Obtaining and Characterization of an Ecologic Wax Emulsions for Finishing Natural Leathers and Furs

OLGA NICULESCU[1,2]*, MINODORA LECA[1], ZENOVIA MOLDOVAN[1], CIPRIAN CHELARU[2]*, DANA GURAU[2], DANIELA MARIANA BERECHET[2]

[1] University of Bucharest-Faculty of Chemistry, 36-46 Mihail Kogalniceanu Blv., 050107, Bucharest, Romania

[2] National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute Bucharest, 93 Ion Minulescu, 031215, Bucharest, Romania

The prepared wax emulsions contain natural ingredients - beeswax and lanolin, as well as stearin, obtained by cleavage of natural fats. They have homogeneous appearance and a particle size ranging between 4 and 8 μm. The mixture of waxes in the aqueous medium was emulsified in the presence of a fully biodegradable non-ionic emulsifier - lauryl alcohol ethoxylated with 7 moles of ethylene oxide. FT-IR spectrum of the film obtained from the prepared emulsions contain bands of all components and the broadband at about 3385 cm^{-1} due to hydrogen bonds formed by the water left in the film. Used in the final dressings of natural nappalan leather, it gives finishing films a waxy feel and better resistance to scratches and water.

Keywords: ecologic wax emulsions, finishing natural leather and fur, FT-IR spectrometry, optical microscopy

Waxes, esters of superior monocarboxylic acids with monohydric primary alcohols superior to the normal chain, are classified as follows:

- animal waxes, produced by some insects or obtained from body parts of marine animals;
- vegetable waxes, harvested from plant parts (leaves or fruit - as Carnauba wax from wax palm);
- synthetic waxes, obtained by synthesis, with different compositions and bearing the commercial names of manufacturing companies.

Some mineral products with similar appearance to natural waxes, such as montan wax of brown coal, can also be considered waxes.

For finishing natural napalan leather and fur, natural and synthetic waxes are used in the form of aqueous emulsions, in order to reduce the stickiness of thermoplastic binders and to obtain a pleasant feel [1-4].

To improve the organoleptic and physico-mechanical properties of finished leather, wax emulsions and silicone oils are used in the final dressing composition, applied by spraying over the surface.

In order to obtain waxy products, the following components are used: silicone polymers, amide derivatives of C_{12}-C_{18} fatty acids, products based on ethylene polymers, wax-based products resulting from the esterification of fatty acids with fatty alcohols and polymeric compounds, products based on mixture of C_{10}-C_{18} fatty acids prepared by oxidation of paraffin [5-7].

Wax emulsion stability is ensured by nonionic emulsifiers [8-14]. The best stabilizing agent is nonylphenol ethoxylate with 9 moles of ethylene oxide, but following the evaluation of ecotoxicity, its use in industrial products was banned through Directive 76/769/EL/2003, as it is only 30% biodegradable. An alternative is represented by ethoxylated fatty alcohols, 100% biodegradable [15].

This paper presents the process of obtaining ecologic wax emulsions by emulsifying a mixture of beeswax, lanolin and ethanolamine monostearate stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide, for finishing natural napalan leather and fur, and their characterization by physico-chemical, microscopic and spectral analyses, and by optical microscopy analysis of leather finished by film-coating using wax emulsions in the final dressing.

Experimental part

Materials and methods

- Beeswax (S.C. Happynatura SRL, Bucharest) – solid substance, with specific odour, yellow colour, melting point 62-65°*C;*
- Lanolin (S.C. Medchim S.RL., Bucharest) – semisolid greasy compound, with specific odour, light yellow colour, melting point 38-42°*C;*
- Strearin (S.C. Stera Chemicals S.R.L., Bucharest) – solid substance, with specific grease odour, white colour, melting point 69-70°*C;*
- Triethanolamine (SC Stera Chemicals S.R.L., Bucharest) – colourless liquid, melting point – 20-21^{0}C, boiling point – 277-279^{0}C, density – 1.124 g/cm^3, refractive index – 1.4852;
- Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (SC Elton Corporation SA., Bucharest), density – 0.95 g/cm^3 at 40^{0}C, *p*H (10% solution) – 7-8.
- 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.
- Crust bovine leathers natural grain assortments, mineral tanned and wet finished by retanning, fatliquoring and dyeing (1.2-1.4 mm thick, dyed black (M1), dyed brown (M2), and dyed yelow (M3)) (National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute Bucharest, Romania).
- Black pigment paste – Casicolor Black (Triderma, Germania), dry substance – 22%, ash – 12%.
- Brown pigment paste – Casicolor Brown R (Triderma, Germania), dry substance – 35 %, ash – 60%.

* *email: o_niculescu@yahoo.com; Tel.: 0213235060*

- Ochre pigment paste – Casicolor Ochre (Triderma, Germania), dry substance – 33%, ash – 68%.

- Roda-cryl 87 (Triderma, Germany), acrylic binder for ground coat, dry substance – 34.50%, *p*H (10% solution) – 6.0, Ford cup viscosity Φ4 – 14, density – 1.025 g/cm^3.

- Roda wax MONO (Triderma, Germany), wax emulsion for ground coat: dry substance – 36.87%, *p*H (10% solution) – 4.2, Ford cup viscosity Φ4 – 12, kinematic viscosity, cSt – 8.97, density – 0.957 g/cm^3.

- Roda-pure 5011 (Triderma, Germany), polyurethane binder used as a fixing agent (final dressing) for finishes applied to natural leather: dry substance – 40%, *p*H (10% solution) – 5.5, Ford cup viscosity Φ4 – 7, density – 1.053 g/cm^3.

The wax mixture was prepared in an equipment consisting of a reaction vessel with 3L capacity and a heating system (electric bath with temperature control).

The 3-necked reaction vessel, made of high-temperature resistant glass, is equipped with a propeller stirrer to homogenize the reaction mass, a thermometer for temperature control and condenser connected to the water source to maintain the temperature constant during the preparation process.

Obtaining the wax mixture

Preparation of wax mixture involves the following:

- obtaining triethanolamine monostearate by esterification of triethanolamine stearin using a fatty acid/amino alcohol mass ratio of 1.0/0.8-1.0. For good stirring during the technological process, the amount of components added to the reaction vessel should be 50-70% of its capacity. We used the following operating parameters: temperature - 120-140°C, stirring at a speed of 60-80 rpm, mixing time - 4 h.

- cooling the reaction mass at 60-80°C, then emptying the reaction vessel.

- preparation of wax mixture - in a heat-resistant glass vessel, the required amount of lanolin was liquefied in a water bath at a temperature of 50-60°C and the beeswax at 80-90°C, in a 3/1 ratio.

- cooling the mixture of the two fluid waxes at the temperature of 60°C.

-introduction of the following components in the mixing vessel: triethanolamine monostearate, lanolin and beeswax in the 7/3/1 ratio.

The following parameters were used in mixing: temperature 60-80°C, stirring at a speed of 60-80 rpm, stirring time - 30 min.

The resulting intermediate substance is a yellowish clear oil. [16-18]

Obtaining wax emulsion

The wax mixture obtained was emulsified in water using 20% mixture and 10% polyoxyethylene lauryl alcohol relative to the amount of wax subject to emulsification, namely 2% relative to the weight of the emulsion, under mechanical stirring at a rotation of 300-500 rpm, at a temperature of 60-80°C. The O/W emulsion obtained (marked AGE 7) is stirred until cooled to room temperature.

Elaboration of dry finishing technologies for natural leather using wax emulsions in the final dressing

Dry finishing technologies have been developed for natural grain black and coloured bovine hides.

The experimental samples P1-P3 contain 20g/L AGE 7 wax emulsion in the final dressing composition, prepared during the experiments performed, an amount commonly used to improve the final feel of finishing films.

The framework technology for dry finishing of natural grain black and coloured bovine leather is presented 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. Magnification was 100X for the wax emulsions and 40X for surface of finished leather.

Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were run with a Jasco instrument (model 4200), in the following conditions: wavenumber range – 600-4000 cm^{-1}; data pitch – 0.964233 cm^{-1}; data points – 3610: apperture setting – 7.1 mm; scanning speed – 2 mm/s; number of scans – 30; resolution – 4 cm^{-1}; filter – 30 kHz; angle of incident radiation – 45° [19-22].

Results and discussions

Characterization of wax emulsion by physico-chemical analyses

Wax emulsion AGE 7 have the physico-chemical caracteristichs: homogeneous, white appearance, dry substance – 19.96, pH (10% solution) – 7.3, Ford cup viscosity Φ4 – 27 s, kinematic viscosity, cSt – 10.48, density – 0.975 g/cm^3.

Characterization of wax emulsion by optical microscopy

Given that emulsions are transparent, in order to be able to differentiate phases, a methyl red solution was used. Optical microscopy measurements have highlighted the following characteristics: type of emulsion, its relative homogeneity and emulsified particle sizes.

Optical images of wax emulsion are presented in figure 1.

Image shows that the prepared emulsion are oil in water emulsion, given that the emulsifier is soluble in the aqueous phase. The emulsion prepared have small-sized particles, with diameters ranging between 4.1 and 8.2 μm, relatively uniformly distributed in the whole mass.

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 570 g/L water Application by spraying (2 passes)
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)
Applying final dressing (fixing)	Dispersion with the following composition: 700 g/L aqueous polyurethane dispersion 20 g/L aqueous wax emulsion for feel (Wax 1-AGE 7) 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 1
FRAMEWORK TECHNOLOGY FOR DRY FINISHING OF BOVINE LEATHERS IN BLACK AND COLOURED BOX NATURAL GRAIN

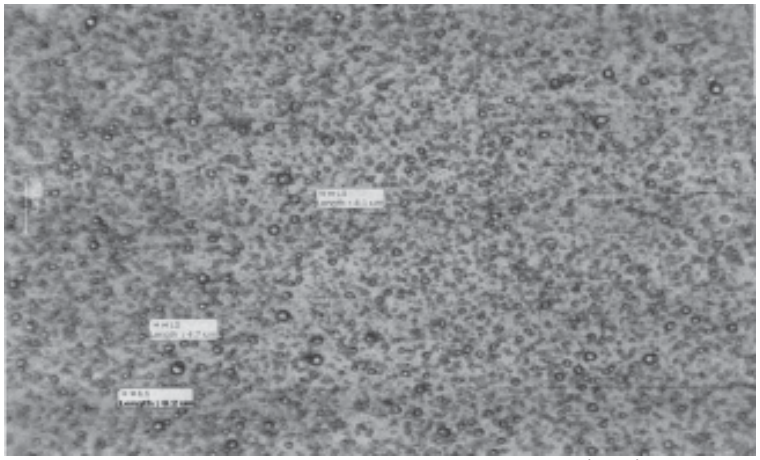

Fig. 1. Optical image of prepared wax emulsion (100X) assortment

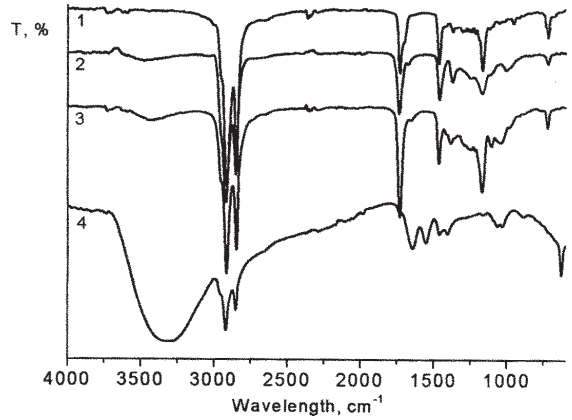

Fig. 2. Overlapping FT-IR spectra of component waxes and the film obtained from emulsion (1- beeswax; 2- lanolin ; 3- triethanolamine monostearate; 4- AGE 7 wax emulsion)

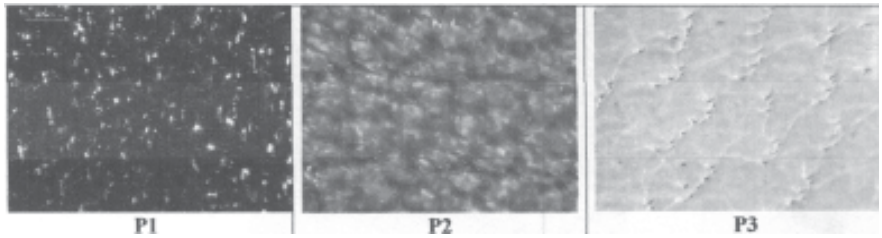

Fig. 3. Optical images recorded for the finished natural grain box bovine leather using wax emulsion in the final dressing

FT-IR characterization of components used and of the wax emulsion obtained

The wax emulsion and additives used were dried over glass slides and films obtained were analyzed by FT-IR spectroscopy.

FT-IR spectra of the following components: beeswax, lanolin, triethanolamine monostearate, and the film obtained after evaporation of the dispersing medium in the wax emulsion are shown overlapping in figure 2.

The figure shows that the beeswax and lanolin have common bands: two intense bands at about 2920, and 2850 cm^{-1}, respectively, assigned to the asymmetric and symmetric stretching vibrations of methylene and methyl groups, a weak band at about 1730 cm^{-1} due to the stretch of C=O bond of ester groups, a weaker band at 1470 cm^{-1} and a very weak one at 720 cm^{-1}, specific to compounds containing long aliphatic chains, slightly more intense for beeswax, and the band at about 1170 cm^{-1} attributed to C-O-C bonds, also more intense for beeswax. The triethanolamine monostearate has all these bands, given by the stearyl radical, and a medium intensity band at 1169.5 cm^{-1}, due to the tertiary amine group of triethanolamine (C-N stretch).

The spectrum of the film obtained by evaporating the emulsion derived from three waxes, stabilized with 10% lauryl alcohol ethoxylate - on average - with 7 moles of ethylene oxide relative to the amount of the wax, contains all characteristic bands of the three components, with the addition of the intense band centered at 3374 cm^{-1} due to hydrogen bonds formed by water left in the film, the relatively weak one at 1645 cm^{-1} - present in stearate and attributed to C=O stretch of hydrogen bonds coupled with C-N stretching vibration, the very weak one at 1559 cm^{-1}, which may be due to the COO^- stretch in the neutralized stearic acid in a proportion of 33% of triethanolamine monostearate, the low to medium intensity band at 1091 cm^{-1} present in triethanolamine monostearate as a very weak band, which may be due to the stretch of C-O-C bonds of the ether groups of the emulsifier.

Optical microscopy analysis of obtained leather assortments

Optical microscopy images were recorded for natural grain box bovine leather assortments finished with black (P1), brown (P2) and yellow (P3) pigment pastes and acrylic thermoplastic binders (in the basecoat) and polyurethane final dressing containing AGE 7 wax emulsion, and are presented in figure 3.

Optical microscopy images show that the finishing films are coated uniformly on the dermal support for the three leather assortments.

FT-IR characterization of obtained leather assortments

Figures 4-6 present the spectral characteristics of the untreated leather samples M1-M3, compared with those of the treated ones P1-P3, used pigment pastes and acrylic thermoplastic binders (in the basecoat) and polyurethane final dressing containing AGE 7 wax emulsion.

The main spectral bands of the ungrafted leather samples M1 and M2 are find in the following regions: 3660–3530 cm^{-1} (NH amide), 2922 and 2856 cm^{-1} (-CH_3, -CH_2-),1643 cm^{-1} (-OC-N), 1540 cm^{-1} (NH), 1446 cm^{-1} (C–H), 1239 cm^{-1} (NH-CO), 1076, and 1028 cm^{-1} (C-O). The spectra of the top coated leather have the following characteristics, compared to those of the untreated ones: the intense peak at about 1642-1649 cm^{-1}, characteristic for C=O and –OC-N groups, from the spectrum of the untreated leather, is absent in the spectra of the treated samples; these last ones present a peak at about 1721-1725 cm^{-1}, corresponding to C=O stretching in saturated ester of polyurethane top coat; the two peaks at about 1240 and 1165 cm^{-1} assigned to the couplings of C-O and C-C stretches and to the stretching vibration of C-O-C of acrylates appear in the spectra of the finished leather; the broad band in the region 3200-3500 cm^{-1}, assigned to hydroxyl and amide groups vibrations, is diminished in the spectra of the top coated leather samples compared with the untreated ones. The above differences between the IR spectra of treated and untreated leather may be considered as a proof for the chemical bonding of the top coat on base coat components [23-24]. Therefore, the top coat not only covers the surface of the leather but it is bound with the base coat, assuring thus a resistant coverage.

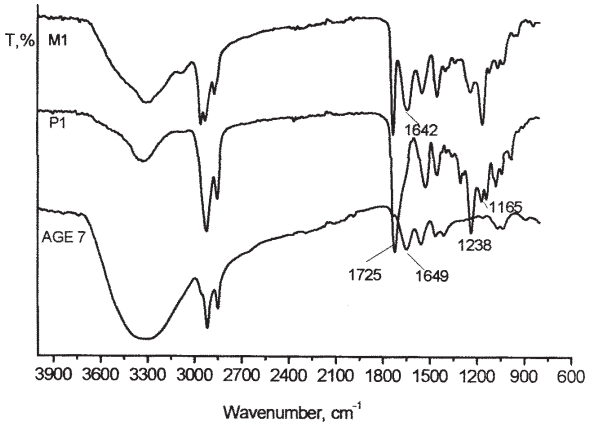

Fig. 4. Superposed IR spectra of unfinished leather M1 and finished sample P1, and of AGE 7 wax emulsion used in the final dressing

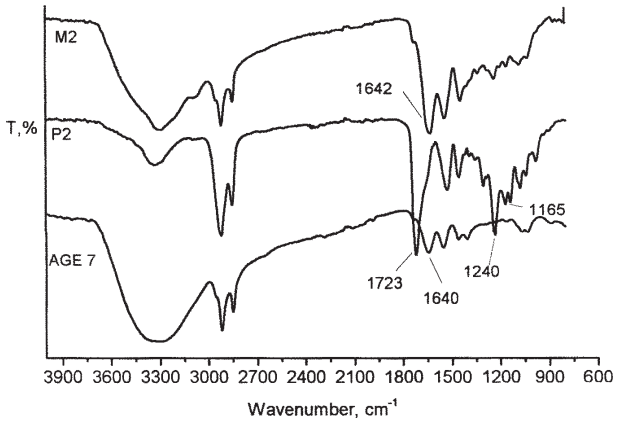

Fig. 5. Superposed IR spectra of unfinished leather M2 and finished sample P2, and of AGE 7 wax emulsion used in the final dressing

The polyuretane top coat containing the prepared emulsion is also bound chemically on base coat. Thus, the band from about 1640 cm^{-1} characteristic for C=O and –OC-N grups from the spectrum of the emulsion film is absent from the spectrum of the finished leather samples.

Conclusions

The prepared wax emulsions contain natural ingredients - beeswax, lanolin and triethanolamine monostearate - resulting from cleavage and esterification of stearin.

To emulsify the wax mixture in an aqueous medium, a fully biodegradable non-ionic emulsifier was used, lauryl alcohol ethoxylated with 7 mol of ethylene oxide.

AGE7 handle emulsions are white poly-dispersed fluids, with homogeneous appearance and drop diameters between 4 and 8 μm, relatively uniformly distributed in the emulsion mass.

The spectrum of the film obtained from the AGE 7 wax emulsion contains all the bands of components and the broad band at about 3385 cm^{-1} due to hydrogen bonds formed by water left in the film. They have different intensities, determined by the proportions in which they were used.

AGE 7 emulsions may be used in surface finishing of natural nappalan leather and fur in the final dressing composition to obtain a waxy feel and better resistance of finishing films to scratches and water.

IR spectra of leather samples treated with polyurethane coating agent, to which the wax-based emulsion was added, show that the latter is chemically bound to the leather surface.

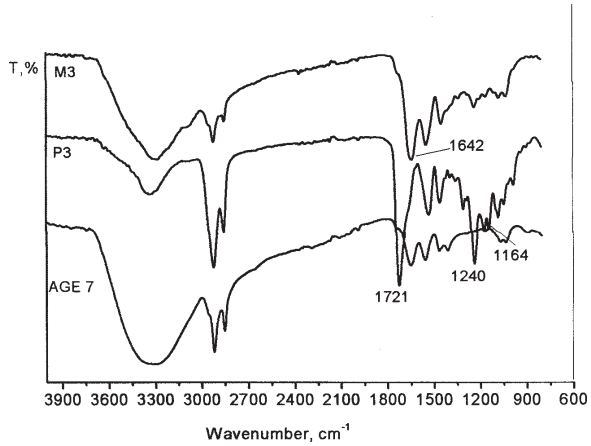

Fig. 6. Superposed IR spectra of unfinished leather M3 and finished sample P3, and of AGE 7 wax emulsion used in the final dressing

Referernces

1. LANGE, J., „Leather Finishing", Leather library vol. V, Umschau, Frankfurt, 1982.
2. LANGE, J., „Assessing quality, flaws, storage and maintenance of leathers", Cap. 12.- Behaviour of leather to water, Leather library vol. X, Umschau, Frankfurt,1982.
3. HEIDEMANN, E., „Fundamentals of Leather Manufacturing", Eduard Roether KG Druckerei und Verlag, Darmstadt, 1994.
4. CHIRITA, Gh., CHIRITA, M., „Tratat de chimia şi tehnologia pieilor şi blănurilor", vol. I şi II, Ed. Gh. Asachi, Iaşi 1999.
5. *** TRIDERMA, Germany – Leather finishing auxiliaries, 2010.
6. ***VECO, Italy – Leather finishing auxiliaries, 2010.
7. BACARDIT, A., OLLE, L., MORERA, J.M., BARTOLI, E., CUADROS, R., COBOS, M., "Study of aqueous patent leather finish with a pull–up effect", J. Amer. Leather Chem. Assoc., **104**, 2009, 103.
8. MANDRU, I., LECA,M., „Chimia coloizilor şi macromoleculelor", Ed. Didactică şi Pedagogică, Bucureşti, 1977
9. VOIUTSKY, S., „Colloid Chemistry", Mir Publishers, Moscow, 1975.
10. KABALNOV, A., WENNERSTROM, H., Coll. Polymer Sci., **1**, 1996, 81.
11. MOHAMMED, R.A., BAILEY, A.I., LUKHAM, F., Coll. Surf. A. Phys. Chem. Eng. Aspects, **71**, 1991, 129.
12. VILLAMAGNA, R., WHITEHEAD, A., CHALTOPADHYAY, A.K., J. Dispersion Sci. Technol., **16**, 1995, 105.
13. PILLARD, C., GAREND, G., Technicuir, **3**, 1989, 169.
14. GUILLAUMIN, R., Rev. Fr. Corps Gras, **18**, 1991, 445.
15. OSPAR Commission- Hazardous Substances Series- Nonylphenol/ Nonylphenoletoxylates, 2004.
16 ***Patent Library of the European Community (http:// www.epo.org).
17. ***Patent Application, NICULESCU, O., MANTA, A., "Waxy product for finishing natural leather and leather items", OSIM A/00532/2013.
18. ***Patent Application, NICULESCU, O., MACOVESCU, G., COARA, G., TONEA, S., „Film-forming composition and finishing process for Nappalan sheepskins", OSIM A/00923/2010.
19. XIE, YI and LI MI, Preparation and Application Properties Analysis of Hyperbranched Polyurethane Leather Finishing Agent, Advanced Materials Research (Vol. 129 - 131), 251-255, 2010.
20. KAUSHIVA, B.D.; WILKES, G.L., Uniaxial orientation behavior and consideration of the geometric anisotropy of polyurea hard domain structure in flexible polyurethane foams. Polymer 41, 2000, 6987-6991
21. SHI, YING; ZHAN, XIAOLI; LUO, ZHENHUAN; ZHANG, QINGHUA; CHEN, FENGQIU, Quantitative IR characterization of urea groups in waterborne polyurethanes, Journal of Polymer Science.
Part A: Polymer Chemistry, 46, (2008), 2433 - 2444.
22. DONGYA YANG, FEIYAN YE, XINSHAN RONG, FENGXIAN QIU, Waterborne polyurethane-acrylic hybrid polymer based on PTMEG: physical and mechanical properties, Journal of Materials Science and Engineering with Advanced Technology, 6, 2012, 19-28.
23. *** SR 1619:1994 standard for natural grain box bovine leathers.
24. *** SR EN ISO 14931:2005 standard for natural grain napa sheep leathers

Manuscript received: 29.04.2014