UNEWS. Leather

Informative Magazine, Nº 29

WATERPROOFING PRODUCTS 2019

CROMOGENIA UNITS

YOUR SPECIALIST FOR SPECIALTIES

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PRESENTATION

The second technical meeting of 2018 was held at the H10 Marina hotel of Barcelona. The range of waterproofing products developed by Cromogenia Units was presented at this meeting.

Designed, edited and published by the Leather Department of Cromogenia Units.
This magazine is addressed to all technicians, representatives, customers and friends who wish to stay informed about our new products as we move forward.
For more information or suggestions, please contact: **oballus@cromogenia.com**

Waterproofing products

The increasingly strict requirements for waterproofed articles have led CROMOGENIA UNITS S.A. to develop new products with different organoleptic properties and excellent results in waterproofing tests.
This issue of Unews presents the new range of waterproofing products and their main characteristics to help both technicians and customers select the best waterproofing product for each type of article.

1. BASIC PRINCIPLES

Waterproofing includes two types of treatment: water repellent leathers and fully waterproofed leathers. The former type is used in treatments where the product covers the surface of the fibers (without chemical bond) and the final leather repels water droplets. The latter type is used in fully waterproofed leathers, where the product must be chemically bound to the fibers. These leathers have high levels of water repellency (they resist water penetration) and water vapor permeability. The different water-related behaviors of water repellent leathers vs. fully waterproofed leathers are shown in Figure 1.

Figure 1. Water repellent leather (left) and fully waterproofed leather (right).

In order to obtain a waterproofed leather, the surface tension of the leather fibers must be changed to make it lower than the surface tension of water, thus preventing moistening. Waterproofing products act by surrounding the collagen fibers of a hydrophobic layer without obstructing the interfibrillary pores so as to obtain a high level of water vapor permeability.

Waterproofing Tests

Waterproofing products contain a hydrophobic part, which provides water repellency to the leather, and a hydrophilic part, which allows it to be emulsified in water (Figure 2).

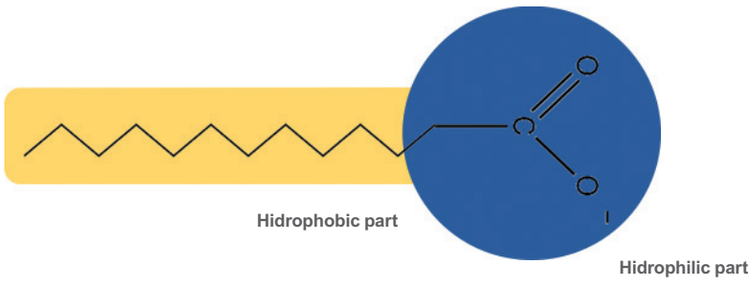


Figure 2. Nature of waterproofing products.

Classification of waterproofing products according to their hydrophobic part:

- **Acrylate-based polymers or copolymers**
- **Phosphoric esters**
- **Combination of silicone with oils or emulsifiers**
- **Fluorocarbonated chemicals**

2. WATERPROOFING TESTS

The main waterproofing tests are:

· BALLY - IUP 10-1 (ISO 5403-1:2011_ EN ISO 5403-1)

This test is mainly used in Europe and measures the time until water penetrates a leather sample, as well as the dynamic absorption of the leather.

· MAESER - IUP 10-2 (ISO 5403-2:2011_EN ISO 5403-2)

This test is mainly used in the US. The number of flexes until water penetrates the leather (usually 15,000 flexes) is determined. This test is stricter than the BALLY test.

Waterproofing Tests

· WATER VAPOR PERMEABILITY – IUP 15 (ISO 14268:2012_EN ISO 14268)
This measures the ability of leathers to allow the passage of water vapor through its fibers without retaining it.

The equipment used for each test is shown in Figure 3.

Figure 3. Bally (left), Maeser (middle) and water vapor permeability (right).

Some of the waterproofing requirements for footwear and protection, as well as for GORE-TEX, are shown in Table I.

Table I. Footwear requirements.

TEST	REQUIREMENTS FOR FOOTWEAR AND PROTECTION METHOD EN 344:1992		GORE-TEX REQUIREMENTS		
Tear load	Min. 120 N		-		
Tensile strength (only suede)	Min. 15 N/mm^2		-		
Water absorption at 60min	Max. 30%		-		
BALLY	Water time penetration	Min. 60min	> 2h		
	Water penetration at 90 min	Max. 2g			
Water vapor permeability	Min. 8mg/h.cm^2		Article	<2,6mm	>2,6mm
			Nubuck	7.5mg/cm^2.h	5.0mg/cm^2.h
			Split	10.0mg/cm^2.h	7.5mg/cm^2.h
			Full grain	5.0mg/cm^2.h	3.5mg/cm^2.h
pH Value	Min. 3.5		-		
Difference figure (only if pH<4)	Max. 0.7		-		
Wicking test	-		1cm after 2h		

The key products of some waterproofed articles and the waterproofing values obtained are shown in Table II.

Table II. Articles and waterproofing values

Reference	Article	BALLY		MAESER		Water vapor permeability ($mg/cm^2.h$)
		Penetration time	Water absorption (2h)	Maeser flexes	Water absorption (15,000 flexos)	
0117 WP	Floater	4h 30'	10%	x	x	9.0
0217 WP	Nubuck	2h 30'	10%	30,000	11%	7.9
0317 WP	Military boot	4h 35'	7%	>100,000	8%	11.4
0417 WP	Split	>24h	5%	>50,000	9%	10.5

REPELAN PSH-171 was used for the WATERPROOFED FLOATER article.

REPELAN HO, REPELAN WR-25 and REPELAN PSH-200 were used for the WATERPROOFED NUBUCK article.

REPELAN HO and REPELAN HC were used for the MILITARY BOOT article.

REPELAN HO, REPELAN HC and REPELAN WR-25 were used for the WATERPROOFED SPLIT article.

For more information about these formulas, please contact: oballus@cromogenia.com, indicating the reference shown in Table II.

3. RANGE OF WATERPROOFING PRODUCTS BY CROMOGENIA UNITS S.A.

Polymers and silicones are currently the most frequently used waterproofing products.

CROMOGENIA UNITS S.A. has a wide range of waterproofing products, from products designed for soft articles (e.g., phosphoric oils) to products for reinforced articles (e.g., silicone polymers).

The waterproofing products, their composition and their main waterproofing and organoleptic characteristics are shown in Table III.

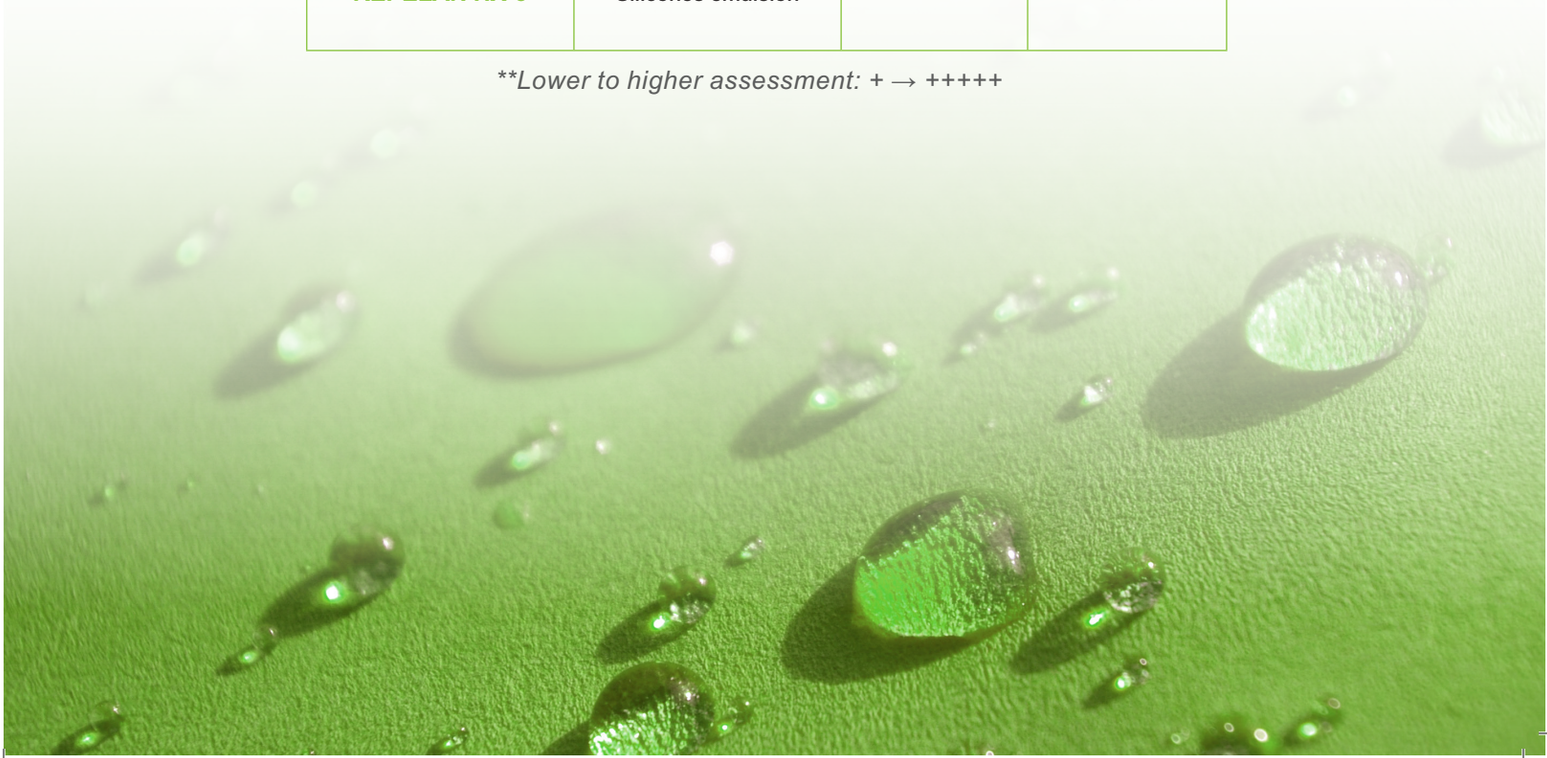
WATERPROOFING PRODUCTS

Range of Waterproofing Products

Table III: CROMOGENIA product range

PRODUCT	NATURE	TOUCH	WATERPROOFING
REPELAN HO	Silicone emulsion with special additives	+	++++
REPELAN HC	Maleic polymer	+++	-
REPELAN HF	Synthetic oils with silicone	+++	+++
REPELAN PSH-171	Acrylic copolymer	+++	++
REPELAN PSH-200	Acrylic copolymer with special additives	+++	++++
REPELAN WR-10	Phosphoric esters	+++++	+
REPELAN WR-25	Phosphoric esters	++++	+
REPELAN HX-3	Silicones emulsion	-	+++++

***Lower to higher assessment: + → +++++*



Range of Waterproofing Products

REPELAN HO is a fatliquoring-waterproofing product based on silicones with special additives, and is particularly recommended for reinforced articles such as military boots. REPELAN HO has high waterproofing ability and is therefore highly suitable for leathers undergoing the Maeser and Bally tests.

REPELAN HC unlike the rest of the products of this range, is not waterproofing by itself but rather helps the rest of waterproofing products reach the interior of the leather fibers, and is therefore equally important within the process.

REPELAN HF is a fatliquoring-waterproofing product based on synthetic oils with silicones, and provides the leather with a soft feel and a high waterproofing effect. It has the advantage that it can be used in all types of articles: split, full grain, suede.

REPELAN PSH-171 is a retanning-fatliquoring product that provides the leather with a high degree of water repellency when the leather is fixed in a separate bath with metal salts (chromium, aluminum, zirconium). Particularly designed for waterproofed or washable leathers and hides.

REPELAN PSH-200 is a retanning-fatliquoring acrylic polymer with additives and is particularly designed for leathers with high waterproofing requirements. Leathers treated with REPELAN PSH-200 have a good feel and excellent fullness.

REPELAN WR-10 y REPELAN WR-25 are products based on phosphoric esters. They provide high fullness and excellent dye levelness. They have high light and heat fastness and can be used alone or combined with other fatliquoring agents at the end of the process, thus providing a natural, silky feel to suede articles.

REPELAN HX-3 is a new waterproofing product based on emulsified silicones. It is particularly designed for leathers with high waterproofing requirements that must undergo the Maeser or Bally tests. We recommend using 1-2% of this product together with REPELAN PSH-200 or REPELAN HO.

4. CLASSIFICATION OF WATERPROOFING PRODUCTS ACCORDING TO THEIR CHEMICAL STRUCTURE

4.1 ACRYLATE-BASED PRODUCTS

PRODUCTS: **REPELAN PSH-171, REPELAN PSH 200, REPELAN HC**

These products contain an acrylate-based polymer to which an alkydic chain (R) is added. The acrylate provides the retanning properties and the alkydic chain provides the fatliquoring properties, thus lending very different properties depending on the proportion of each. Its structure is shown in Figure 4.

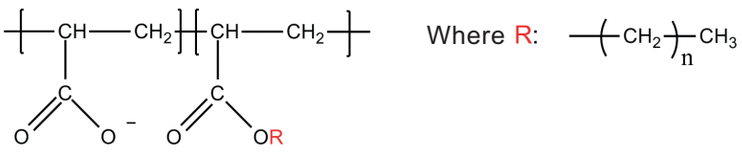


Figure 4. Structure of an acrylate-based waterproofing product.

As shown in Figure 5, these products can bind to chromium (Cr)or to the collagen fibers (-NH_3^+) through their carboxylic groups.

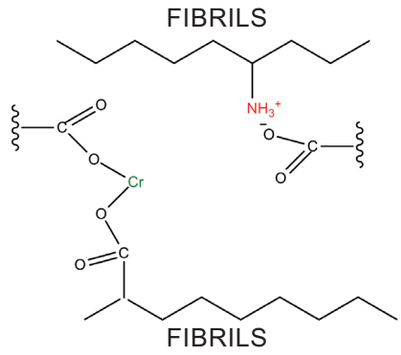


Figure 5. Binding mechanism of acrylate-based waterproofing products.

Maleic polymers have a similar structure to that of acrylic polymers and therefore we consider them within the same family.

These products contain on one hand a fatliquoring agent and, on the other hand, the maleic polymer. In Figure 6 the structures of the two components are shown.

The mechanism of attachment to leather would be the same as in the case of acrylate-based products, that is, they are fixed thanks to their carboxylic groups to both chromium and collagen fibers.

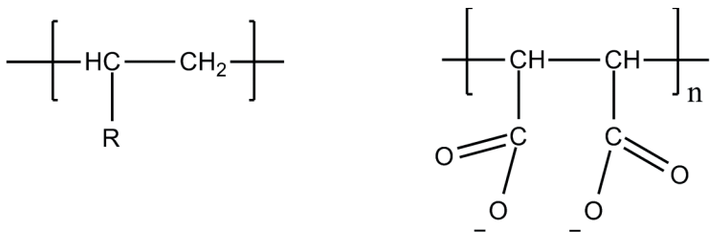


Figure 6. Structure of the maleic polymer.

4.2. PHOSPHORIC ESTERS

PRODUCTS: **REPELAN WR-10, REPELAN WR-25**

Phosphoric esters are formed by a phosphorus atom surrounded by four oxygen atoms and one alkyl group. These groups form complexes with chromium (Figure 7), and the alkydic chain (R) lends the leather a hydrophobic character.

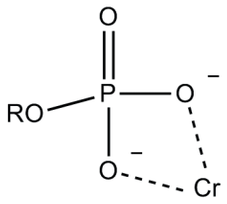


Figure 7. Structure and chromium-binding mechanism of phosphoric esters.

Classification of Waterproofing Products

4.3. SILICONE-BASED PRODUCTS

PRODUCTS: **REPELAN HO, REPELAN HF and REPELAN HX-3**

Silicones are formed by Si and O atoms to which different groups are added to obtain different properties. These products can bind to collagen through the oxygen atoms. Silicon atoms and radicals thereof, which are usually apolar, are oriented around the fibers to lend the leather a hydrophobic character (Figure 8).

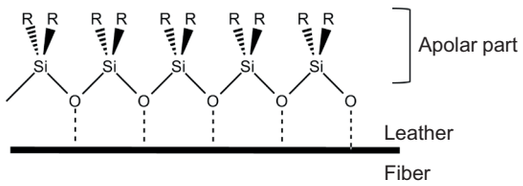


Figure 8. Structure and binding mechanism of silicone-based products.

4.4. FLUOROCARBONATED COMPOUNDS

These are organic compounds that have fluorine atoms in their structure. Their leather-binding mechanism is shown in Figure 9.

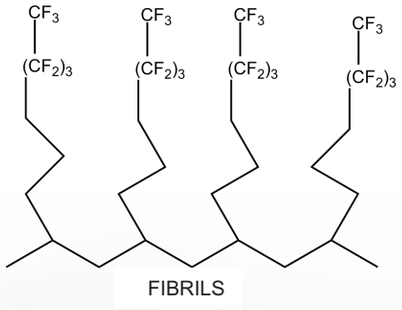


Figure 9. Structure and leather-binding mechanism of fluorocarbonated compounds.

The main difference between fluorocarbonated compounds and silicone-based compounds lies in their ability to repel dirt and oils.

While silicone-based products only have waterproofing properties, fluorocarbonate-based products also have oil repellent properties. The waterproofing and oil repellent properties of each compound are shown in Figures 10 and 11.

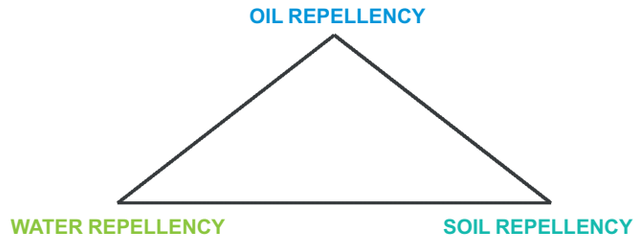


Figure 10. Waterproofing and oilproofing properties of fluorocarbonate-based products.

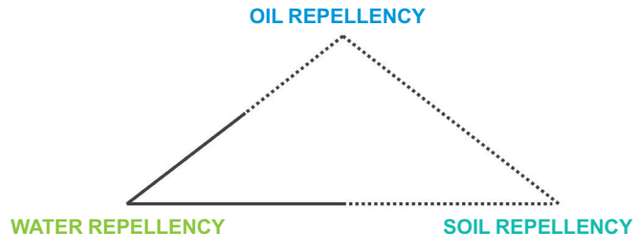


Figure 11. Waterproofing and oilproofing properties of silicone-based products.

5. FACTORS INFLUENCING WATERPROOFING

Waterproofing is a delicate process that must be controlled from the beamhouse to finishing.

Here are a few tips to obtain good-quality waterproofed leathers.

Factors Influencing Waterproofing

5.1. RAW MATERIAL

The type of tanning has a great influence on the waterproofing process.

Wet blue leathers are considered as relatively hydrophobic, whereas wet white leathers are hydrophilic and therefore much harder to waterproof.

Figure 12. Wet blue, hydrophobic leather.

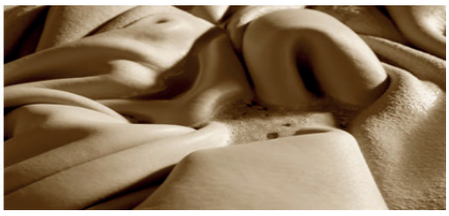


Figure 13. Wet white, hydrophilic leather.

5.2. BEAMHOUSE PROCESSES

Because surfactants and salts reduce waterproofing, minimum quantities of these products should be used in beamhouse processes.

5.3. NEUTRALIZATION-ANIONIZATION

For the leather to be neutralized, products must penetrate the entire section, the pH must be high enough to prevent leather-product interactions, and neutralization must be deep and effective. For complete neutralization-anionization, and hence correct waterproofing, we recommend using naphthalene-sulfonic auxiliary products such as RETANAL A-4, RETANAL HD or RETANAL A-40.

These products reduce the isoelectric point (pI) of the leather and allow neutralization at pHs lower than usual, thus ensuring complete product penetration at low pHs.

5.4. RETANNING

It is recommended not to use hydrophilic products in retanning processes.

CROMOGENIA UNITS S.A. has studied its retanning products according to their ability to reduce or affect the waterproofing results.

Some of the products that may be used when retanning waterproofed articles are shown below:

Acrylic resins:
RETANAL RC-200
RETANAL CLE
RETANAL RCN-40
RETANAL RST

Phenolic retanning agents and sulfones:
RETANAL BDF
RETANAL SUL
RETANAL XD
RETANAL A FF

Melamines / Dicyandiamides:
RETANAL MV EXTRA
RETANAL DIC
RETANAL MEL
RETANAL D-57

While these are some of the products recommended for retanning waterproofed articles, **CROMOGENIA UNITS S.A.** has a wide range of retanning products and all of them have been studied.

5.5. DYEING

Concentrated dyestuffs are recommended. Because salts are hygroscopic products (products that absorb water), they should be avoided in waterproofing processes.

5.6. FATLIQUORING

Fatliquoring products particularly designed for the processes must be used: fatliquoring products that incorporate emusifiers must not be used.

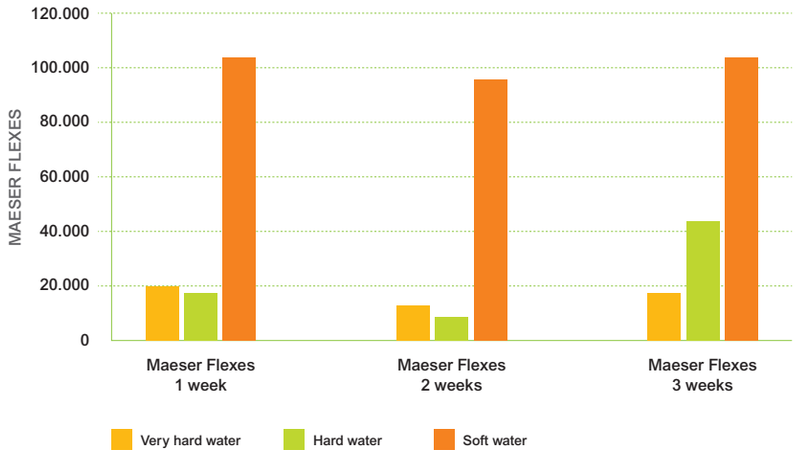
5.7. OTHER

Electrolytes, salts: Ions attract water, and therefore should be avoided. In any event, washing helps eliminate this type of products.

Water hardness: The hardness of the water used during the process has a great influence on the waterproofing process. The influence of water in the Maeser test is shown in Graph 1.

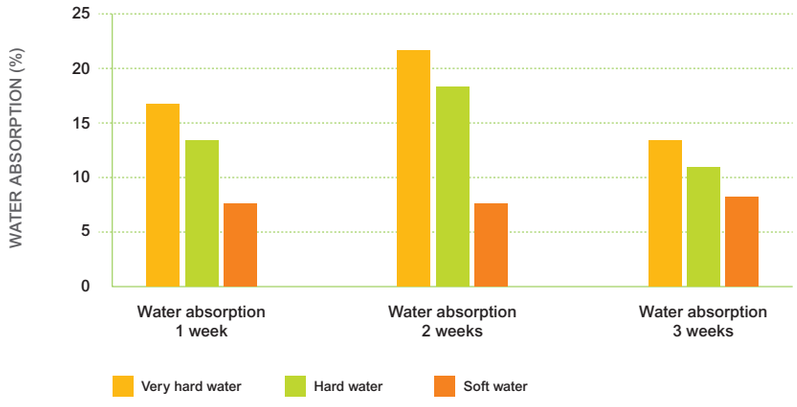
Factors influencing waterproofing

If the water used is very hard, waterproofing is reduced from 100,000 flexes to approximately < 20,000 flexes in the Maeser test, measured one week after drying the leather. This tendency is observed over time.



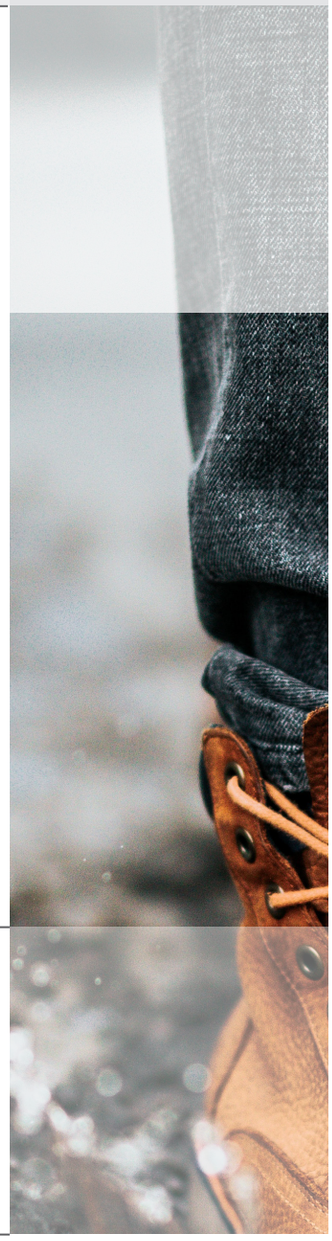
Graph 1. Time-related waterproofing results according to water hardness.

Water hardness affects both flexes and water absorption. Graph 2 shows the increase of water absorption with increased hardness, from an absorption of approximately 8% with soft water to an absorption of approximately 17% with very hard water, measured one week after drying the leather.



Graph 2. Time-related water absorption according to water hardness.

On account of reduced waterproofing in both flexes and water absorption when hard waters are used, we recommend using waters as soft as possible.



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