

Absorption and Water Resistance of Natural Leathers Finished with Ecological Touch Emulsion in the Final Dressing

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An ecologic emulsion for leather touch was prepared by emulsifying a mixture of beeswax, lanolin and triethanolamine monostearate stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide. It has a homogenous appearance and particle sizes ranging between 2 and 4 μm . Used in amounts of 20-100% in polyurethane, nitrocellulose or acrylic final dressing, it improves feel and water resistance of finished leather. For a given amount and time, this wax emulsion leads to lower amounts of water absorbed than a silicone oil emulsion used as control. The lowest values for water absorption in leather were obtained by adding the emulsion in polyurethane dressing, and the highest values – in acrylic dressing.

Keywords: ecologic wax emulsions, leather finishing, final dressing, waxy feel

Finishing is the last operation in natural leather processing. It imparts the appearance and the value to the finished product and has as goal the embellishing, providing luster and a pleasant feel, covering defects and forming a surface layer to protect the leather during wear [1-3].

The following auxiliary materials are used in the composition of disperse finishing systems: pigments, binders, dyes, waxes, preservatives, plasticizers, thickeners, fillers, penetration agents [4-6].

The handle modifiers (wax and oil emulsions) are used to change the feel of the finished product, which can be oily, waxy or silky, as well as to improve the physical properties of the finished leather [7-10].

Both the natural and synthetic waxes used in natural leather finishing reduce the stickiness of thermoplastic binders and lead to a pleasant feel or to an effect of darkening of colour (in waxed leather assortments, fashionable now) [11].

Natural waxes, such as beeswax, are mixtures of esters with varying amounts of free acids and alcohols and alkanes.

Emulsion stability – their ability to maintain the initial properties on time – [12-16] is provided by emulsifiers. They are amphiphilic compounds which interact both with oil and water, producing the decreasing of the interfacial tension and preventing the coalescence of droplets. [17, 18]

The best wax emulsion stabilizing agent is nonylphenol ethoxylated with 9 moles of ethylene oxide, but its use in industrial products is forbidden by the Directive 76/769/EL/2003, as a consequence of assessment of its ecotoxicity which shows a biodegradability of only 30%. An alternative to the ethoxylated nonylphenol are ethoxylated fatty alcohols, 100% biodegradable [19, 20].

The paper presents the preparation, characterization and testing of a wax emulsion to be used in the final dressing for the dry finishing of natural leather and the characterization of the film-coated leather in terms of water absorption and water resistance [8-10, 21].

Experimental part

Materials and methods

- Beeswax (Bucharest) – solid substance, with specific odour, yellow colour, melting point 62-65°C;

- Lanolin (Bucharest) – semisolid greasy compound, with specific odour, light yellow colour, melting point 38-42°C;

- Stearin (Bucharest) – solid substance, with specific grease odour, white colour, melting point 69-70°C;

- Triethanolamine (Bucharest) – colourless liquid, melting point – 20-21°C, boiling point – 277-279°C, density – 1.124 g/cm³, refractive index – 1.4852;

- Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (Bucharest), density – 0.95 g/cm³ at 40°C, pH (10% solution) – 7-8.

- Roda-cryl 87 (Germany), acrylic binder for ground coat, dry substance – 34.50%, pH (10% solution) – 6.0, Ford cup viscosity F4 – 14, density – 1.025 g/cm³.

- Roda-pure 302 (Germany) polyurethane binder for ground coat: dry substance – 30.87%, pH (10% solution) – 7.5, Ford cup viscosity F4 – 15, density – 1.076 g/cm³.

- Roda wax MONO (Germany), wax emulsion for ground coat: dry substance – 36.87%, pH (10% solution) – 4.2, Ford cup viscosity F4 – 12, kinematic viscosity, cSt – 8.97, density – 0.957 g/cm³.

- Roda-pure 5011 (Germany), polyurethane binder used as a fixing agent (final dressing) for finishes applied to natural leather: dry substance – 40%, pH (10% solution) – 5.5, Ford cup viscosity 4 – 7, density – 1.053 g/cm³.

- Roda lacquer 93 (Germany), nitrocellulose emulsion used as a fixing agent (final dressing) for finishes applied to natural leather: dry substance – 15%, pH (10% solution) – 5.5, Ford cup viscosity F4 – 125, flash point – 82°C.

- Medacril EFP34 (Medias), acrylic copolymer based binder with an addition of epoxy resin used as a fixing agent (final dressing) for finishes applied to natural leather: dry substance – 39%, pH (10% solution) – 5.5, Ford cup viscosity F4 – 12, kinematic viscosity, cSt – 7.05, density – 1.033 g/cm³.

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Characteristic/wax	RODA feel KTA 950	AGE 7 wax
Dry substance, %	12.39	19.96
pH	5.5	7.3
Ford cup viscosity $\Phi 4$, s	13	27
Kinematic viscosity, cSt	8.45	10.48
Density, g/cm ³	0.948	0.975

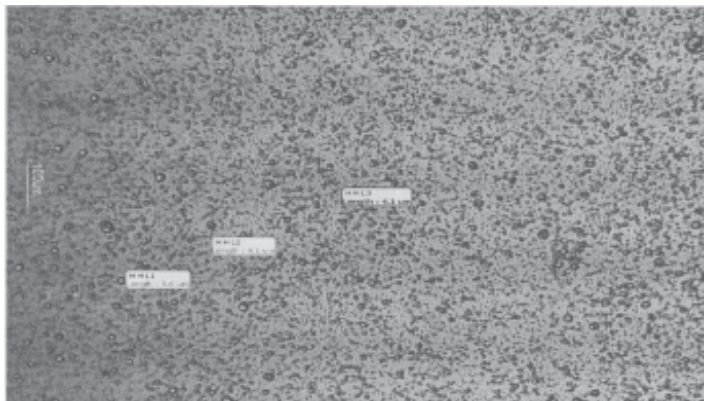


Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF STUDIED WAX EMULSIONS

Fig. 1. Optical image, 100X, of AGE 7 wax emulsion

Operation	Composition of dispersion/Method of application
Applying dispersion I (basecoat)	100 g/L pigment paste 30 g/L wax emulsion 300 g/L acrylic dispersion or 150 g/L acrylic dispersion and 150 g/L polyurethane dispersion 570 g/L water Application by spraying (2 passes of dispersion I)
Intermediate pressing	In hydraulic press using mirror or steam plate, parameters: - temperature – 50-60°C - pressure – 50-100 bar
Applying dispersion I	By spraying (2-3 passes of dispersion I)
Applying final dressing (fixing)	Emulsion/dispersion with the following composition: 700 g/L aqueous nitrocellulose emulsion or acrylic or polyurethane dispersion 20-100 g/L aqueous wax emulsion for feel (Wax AGE 7) or 20-100 g/L aqueous wax emulsion for feel (Roda feel KTA 950) 200-280 g/L water Application by spraying (2 passes of final dressing)
Final pressing	In hydraulic press using mirror plate, parameters: - temperature – 70-80°C - pressure – 50-100 bar

Table 2
FRAMEWORK TECHNOLOGY FOR DRY FINISHING OF BOVINE LEATHERS IN BLACK AND COLOURED BOX NATURAL GRAIN ASSORTMENT

- Roda feel KTA 950 (Germany), silicone oil emulsion used as handle modifier: dry substance – 12%, pH (10% solution) – 5.5.

- Wax emulsion AGE 7 used as handle modifier (made from beeswax, lanolin and triethanolamine monostearate and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide: dry substance – 12%, pH (10% solution) – 7.0.

Wax emulsion viscosities were determined with Ubbelohde KPG capillary viscometers, Schott, Jena^{er} Glaswerk Schott & Gen. Mainz, Germany [12, 13].

The physico-chemical properties of the wax emulsion AGE 7 and imported product RODA feel KTA 950 tested as control handle modifier are shown in table 1

Optical microscopy images were captured using a Leica stereomicroscope S8AP0 model with optic fiber cold light source, L2, with three levels of intensity. [26] Magnifying was 100X.

The microscopic image obtained for the prepared emulsion is presented in figure 1.

Wet finished natural grain box bovine leathers, non-hydrophobized (P1-P30 samples) and hydrophobized (H1-H10 samples) were dry finished by the framework technology presented in table 2, using the prepared AGE 7 emulsion and Roda feel KTA 950 as control in the final dressing (nitrocellulose, acrylic or polyurethane) [21-25].

Water absorption was determined for finished leathers using a Bally penetrometer, according to SR EN ISO 5403:2003 for natural grain box bovine leathers [27-28]. Water resistance of the finishing films (after final pressing) was assessed by the water drop method, simulating rain, 24 h after drop deposition.

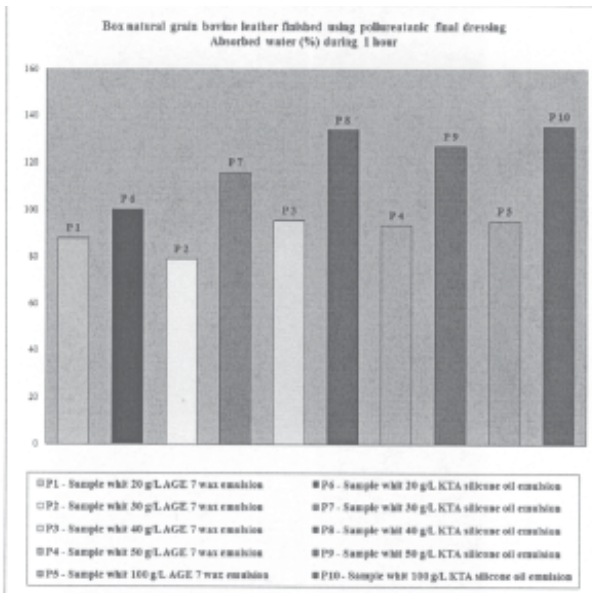
Results and discussions

Both AGE 7 handle emulsion and Roda feel KTA 950 are white fluids having a homogenous appearance.

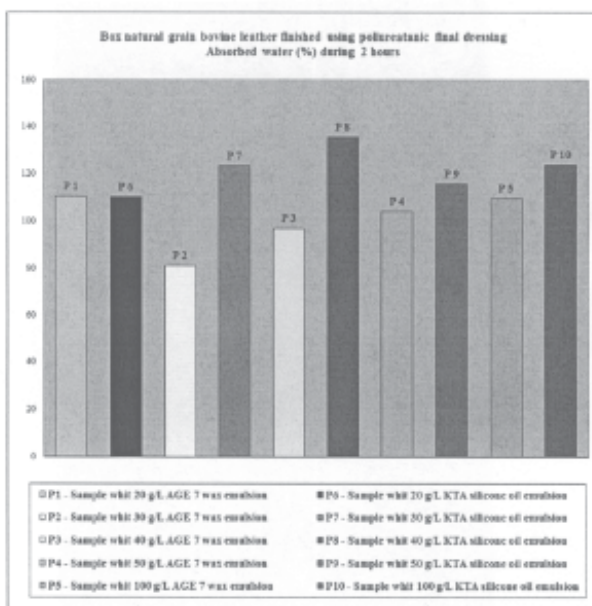
Figure 1 shows that AGE 7 wax emulsion has droplets of different size, as expected, and most of them have diameters ranging between 4 and 6 μm , distributed relatively uniform within the emulsion mass. To differentiate the two phases of the emulsion, a methyl red solution was used.

The AGE 7 emulsion was added into the nitrocellulose, acrylic or polyurethane final dressing, and Roda feel K 950 silicone oil emulsion, the most commonly used product for water resistant leathers having agreeable handle (silky), was used as control.

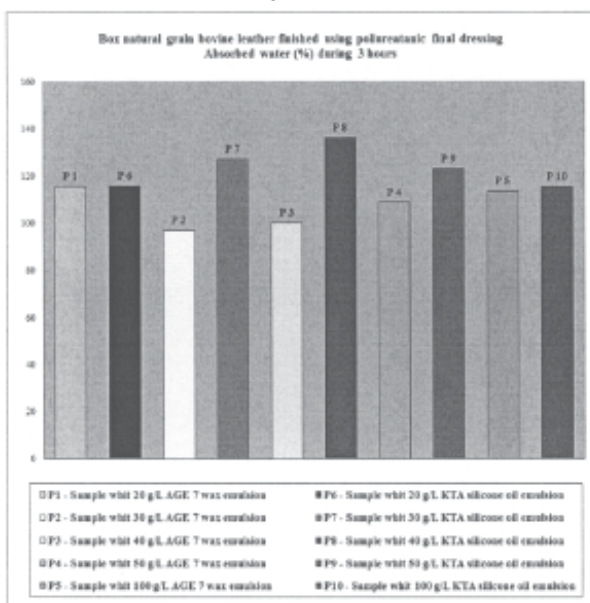
Figures 2a-c present the amounts of water (%) absorbed during 1, 2 and 3 h by the leather samples P1-P10 finished with polyurethane final dressing containing the prepared emulsion and the control in the five ratios specified on figures.



a



b



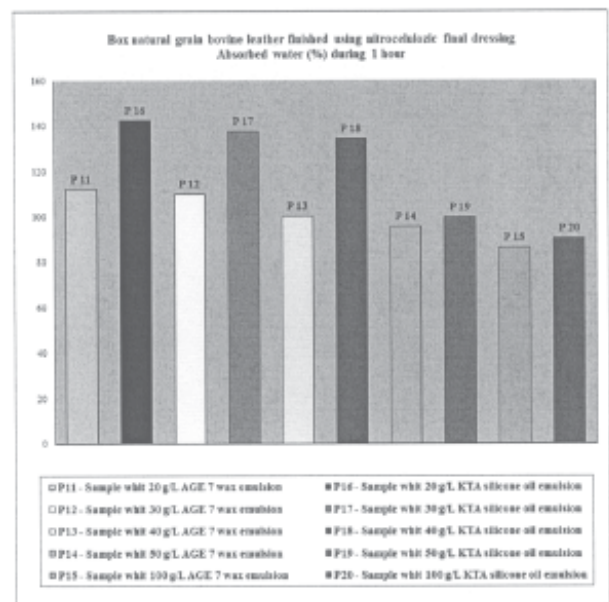
c

Fig. 2a-c. Water absorption for the specified final dressing, handle modifiers and time

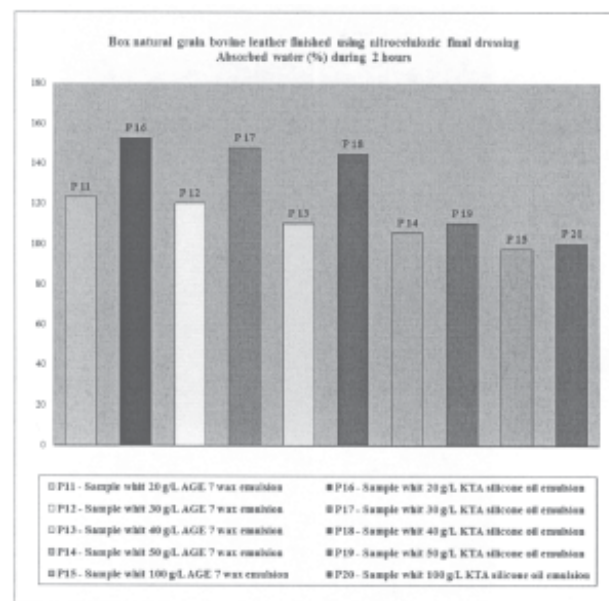
Figures 2a-c show that there is a decrease of water amounts absorbed by leather, at a given absorption time, with the increasing of handle modifier amount for both emulsions, but the values are lower for all the five proportions and three times used when the handle modifier is AGE 7. The differences are high – 35-40% – when handle emulsion amounts are low (20, 30 and 40 g/L) and decrease for 50 g/L (by 5%), and the values are much closer for 100 g/L, the differences not exceeding 3%.

Figures 3a-c present the amounts of water absorbed during the same periods of times by the samples P11-P20 finished with the nitrocellulose final dressing using the prepared and the control emulsions in five specified ratios.

In comparison with the data of the previous figure, it is found that, when using nitrocellulose dressing, water absorption values are slightly higher for a given time and handle emulsion than as expected, knowing that the polyurethane final dressing gives the highest water resistant finished leather. But the dependency on the nature of the handle modifier, the amount used and time of absorption is the same as in the previous case.



a



b

Fig. 3 a-b. Water absorption for the specified final dressing, handle modifiers and time

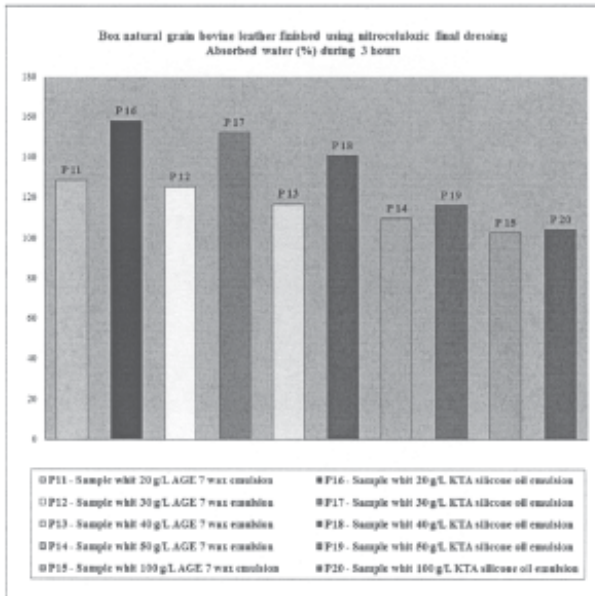


Fig. 3c. Water absorption for the specified final dressing, handle modifiers and time

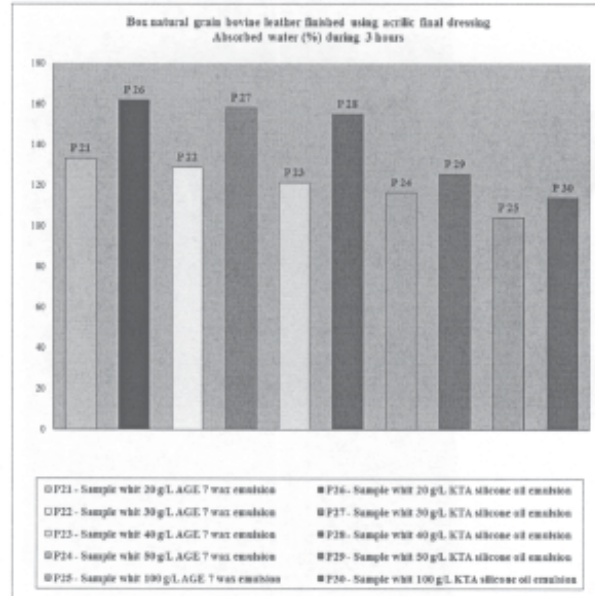


Fig. 4c. Water absorption for the specified final dressing, handle modifiers and time

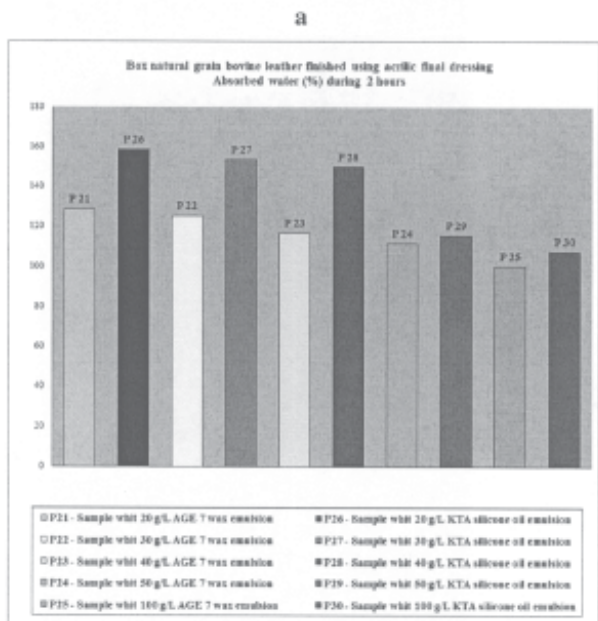
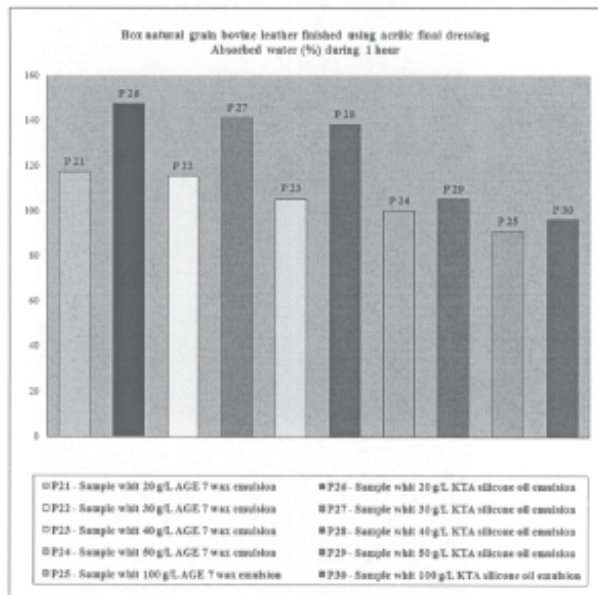


Fig. 4a-b. Water absorption for the specified final dressing, handle modifiers and time

Figures 4a-c present the water absorption, under the same conditions, for the samples finished with the acrylic final dressing containing the prepared emulsion and control in the five specified ratios – samples P21-P30.

In the case of acrylic dressing variations in the amounts of water absorbed with the amount of handle modifier, its nature and the absorption time are the same, but the quantities of water absorbed in leather are even higher than when using nitrocellulose dressing.

Figures 5a-c present the water amounts absorbed by H1-H10 hydrophobized samples finished using polyurethane final dressing containing AGE 7 emulsion and the control one in the same ratios as for the non-hydrophobized ones.

They absorb 9-13 times less water than samples in figure 2a-c finished using the same final dressing, but the variation on the nature of the handle modifier, added amount and water contact time is preserved.

Water drop test also shows that the leather finished using acrylic dressing with the two handle modifiers shows the

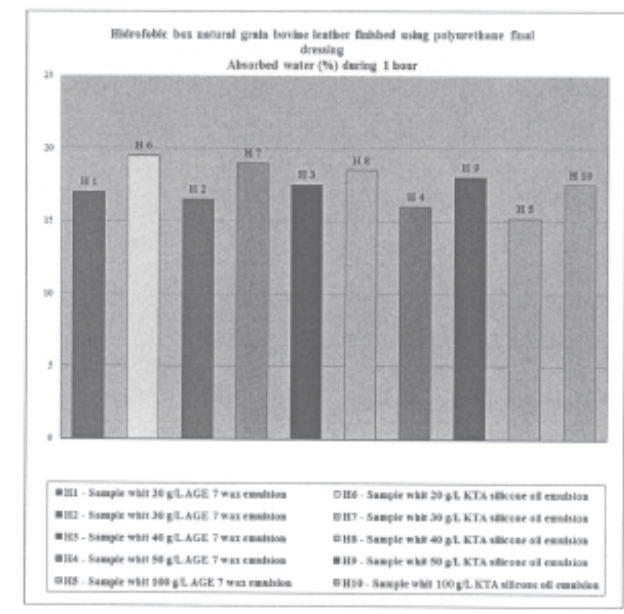


Fig. 5a Water absorption for the specified hydrophobized leathers, final dressing, handle modifiers and time

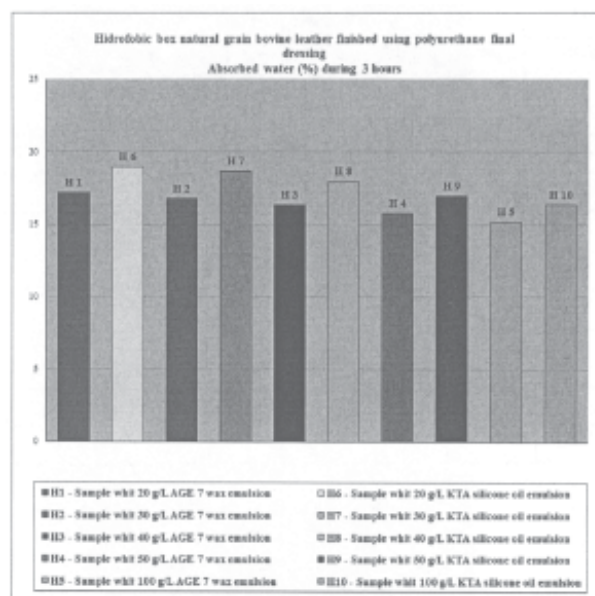
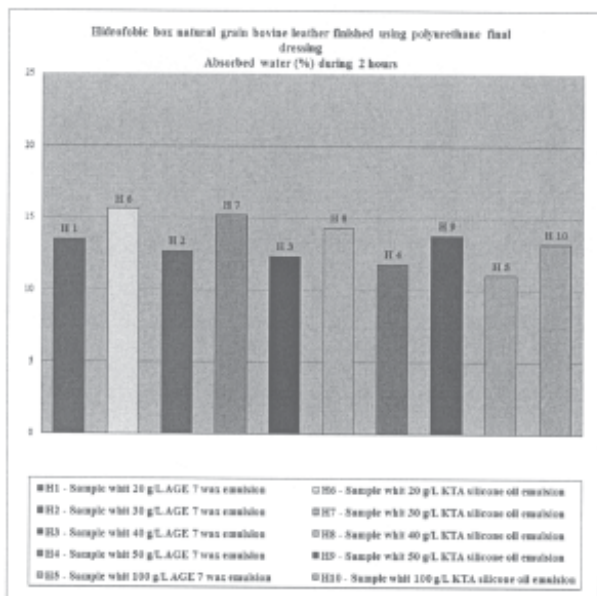


Fig. 5b-c. Water absorption for the specified hydrophobized leathers, final dressing, handle modifiers and time

lowest water resistance, but leather coating does not show significant deterioration, the resistance of the dyed samples to water drop ranking between 4-5 and 5 on a scale of 1 to 5.

In the case of using polyurethane nad nitrocellulose dressing, the resistance of the dyed samples to water drop is rated 5.

Conclusions

The emulsion obtained by emulsifying a mixture of beeswax, lanolin and triethanolamine monostearate stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide has homogenous appearance and particle sizes ranging mostly between 2 and 4 μm .

AGE 7 emulsion added in polyurethane, nitrocellulose or acrylic final dressing it leads – for a given amount and time – to lower water absorption values than Roda feel KTA 950 emulsion, the most used handle modifier.

Finished leathers finished with polyurethane dressing absorb the lowest amounts of water, while those treated with acrylic dressing absorb the highest amounts.

The resistance of the finished leather samples to water drop ranks between 4-5 and 5 on a scale of 1 to 5.

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