MATERIALS FOR SURFACE DESIGN AND FINISHING FOR CONTEMPORARY FOOTWEAR – PART 2

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Leather has a natural beauty that, unlike many materials, improves with age, and has long been a component of luxury goods such as footwear, leather goods and clothing. It is a natural and durable material, unmatched by any synthetic product, in terms of hygienic and protective properties. Thanks to the skills of leather producers, who take the same basic raw material, natural leathers are processed through different technological processes and transformed into finished leathers for various clothing items with high-performance properties. Finishing is achieved through a series of technologies, using materials that provide the finished leather with the desired aesthetic characteristics related to fashion, colors and special effects (pearl, two-tone, antique, printed, glossy, matte, waxed, etc.). Hand-painted natural leather shoes are also in fashion, to give a personal touch to a luxury item. The work presents surface finishing technologies of ecological natural leathers (tanned without metals), using pigment pastes with a metallic effect, in combination with acrylic and polyurethane polymers, with resistance to light and aging. White and pastel finished leathers with silver and gold effect can be used in creative industries for artistic and luxury footwear (especially for women).

Keywords: natural leather, pigment pastes, surface design, creative industries

INTRODUCTION

Leather is fashionable in all colours while maintaining outstanding technical performance. The current ecological standards impose strict regulations in all processes technological and social, so that the carbon footprint is as small as possible (ETAD, 2004; SG, 2006; Directive 2010/75/EU).

In the field of eco-design, ethical-fashion, green product, etc., the theme of sustainability is not just a trend but a constant research topic under all aspects of the human-product-technology-consumption-environment relationship, developing the circular economy, based on four pillars: environment, economy, social and culture (Burdujan and Kral, 2015).

The global sustainability of products represents the coexistence of scientific, technical and cultural sustainability parameters, which, in the case of leather, through its ecological structure, involves modern finishing technologies and the eco concept of surface design (Pop and Horatau, 2019). In the fashion industry the added value is only reflected by an efficient surface design, but the Surface Design is not just a type of finish, it is an art-science act that, if well-known and coordinated, can be spectacular and sustainable at the same time (Pop *et al*., 2019).

Leather is finished (by spraying or using ecological finishing machines with rollers) using dispersed systems which contain: pigments, binders, waxes, preservatives, plasticizers, thickening agents, fillers, odorizing substances, penetrators, solvents etc. Environmental and toxicity concerns have led to new alternatives for finishing ancillary industry (Niculescu *et al*., 2015; Niculescu and Manta, 2019; Niculescu, 2022).

Finishes with special effects are applied to leather to improve the organoleptic and aesthetic properties, related to fashion, such as: metallic, bicolor, antique, waxed, etc.

The paper presents the dry leather finishing technologies using ecological materials (pigment pastes with a metallic effect) that provide the desired aesthetic characteristics for shoes. The bovine leathers were tanned (without metals) with syntans based on phenolsulfonic acids and aromatic oxysulfones and finished with ecological materials.

https://doi.org/10.24264/icams-2022.V.6

(Triderma, 2020). White and pastel finished leathers with special effect finish (silver and golden effect) can be used in creative industries for artistic and luxury footwear (especially for women).

EXPERIMENTAL

Materials

The nappa bovine leathers, tanned with syntans based on phenolsulphonic acids and aromatic oxysulfones and wet finished by retanning, fatliquoring (1.0-1.2 mm thick, white) (INCDTP – Division ICPI Bucharest, Romania).

Pigment pastes with silver effect (marked PPS), viscous and homogenous fluid, dry substance – 32-35%, pH (10% solution) – 7.0-8.0, ash – 25-8% (INCDTP – Division ICPI Bucharest, Romania).

Pigment pastes with golden effect (marked PPG), viscous and homogenous fluid, dry substance – 31-35%, pH (10% solution) – 7.0-8.0, ash – 27-29% (INCDTP – Division ICPI Bucharest, Romania).

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

Roda-Pur Wx 1418 (Triderma, Germany) polyurethane binder for ground coat: dry substance – 19-21%, pH (10% solution) – 7.5-9.5.

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

Roda feel KTA 950 (Triderma, Germany), aqueous wax emulsion for handle: dry substance – 12%, pH (10% solution) – 5.5.

Roda-Pur 5011 (Triderma, Germany), polyurethane dispersion (marked PU5011), dry substance – 40%, pH (10% solution) – 5.5, Ford cup viscosity Φ4 – 7, density – 1.053 g/cm^3.

Roda lacquer 93 (Triderma, Germany), nitrocellulose emulsion (marked LAC93), dry substance –15%, pH (10% solution) – 5.5, Ford cup viscosity Φ4 – 125, flash point – 82°C.

Methods

Physical-mechanical characteristics of finished leather assortments were determined according to the following standards: dry and wet abrasion (1-5 ranking) – SR EN ISO 11640:2002; resistance to repeated bending, number of flexions – SR EN ISO 5402:2012.

Finished leathers were artificially aged and tested according to ISO 17228/2015 standard, using Xenotest Apolo.

Optical microscopy images were captured using a Leica stereomicroscope S8AP0 model with optic fiber cold light source, L2, with three levels of intensity, and magnification 20X.

Elaboration of Dry Finishing Technologies for Natural Leathers for Shoes

Dry finishing technologies (application by spraying) have been developed for bovine hides into natural grain nappa, with silver and golden effect. The framework technology for dry finishing of bovine hides into natural grain nappa, with new pigment pastes, with silver and golden effect, is presented in Tables 1 and 2. Application of the final dressing was performed in two variants: P – polyurethane – Roda pur 5011 and N – nitrocellulose – Roda lac 93 (Triderma, 2020).

https://doi.org/10.24264/icams-2022.V.6

Table 1. Framework technology for dry finishing of bovine hides into natural grain nappa with silver effect (white and pastel)

Operation	Dispersion composition/application method
Applying dispersion I (basecoat)	100-120 g/L pigment paste (PPS) 2-5 g/L pigment paste (red, yellow, blue)* 150 g/L aqueous acrylic dispersion (Roda-cryl 87) 150 g/L aqueous polyurethane dispersion (Roda-pur 1418) 30 g/L aqueous wax emulsion (Roda wax MONO) 545-568 g/L water Application by spraying (2 passes dispersion I)
Intermediate pressing	In hydraulic press with the mirror or fog plate, parameters: - temperature – 50-60°C; pressure – 50-100 atm.
Applying dispersion I	By spraying (4-5 passes dispersion I)
Applying final dressing (fixing)	Emulsion/dispersion with the following composition: 700 g/L aqueous polyurethane dispersion (Roda pur 5011) or 700 g/L aqueous nitrocellulose emulsion (Roda-lac 93) 20 g/L aqueous wax emulsion (Roda feel KTA 950) 280 g/L water Application by spraying (2 passes final dressing)
Final pressing	In hydraulic press with the mirror plate, parameters: - temperature – 80-100°C; pressure – 50-100 atm.

* For finishing leathers in pastel colors with a silver effect, 2-5 g/L red, yellow or blue pigment pastes (Triderma SRL) were added in combination with the silver white pigment (PPS).

Table 2. Framework technology for dry finishing of bovine hides into natural grain nappa with golden effect

Operation	Dispersion composition/application method
Applying dispersion I (basecoat)	100-120 g/L pigment paste (PPG) 150 g/L aqueous acrylic dispersion (Roda-cryl 87) 150 g/L aqueous polyurethane dispersion (Roda-pur 1418) 30 g/L aqueous wax emulsion (Roda wax MONO) 550-570 g/L water Application by spraying (2 passes dispersion I)
Intermediate pressing	In hydraulic press with the mirror or fog plate, parameters: - temperature – 50-60°C; pressure – 50-100 atm.
Applying dispersion I	By spraying (4-5 passes dispersion I)
Applying final dressing (fixing)	Emulsion/dispersion with the following composition: 700 g/L aqueous polyurethane dispersion (Roda pur 5011) or 700 g/L aqueous nitrocellulose emulsion (Roda-lac 93) 20 g/L aqueous wax emulsion (Roda feel KTA 950) 280 g/L water Application by spraying (2 passes final dressing)
Final pressing	In hydraulic press with the mirror plate, parameters: - temperature – 80-100°C; pressure – 50-100 atm.

Testing Artificially Aged Finished Leather

The characteristics of finished natural grain nappa leather assortments aged with artificial light (Xenotest) for 7 days were determined.

The samples were marked:

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- PPS-P (metal pigment-aluminum, poppy oil/ fixing with polyurethane dispersion);
- PPS-N (metal pigment-aluminum, poppy oil/ fixing with nitrocellulose emulsion);
- M1-P (metal pigment-aluminum, castor oil/ fixing with polyurethane dispersion);
- M1-N (metal pigment-aluminum, castor oil/ fixing with nitrocellulose emulsion);
- PPG-P (bronze powder, poppy oil/ fixing with polyurethane dispersion);
- PPG-N (bronze powder, poppy oil/ fixing with nitrocellulose emulsion);
- M2-P (bronze powder, castor oil/ fixing with polyurethane dispersion);
- M2-N (bronze powder, castor oil/ fixing with nitrocellulose emulsion).

RESULTS AND DISCUSSION

Characterization of Finished Leathers by Mechanical Methods

Physical-mechanical characteristics (resistance to dry/wet friction, resistance to repeated bending) and fastness to light (of leathers aged with artificial light-Xenotest, for 7 days) are shown in Table 3.

Table 3. Physical-mechanical characteristics of bovine hides into natural grain nappa

Samples	Resistance to dry friction (mark)	Resistance to wet friction (mark)	Resistance to repeated bending, number	Fastness to light after artificial ageing (1-8 ranking)
PPS-P	5/5	4/5	200.000	8
PPS-N	5/5	4/5	200.000	7-8
M1-P	5/4-5	4/4	190.000	7-8
M1-N	5/4	4/4	180.000	7
PPG-P	5/5	4/5	200.000	8
PPG-N	5/4-5	4/5	190.000	7-8
M2-P	5/4-5	4/3	180.000	7-8
M2-N	5/4	4/3	170.000	7
Standard	SR EN ISO 11640:2002	SR EN ISO 11640:2002	SR EN ISO 5402:2012	SR EN ISO 105-B02:2003

Leather samples (nappa) finished using prepared pigment pastes, according to the technologies presented in Tables 1 and 2, are within the limits specified in standards (ST 1619:1994), for natural leathers for shoes (min. 5/3 mark for resistance to dry friction, min. 4/2 mark for resistance to wet friction, min. 150.000 number for resistance to repeated bending).

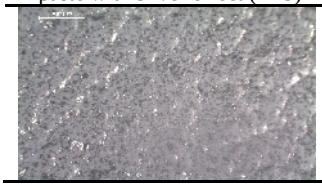
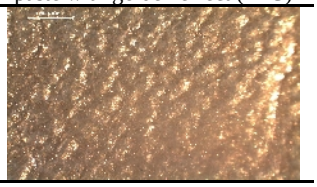
Leather finished using the prepared pigment pastes (PPS and PPG) and polyurethane binder (final dressing) have higher marks for fastness to light after artificial ageing (8 on a scale of 1 to 8), and leather finished with nitrocellulose dressing have the mark 7 or between 7 and 8. Poppy seed oil, used as plasticizer, improves resistance to yellowing of coating films.

Analysis of Leathers Finished with New Pigment Pastes by Optical Microscopy

Table 4 illustrates optical images of leathers finished with pigment pastes with silver effect (PPS) and with golden effect (PPG). The resulting shades can be used to finish leather for footwear in a modern style.

https://doi.org/10.24264/icams-2022.V.6

Table 4. Optical images at 20X of the leathers finished with pigment pastes

Leather finished with pigment paste with silver effect (PPS)	Leather finished with pigment paste with golden effect (PPG)
	

Macroscopic Images of Finished Leather for Creative Industries

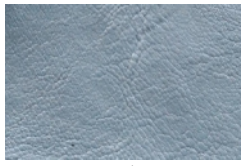
Macroscopic images of leathers finished for creative industries are presented in Figures 1 (a-e), 2 and 3.

a)

b)

c)

d)



e)

Figure 1. Leathers finished with pigment pastes with silver (a) and golden (b) effect; leathers finished in pastel colors with pigment pastes (with silver and golden effect) (c-e)

Figure 2. Hand painted leather with pigment pastes (with silver and golden effect)

https://doi.org/10.24264/icams-2022.V.6

Figure 3. Leathers for artistic and luxury footwear

CONCLUSIONS

- Leather finished with pigment paste with silver and golden effect can be used for modern footwear.
- The highest resistance to light after aging under the influence of artificial light was found for leather finished with polyurethane dressing in comparison with leather finished with nitrocellulose dressing. Poppy seed oil, used as plasticizer, improves resistance to yellowing of coating films.
- The finishing composition can be used for the surface finishing of natural leather (white and pastel) for shoes (especially for women), to improve the organoleptic and aesthetic properties (related to fashion).
- Leather with silver and golden effect finish can be used in creative industries for artistic and luxury shoes (hand-painted natural leather shoes).

Acknowledgements

This research was funded by the Romanian Ministry of Research and Digitalization, CCCDI - UEFISCDI, PNCDI III - Program 1 – Development of the national RD system, Subprogram 1.2-Institutional Performance-RDI excellence funding projects, Contract no. 4PFE/ 2022 and Contract no. E!254/2021 (BIOSAFE LEATHER).

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