, characteristics which have to be durable under static and dynamic conditions as well. At the same time these leathers should show reasonable water vapour permeability in order to ensure a high wearing comfort (shoe upper) and sitting comfort (upholstery leather), respectively.

In relation to the leather equipment basically, two different modes of hydrophobing can be distinguished: the "closed hydrophobing", where in principle all the fibre interstices are filled with water repellent substances, and the "open hydrophobing", where the fibres are enwrapped with a kind of hydrophobic net, without filling fibre gaps.

So, by embedding water-in-oil-emulsifiers (certain dicarboxylic acid derivatives), water penetrating in the fibre interstices is bound in a water-in-oil emulsion, consequently generating 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 binding mode to the chrome tanned leather matrix: the carboxyl groups form a chelate complex with chromium, while the hydrophobic alkyl chains are oriented away from the fibre thus protecting it.

A similar mechanism of action can be assumed /2/ for other carboxyl-groups-containing hydrophobing agents (e. g. chromium and aluminium soaps of fatty acids, fluorinated carboxylic acids), which enclose the leather fibre with a network of hydrophobic ends ("open hydrophobing”). In case of polysiloxanes a bond to the fibre via oxygen is possible. The hydrophobic alkyl-silyl-end on the other hand points towards the water.

The water-repellent effect of fluorochemicals can be attributed to the special interface properties of these substances. By generating a negative capillary pressure wetting and penetration of water are impeded. Using products on the basis of so-called “fluortelomers” even a supplemental oil repellence can be achieved /3/.

According to the available experience, the quality of the obtainable hydrophobing in manufacturing waterproof leather depends on a series of essential factors:

- The selection of raw material (hides) and the conduct of beamhouse and tanning processes in such way to result in dense structured hide material /4/.
- Minimization in the application of chemicals with hydrophilic-making effects on leather (salts, wetting agents) /5/.
- Intensive washing in order to remove salts from the leather /6/.
- Neutralisation all through the hide cross-section is the basis for good penetration of hydrophobing chemicals /7/.
- Higher process temperatures improve the attainable hydrophobic effect by gaining better penetrating emulsions.

In support of manufacturing waterproof leather a series of hydrophobing agents and systems are available. The so-called reactive hydrophobing agents on the basis of polymers bind it selves by means of a polar chrome-affine structure unit to the chromium-collagen-complex making a subsequent fixation with chromium-salt dispensable /8/. The positive influence of such products, also named polymeric fatting agents, is described by other authors, too /9/.

Modern polymeric hydrophobing systems are typically composed of co-polymers of acrylic acid, methacrylic acid and maleinic acid, containing longer hydrophobic side chains with a fatting action /10/. Likewise, combined systems consisting of poly-acrylates and polysiloxanes are applied successfully /11/. In more recent developments in leather-hydrophobing a two-component system based on a special polyacrylate and an anionic polysiloxane is used, which can be fixed to the leather fibre by only acidifying with formic acid, making metal salt fixation superfluous /12/.

In case of chrome-tanned leathers, which account 80 – 85 % of the leather produced world wide, hydrophobing does not usually present difficulties. Considering all know-ledge according to the state-of-the-art and with several suitable systems developed by the chemical industry, the requirements of the market can be met.

Nevertheless, in important areas of leather processing an increasing interest in using free of chrome tanned leathers exists. This applies especially for the automotive industry, where, in case of leathers used for lamination high requirements regarding shrinkage stability have to be fulfilled. At present, this is best achievable with leather based on wet white and produced using combined vegetable-synthetic tannage / retannage procedures. The increasing demand in the area of shoe upper leather for leathers “free-of-chrome” is determined by ecological reasons or by the possibility of allergy problems.

As compared with chrome tanned leather, the possibilities of waterproofing free-of-chrome leather are falling far short. Due to this tanning technique, the preferred bonding locations are lacking. Additionally, in production of “free of chrome” leathers the use of chrome salts to fix the hydrophobing system to the whole leather substrate is unacceptable. Therefore it seemed to be necessary to investigate systematically the feasibility of producing waterproof chrome-free leather.

2. Materials and Methods

Starting from South-German raw hides attempts were made to produce hydrophobic chrome-free tanned shoe upper with a 1.6 mm thickness. An open hydrophobing was aimed in order to keep the ventilating properties at a reasonable level. For this purpose a wet white procedure was used and the influence of particular processes, not including finish application, on leather hydrophobing was studied.

In pelt preparation a generally applied beamhouse procedure (soaking without wetting agents, hair-destroying calcium hydroxide / sodium sulphide liming, fleshing, splitting, deliming on the basis of inorganic and organic acids, bating) was compared with other technological variants. The individual pelt preparing experiments were combined with different pretannage options. The following processes were conducted for all trials in the same manner.

Semi-finished products produced according to the same common beamhouse and pretannage procedure were used for other test series starting from a later point in leather manufacture. So, the influence of vegetable tannins on waterproof properties of the resulting leathers was investigated. Different hydrophobing systems were tested by changing the time of application of these chemicals, as well. By using specific amphoteric or cationic auxiliaries and retanning agents respectively, it was tried to create better attachment alternatives for hydrophobing chemical compounds. In this context the possibilities to fix the hydrophobing agents to the leather substrate were examined more closely.

Generally, the leathers produced in the test series were vacuum-dried at 55 °C. Several selected leathers were used for drying experiments. For that reason two different vacuum-drying options (42 °C and 55 °C) were compared with frame-drying.

In addition, the durability of the obtained waterproofness and the influence of the time factor on the degree of hydrophobing were investigated.

The evaluation of the hydrophobic properties of the test leathers (without finish) 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 shoe upper leather by the Maeser water penetration tester (ASTM D2099)
- Colour fastness to water spotting (EN ISO 15700, modified).

In order to perceive the influence of hydrophobing on other relevant leather properties, particular leathers were submitted to the following supplemental 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).

Sampling occurred, if possible, in accordance with EN ISO 2418. All the tests were performed on conditioned specimens (EN ISO 2419, 23 °C / 50 % rel. humidity). Alongside with the tests visual appearance and feel of the leathers were assessed.

3. Results

3.1 Liming experiments

After analysing and modifying a suitable shoe upper leather recipe in order to eliminate hydrophilic chemicals or at least minimise their amount, the pelt preparing experiments focussed on the following options:

- hair-destroying calcium hydroxide / sodium sulphide liming, deliming with inorganic and organic acids
- sulphide-free liming with reduced swelling
- liming system on the basis of water-glass (sodium silicate).

The following processes were the same for all variants: pickling with sodium chloride / formic acid / sulphuric acid, pretannage by means of modified glutaraldehyde / syntan. For retanning a polymeric product was applied. Dyeing and fatliquoring / hydrophobing were conducted always in the same manner. The hydrophobing system included several products based on polyorganosiloxanes and other polymeric compounds (oleylsarcosides) together with specific auxiliaries to improve the penetration. The hydrophobic agents were fixed to the leather fibre with the aid of a metal salt (Al). After two washing steps the leathers were vacuum-dried. After storage for two weeks the leathers were conditioned and tested.

The resulting leathers showed no variation in visual appearance and feel. Even in relation to the static and dynamic water uptake, as well as the penetration time of a water drop no significant differences could be observed. Only the water resistance values permit a distinction between the experiments (see table 1).

Test procedure	**Liming variant**		
	Calcium hydroxide / sodium sulphide	Sulphide-free, reduced swelling	Water-glass, reduced pH
Static water uptake			
Water uptake (%)			
after 30 min	23,1	23,8	25,7
after 2 h	40,5	33,7	43,2
Penetrometer (Bally)			
Water penetration (min)	> 480	173	253
Water uptake % in 1 h	5,3	5,5	5,6
Water uptake % in 2 h	7,3	7,7	7,4
C. f. to water spotting, m.*	150 µl	150 µl	150 µl
Wetting time (s)	20	20	20
Penetration time (min)	378	394	393
Assessment			
immediately	dark spot	dark spot	dark spot, swelling
after 16 h	no changes	white borders	white borders

Table 1: Liming experiments in comparison

* C. f. to water spotting means “colour fastness to water spotting”.

3.2 Pretanning experiments

The different liming variants were combined each with four different pretanning modalities. The ensuing processes were conducted analogous to the liming experiments.

The pretanning experiments comprised the following procedures:

- (1) Application of a sodium chloride / formic acid / sulphuric acid pickling, pretannage with modified glutaraldehyde and syntan
- (2) Application of a salt-free pickling followed by the same pretannage as aforementioned
- (3) Application of a sodium chloride / formic acid / sulphuric acid pickling, pretan with syntan
- (4) Fibre stabilisation with sodium silicate (water-glass).

Test procedure	**Pretannage**			
	1	**2**	**3**	**4**
Static water uptake				
Water uptake (%)				
after 30 min	23,1	17,0	19,0	18,9
after 2 h	40,5	29,3	33,4	35,9
Penetrometer (Bally)				
Water penetration (min)	> 480	> 480	53	107
Water uptake % in 1 h	5,3	4,5	8,8	5,4
Water uptake % in 2 h	7,3	5,9		8,7
C. f. to water spotting, m.	150 µl	150 µl	150 µl	150 µl
Wetting time (min)	20 s	130	180	not observable
Penetration time (min)	378	>480	>480	>480
Assessment				
immediately	dark spot	dark spot	dark spot	dark spot
after 16 h	no changes	no changes	no changes	no changes

Table 2: Different pretanning procedures after calcium hydroxide / Na-sulphide liming

In the test run on the basis of sulphide-containing liming liquor (Table 2) the first two variants showed relatively good hydrophobic properties together with suitable feel and visual appearance. The application of salt-free pickling liquor resulted in significantly better Maeser values compared with the experiment version (1): 11300 (2) and 4600 (1) flexes, respectively.

The variants 3 and 4 yielded a considerable decrease of water resistance. The relatively long penetration times of water drops are given by the distribution of fatting and hydrophobing agents in the leather. These are located mostly on the surface, which is confirmed by the greasy feel of the corresponding leathers.

The latter observations apply also to the other two test series (tables 3 and 4). These results can be explained by an insufficient penetration of the hydrophobing recipe components in the leather. As the creation of optimal conditions (application of specific auxiliaries, mechanical effects) in repeated experiments generated no improvement, the negative influence can be assigned to the respective pretannage procedures.

Test procedure	**Pretannage**			
	1	**2**	**3**	**4**
Static water uptake				
Water uptake (%)				
after 30 min	23,8	22,4	18,1	19,0
after 2 h	33,7	33,1	30,1	28,0
Penetrometer (Bally)				
Water penetration (min)	173	278	43	78
Water uptake % in 1 h	5,5	4,9	7,2	5,0
Water uptake % in 2 h	7,7	6,9		
C. f. to water spotting, m.	150 µl	150 µl	150 µl	150 µl
Wetting time (min)	20 s	180	180	170
Penetration time (min)	394	>480	>480	>480
Assessment				
immediately	dark spot	dark spot	dark spot	dark spot
after 16 h	white borders	no changes	no changes	no changes

Table 3: Different pretanning procedures after sulphide-free liming

Test procedure	**Pretannage**			
	1	**2**	**3**	**4**
Static water uptake				
Water uptake (%)				
after 30 min	25,7	20,4	18,9	19,5
after 2 h	43,2	32,0	32,3	33,3
Penetrometer (Bally)				
Water penetration (min)	253	> 480	134	133
Water uptake % in 1 h	5,6	5,6	4,9	4,6
Water uptake % in 2 h	7,4	7,4	7,0	6,3
C. f. to water spotting, m.	150 µl	150 µl	150 µl	150 µl
Wetting time (min)	20 s	200	90	90
Penetration time (min)	393	> 480	479	469
Assessment				
immediately	dark spot, swelling	dark spot	dark spot	dark spot
after 16 h	white borders	no changes	no changes	no changes

Table 4: Different pretanning procedures after water-glass-liming option

3.3 Post-tanning experiments

3.3.1 Hydrophobing systems

Different waterproofing systems were investigated. The crux of the matter proved to be the fixing of the hydrophobic system to the leather substrate. As, due to the chrome-free tanning technique the preferred bonding locations are lacking, several attempts were made to create better possibilities for the attachment of hydrophobing chemicals by using diverse amphoteric and cationic auxiliaries and specific retanning agents, respectively. These chemicals proved to be completely inadequate for this purpose.

Applying different fixing variants, the accordant test results showed that metal salt fixing is inevitable with the waterproofing systems available at the time. Comparing the ensuing leathers, zirconium salt fixing achieved the best results. So, the leather produced using the hydrophobing system H2 (anionic polyorganosiloxane / derivatives of higher fatty acids) and fixed with zirconium-salt resisted to 15000 Maeser flexes.

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						
Water uptake (%)						
after 30 min	127,4	28,3	44,7	117,2	56,8	69,0
after 2 h	129,7	70,5	72,3	121,8	135,0	86,2
Penetrometer (Bally)						
Water penetration (min)	5	46	> 480	3,3	86	>480
Water uptake % in 1 h	89,8	21,2	5,9	86,0	24,3	11,0
Water uptake % in 2 h			8,2		54,0	16,7
C. f. to water spotting	150µl	150µl	150µl	150µl	150µl	150µl
Wetting time (s)	5,5	30	30	1,5	20	30
Penetration time (min)	3,5	350	405	1,5	228	385
Assessment						
immediately	dark spot	dark spot	dark spot	dark spot	dark spot	dark spot
after 16 h	dark spot	dark spot	dark spot	dark spot	dark spot	dark spot

Table 5: Comparison of different fixation options

The effective fixation with Zr-salt presents a series of drawbacks. Leathers manufactured in this manner show low pH-values of the aqueous leather extract together with a high difference figure. Reducing the amount of Zr-salt the limit of effectiveness was reached without solving the problem. Neutralising with sodium formate was helpful, but increased the running time very much.

Several experiments with fluorocarbon resins resulted in good hydrophobic effects, especially when no metal-salt-fixation occurred. In this context a positive influence particularly on the wetting behaviour could be observed. Treating recently manufactured leathers with heat at relatively low temperatures (50 °C) helps fixing these resins to the leather substrate, consequently improving the water repellence. However, when fluorocarbon compounds were applied in addition to an adequate hydrophobing system fixed with metal salts no further improvement with respect to water resistance was observable.

Bearing the drawbacks of Zr-salt-fixation in mind, the attempts were concentrated on the improvement of the Al-salt alternative. So, starting from a recipe based on a glutardialdehyde / syntan tanning system and replacing one retanning agent (polymeric compound) with vegetable tannins, no significant changes of the water-resistance of the resulting leathers were observed. The point at which hydrophobing agents were employed in the manufacturing procedure had only a slight influence on the penetration time of a water drop (table 6). A considerable differentiation of the test leathers was not possible even by Maeser-values. A possible explanation for that might be the composition of the recipe used and the specific experimental conditions as well.

Test procedure	**Reference recipe**	**Hydrophobing prior to retanning**	
		partly	**completely**
Static water uptake			
Water uptake (%)			
after 30 min	23,2	31,1	31,6
after 2 h	33,2	38,6	39,9
Penetrometer (Bally)			
Water penetration (min)	115 >480	> 480	> 480
Water uptake % in 1 h	5,1	5,8	6,0
Water uptake % in 2 h	7,2	7,7	7,7
C. f. to water spotting	150 µl	150 µl	150 µl
Wetting time (min)	63	not observable	not observable
Penetration time (min)	355	480	480
Assessment			
immediately	dark spot	dark spot	dark spot
after 16 h	no changes	no changes	no changes

Table 6: The influence of the application point of hydrophobing agents

The uniformity of hydrophobing seems to constitute a problem even with optimized test conditions (mechanical conditions, running time, pH). Both over the area of a hide and between hides of the same batch partly substantial differences are likely. This fact is illustrated in the following tables (tables 7 and 8) by means of the test results of two different recipe-options. The values in accordance with the standardized sampling area are compared with those corresponding to other three different locations:

- S1 – shoulder
- S2 – upper part of the butt
- S3 – belly, in vicinity to standardized sampling location

The consistency of hydrophobing through the leather cross-section was not tested, because at the given thickness it proved to be impossible to get usable split layers.

In case of a good waterproofness the test procedure using the Bally-penetrometer permits no differentiation between the different leathers. Even an increase of the compression amplitude up to 15 % can be inappropriate if tests have to be interrupted in the end of a working day (8 h).

Test procedure	**Al-salt-fixation**			
	Standardized area	**S1**	**S2**	**S3**
Static water uptake				
Water uptake (%)				
after 30 min	16,9	23,7	25,6	23,5
after 2 h	30,8	33,6	40,5	37,2
Penetrometer (Bally)				
Water penetration (min)	>480 137	68	212	146
Water uptake % in 1 h	4,7	5,8	5,8	7,7
Water uptake % in 2 h	5,3	7,5	7,4	8,4
Maeser				
Water penetration (flexes)	1150	760	1800	900
Water uptake % (5700 fl.)	6,4	5,1	4,4	5,7

Table 7: Uniformity of hydrophobing over the area of a hide (Al-salt-fixation)

Test procedure	**Zr-salt-fixation**			
	Standardized area	**S1**	**S2**	**S3**
Static water uptake				
Water uptake (%)				
after 30 min	19,9	17,1	17,7	19,7
after 2 h	30,9	32,4	31,9	41,4
Penetrometer (Bally)				
Water penetration (min)	>480	>480	>480	>480
Water uptake % in 1 h	4,7	4,6	4,7	4,6
Water uptake % in 2 h	5,8	6,4	6,7	6,6
Maeser				
Water penetration (flexes)	12390	>45600	>45600	8400
Water uptake % (5700 fl.)	1,6	2,2	2,5	2,5
Water uptake % (11400 fl.)	2,6	3,0	3,4	3,3

Table 8: Uniformity of hydrophobiing over the area of a hide (Zr-salt-fixation)

Additionally, it was investigated whether the obtained hydrophobing is long-lasting even after repeated treatment with water. After the initial test the specimens were gently dried, reconditioned in standard atmosphere (23 °C / 50 % r. h.) and tested again (2 – 3 repetitions). Depending on the fixing mode of the hydrophobic system the results showed to be contrary. For leathers manufactured using Al-salt-fixation no significant changes were observable. The realised Maeser flexes are constantly low (ca. 1000), while the water resistance measured with Bally-penetrometer reached test periods > 480 minutes. Presenting higher values, in case of Zr-salt-fixed hydrophobing systems (Table 9) variations could be better noticed. It is questionable, if these variability is caused by changes in the degree of hydrophobing or if it has to be attributed to failings of the test procedure.

Test procedure/ Number of repetitions	**Hide B**				**Hide A**		
	Initial	**1**	**2**	**3**	**Initial**	**1**	**2**
Static water uptake							
Water uptake (%)							
after 30 min	20,0	18,9	19,8	20,8			
after 2 h	30,9	27,9	31,6	30,8			
Penetrometer (Bally)							
Water penetration (min)	>480	>480	>480	>480	>480	>480	>480
Water uptake % in 1 h	4,7	5,0	5,2	5,2	5,1	4,6	5,2
Water uptake % in 2 h	5,8	6,0	6,6	6,5	6,1	7,0	6,8
Maeser-tester							
Water penetration (flexes)	12390	15200	8390	7300	22200 22800	13070 >45600	38800 >45600
Water uptake % (5700 fl.)	1,6	2,0	2,2	2,4	2,1	2,6	2,9
Water uptake % (11400 fl.)	2,6	2,6	2,9	3,3	2,9	3,4	3,7

Table 9: Durability of hydrophobing in case of Zr-salt-fixation

The time has a positive effect on the hydrophobic properties of leather. Testing leathers at well-defined time intervals a steady improvement was noticed. So, leather made hydrophobic (Al-salt-fixation) resisted to water penetration (penetrometer) immediately after manufacturing for 99 minutes, but 8 weeks later 200 minutes could be realised, reaching > 480 minutes after 12 weeks.

3.3.2 Influence of drying

Three different drying modes were used: two by means of vacuum but with different parameters (55 °C, 42 °C) and one using a chamber toggle dryer. Drying acts on hydrophobing of chrome-free leather in a way comparable with that already known for waterproof chrome tanned leather. The effect of the leather structure on the hydrophobic characteristics as well as on the ventilating properties is illustrated in table 10. The compactness of the fibre structure results in reduced water vapour permeability and water uptake and in improved water resistance irrespective of the recipe composition.

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^2h)	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									
Water uptake (%)									
after 30 min	90,3	112,4	142,1	19,7	22,1	28,2	24,0	18,3	23,1
after 2 h	93,7	118,6	148,8	36,9	39,9	36,4	34,7	31,3	35,5
Penetrometer (Bally)									
Water penetration (min)	10	10	11	138	122	117	108	81	21
Water uptake % in 1 h	71,3	94,3	100,4	7,7	9,0	7,9	7,0	7,7	9,3
Water uptake % in 2 h				12,5	15,4	11,2	12,9	12,5	

Table 10: Different drying procedures in comparison

4. Conclusions

The results of the performed investigations on particular processes of hydrophobic chrome-free leather manufacture may be summarized as follows:

- In preparing pelts experiments two liming/pickling systems proved to be the best with respect to hydrophobing: calcium hydroxide/sodium sulphide liquor combined with a pickling float on the basis of sodium chloride/formic acid/sulphuric acid as well as the same liming in combination with a pickling float on the basis of “non-swelling” sulphonic acids. In both cases pretannage was made with modified glutaraldehyde and syntan.
- In case of chrome-free tanned leather a metal-salt-fixation of hydrophobing agents is indispensable.
- A further improvement of an efficient waterproofing obtained by means of metal-salt-fixation can not be achieved by additional treatment with fluorocarbon compounds.
- Trials to improve the possibilities for hydrophobing agents to attach to the leather fibre by means of different other auxiliaries were unsuccessful.
- In certain cases the substitution of polymeric retanning agents by vegetable tanning agents can improve hydrophobing to some extent.
- As expected, the effect of drying conditions on the degree of waterproofness was significant. At the same time, due to changes occurred to the leather structure, an influence on water vapour permeability could be observed as well.
- With zirconium-salt-fixation of the hydrophobing chemicals problems arose with pH and difference figure of the resulting leather, but could be solved. The achieved hydrophobic effect showed to be durable, but the uniformity over the whole hide was not optimal.
- Analogous to chrome tanned waterproof leathers hydrophobing increases with time.

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