SPECIAL EFFECT FINISH FOR BOOKBINDING LEATHER

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The art of bookbinding requires not only skills in the old craft of bookbinding but also materials that can transform a simple book into a high-quality artistic product. Due to its unique properties, leather still remains the first-choice material in the case of art and archival bindings. However, the long-term durability of modern leather is not known since there is little commercial interest in long periods of durability and the market of leather for art, design and archival purposes is very small. It is worth noting that deterioration is influenced by the manufacturing technology, and especially by the chemical ingredients used in the various steps of leather making, from dehairing to tanning and finishing. It is therefore very likely that modern and contemporary artworks made of/with modern leather undergo faster degradation than ancient and medieval artworks. Thus, leather finishing is very important for both artistic and sustainable points of view. In fact, finishes with special effects such as antique, bicolour, printed, cracked, waxy are highly sought for vegetable tanned leather used for artistic and luxury bookbinding, archival bookbinding and restoration purposes. The evolving leather finishing technology of chrome-free leather (i.e. vegetable tanned leather) has enabled us to protect and improve the quality, look and feel of leather and to make it suitable for contemporary art bindery.

Keywords: durable, finish, bookbinding leather

INTRODUCTION

Due to its unique properties, leather still remains the first-choice material in the case of art and archival bindings. Ancient and medieval works of art, but also modern and contemporary works of art made of/with modern leather can suffer a certain degradation over time.

Finishing the skin is very important both artistically and sustainably, and aims to beautify, obtain a pleasant gloss and touch, cover defects, form a protective surface layer during use, as well as improve resistance to external factors (light, friction, scratches, water) of objects made from leather.

The finishing is carried out by spraying or with the help of ecological roller finishing machines, applying on the dermal support of some dispersed systems, in the composition of which the following auxiliary materials are used: pigments, binders, natural waxes and synthetics, preservatives, plasticizers, thickeners, fillers, odorants, penetrants, solvents (Lange, 1982; Heidemann, 1994).

Binders are film-forming macromolecular compounds used in all stages of finishing to give leather flexibility, adhesion and resistance to wear and to external factors. The composition of leather surface finishing systems includes acrylic, polyurethane, butadiene and nitrocellulose binders. Depending on molar masses and hardness, binders are used in various finishing coats (basecoat or dressing) to obtain the desired finish.

The types of finishes differ in terms of the working procedures or the effects obtained. By varying the components or working methods, even the same finishing process can lead to different gloss, matting or coating effects (Niculescu *et al.*, 2015a; 2015b; 2015c; Niculescu and Mendea, 2019). Thus, finished natural leathers can be made by modern means, imitating ancient natural leathers.

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For bookbinding, leathers can be used with contrasting, antique, cracked, wrinkled, pleated, polished, printed, glossy, matte, pearlescent effect, with a silky, waxed, aniline, semianiline touch, in a wide range of colors, finished with materials which provide the desired characteristics of the finished product, for artistic and luxury bookbinding, archival bookbinding and restoration purposes.

The paper presents the surface leather finishing technologies that can be used for bookbinding leather with special effect finish. The auxiliary finishing materials selected, both for the basecoat and for the final finishing coat, as well as the working procedures used, led to obtaining assortments of natural leather finished with antique and cracked effect, which can imitate old, used leathers for valuable book covers.

EXPERIMENTAL

Materials

- Roda-Cryl 87, Roda-pure 302, Roda Wax MONO, Roda-Pur 5011, Roda lacquer 93, Roda feel KTA 950, Roda Casicolor Ochre, Roda Casicolor Brown R (Triderma, Romania).
- Eukesol OL Grund AB-1, LURON Glanz E, LURON Top, Eukesolar (STHAL, Holland).
- The crust bovine (calves) leathers natural grain assortments, vegetable tanned and wet finished by retanning, and fatliquoring (1.2-1.4 mm thick) (INCDTP – Division Leather and Footwear Research Institute Bucharest, Romania).

Methods

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

Finished leathers were artificially aged and tested by colorimetric measurements were performed using a MINOLTA spectrophotometer (CM 2002), with light impulses from a xenon lamp with 0.8 cm aperture. Light reflection is focused on a silicon photo diode with wavelengths between 400 and 700 nm (10 nm steps) and $L^*a^*b^*$ values (chromatic coordinates: brightness, red/green and yellow/blue), according to the CIE LAB system. Parameters of colour difference between aged samples using IT1, IT2, and IL methods (T) and unaged ones (R) were calculated using the following equations:

$$\Delta a^* = a^*_T - a^*_R \quad (1)$$

$$\Delta b^* = b^*_T - b^*_R \quad (2)$$

$$\Delta L^* = L^*_T - L^*_R \quad (3)$$

Chromatic deviation or shift ΔE^* was calculated with equation:

$$\Delta E^* = [\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}]^{1/2} \quad (4)$$

Elaboration of Dry Finishing Technologies for Natural Leathers for Bookbinding

Dry finishing technologies have been developed for natural grain coloured bovine hides with contrasting, antique and cracked effect (Triderma, 2019; STAHL, 2019).

The framework technology for dry finishing of bovine leather into natural grain box assortments for bookbinding, with contrasting effect, marked P1(P), with antique effect,

marked P2(P) and with cracked effect, marked P3(P) and polyurethane final dressing, is presented in Tables 1-3.

Table 1. Framework technology for dry finishing of bovine leathers into natural grain box with contrasting effect

Operation	Dispersion composition/application method
Application of dispersion I (basecoat)	80-100 g/L pigment paste (Roda Casicolor Ochre) 30-50 g/L aqueous wax emulsion (Roda wax MONO) 250 g/L acrylic binder (Roda-cryl 87) 600-640 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
Application of dispersion II	30-50 g/L metalcomplex dye (Roda Brown H) 30-50 g/L ethanol 250 g/L acrylic binder (Roda-cryl 87) 650-690 g/L water Application by spraying (2 passes dispersion I) The skins are wrinkled before applying dispersion II
Application of final dressing (fixing)	700 g/L aqueous polyurethane dispersion (Roda pur 5011) 20 g/L aqueous wax emulsion for handle (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 – 70-80°C; pressure – 50-100 atm.

Table 2. Framework technology for dry finishing of bovine leathers into natural grain box with antique effect

Operation	Dispersion composition/application method
Application of dispersion I (basecoat)	60-80 g/L pigment paste (Roda Casicolor Ochre) 30-50 g/L aqueous wax emulsion (Roda wax MONO) 200 g/L acrylic binder (Roda-cryl 87) 100 g/L polyurethane binder (Roda-pure 302) 570-610 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
Application of dispersion II	80-100 g/L pigment paste (Roda Casicolor Brown) 30-50 g/L aqueous wax emulsion (Roda wax MONO) 100 g/L acrylic binder (Roda-cryl 87) 100 g/L polyurethane binder (Roda-pure 302) 650-690 g/L water Application by spraying (2 passes dispersion II)
Drumming	It is executed in the drum, 2-4 hours
Application of final dressing (fixing)	700 g/L aqueous polyurethane dispersion (Roda pur 5011) 20 g/L aqueous wax emulsion for handle (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 – 70-80°C; pressure – 50-100 atm.

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Table 3. Framework technology for dry finishing of bovine leathers into natural grain box with cracked effect

Operation	Dispersion composition/application method
Application of dispersion I (basecoat)	150 g/L cationic oil (Eukesol OLGrund AB-1) 850 g/L water Very good drying
Application of dispersion II	50 g/L metal complex dye (Eukesolar) 200-250 g/L protein binder (LURON Glanz E) 350-400 g/L protein binder (LURON Top) 300-400 g/L water Application by spraying (2 passes dispersion II)
Intermediate pressing	In hydraulic press with the mirror plate, parameters: - temperature – 90°C; pressure – 100 atm
Staking	It is executed on the Mollisa staking machine (2 passes)
Application of dispersion II	Application by spraying (2 passes dispersion II)
Intermediate pressing	In hydraulic press with the mirror plate, parameters: temperature – 90°C; pressure – 100 atm
Drumming	It is executed in the drum, 2-4 hours
Application of final dressing I (fixing)	700 g/L aqueous polyurethane dispersion (Roda pur 5011) 300 g/L water Application by spraying (2 passes final dressing)
Final pressing	In hydraulic press with the mirror plate, parameters: temperature – 80°C; pressure – 100 atm
Application of final dressing II (fixing)	700 g/L aqueous polyurethane dispersion (Roda pur 5011) 20 g/L aqueous silicone oil emulsion (Roda feel KTA 950) 280 g/L water Application by spraying (2 passes final dressing)

Application of the final dressing was performed in two variants: P – polyurethane (Roda pur 5011) and N – nitrocellulose (Roda lac 93). Finished leathers for bookbinding using the technologies (application by spraying) for dry finishing presented in Tables 1-3, and nitrocellulose final dressing, with contrasting effect, were marked P1(N), with antique effect, marked P2(N) and with cracked effect, marked P3(N).

Finished natural leathers for bookbinding can be made by applying dispersed systems on the surface of crust leathers, and with the help of modern ecological finishing machines with rollers, which have certain designs, thus obtaining special effects.

Testing Artificially Aged Finished Leather

Finished leathers were artificially aged and tested according to ISO 17228/2006 standard. Mechanical characteristics of finished natural grain box assortments in the same variants but artificially aged were determined. The following abbreviations were used:

- IT1 – leather aged at 50°C for 7 days;
- IT2 – leather aged at 70°C for 7 days;
- IL – leather aged with artificial light (Xenotest) for 7 days.

RESULTS AND DISCUSSION

Optical Microscopy Analysis of Obtained Leather Assortments

Optical microscopy images were recorded for bovine hides into natural grain box with contrasting effect, marked P1(P), antique effect, marked P2(P) and cracked effect, marked P3(P) and polyurethane final dressing are presented in figure 1.

Figure 1. Optical images recorded for the finished natural grain box bovine leather with contrasting, antique and cracked effect

Assortments of bovine (calves) finished using in the final dressing, aqueous polyurethane dispersion, have a matte appearance, and those finished with aqueous nitrocellulose emulsion, in the final dressing, have a glossy appearance.

Characterization of Finishing Leathers by Colorimetric Method

Finished leathers were artificially aged and tested according to the CIE LAB system. Chromatic characteristics of natural grain box leather samples P1(P)-P3(P) and P1(N)-P3(N) non-aged and aged using the methods IT1, IT2 and IL, are given in Table 4.

Table 4. Values of colorimetric parameters for finished natural grain box leather samples

Sample	CIE L*	CIE a*	CIE b*	CIE C*	CIE H*
P1(P)	45.38	25.54	26.72	35.69	49.49
P2(P)	45.67	25.61	26.98	35.95	49.73
P3(P)	45.42	24.83	25.73	25.73	49.19
P1(N)	44.89	24.35	26.47	34.78	50.75
P2(N)	45.20	24.48	26.60	34.88	50.74
P3(N)	45.92	24.46	26.36	34.68	50.45

Variation of colorimetric parameters for finished natural leather samples P1(P)-P3(P) and P1(N)-P3(N), aged using IT1, IT2 and IL methods is shown in Table 5.

Table 5. Variation of colorimetric parameters for finished aged natural grain box leather samples using IT1, IT2, and IL methods

Sample	MI	ΔL^*	Δa^*	Δb^*	ΔE^*
P1(P)	IT1	-0.30	-0.02	-0.08	0.33
	IT2	-0.32	-0.36	-0.48	0.65
	IL	-0.38	-0.86	-0.88	1.29
P2(P)	IT1	-0.28	-0.15	-0.09	0.28
	IT2	-0.29	-0.04	-0.42	0.55
	IL	-0.30	-0.32	-0.07	0.86
P3(P)	IT1	-0.24	-0.44	-0.08	0.26
	IT2	-0.20	-0.06	-0.20	0.42

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Sample	MI	ΔL^*	Δa^*	Δb^*	ΔE^*
P1(N)	IL	-0.19	-0.09	-0.08	0.24
	IT1	0.66	0.56	0.79	1.02
	IT2	0.78	0.39	0.87	1.28
P2(N)	IL	0.27	0.28	0.36	0.62
	IT1	0.54	0.45	0.72	1.32
	IT2	0.68	0.29	0.88	1.12
P3(N)	IL	0.22	0.21	0.30	0.74
	IT1	0.86	0.63	0.65	1.25
	IT2	0.72	0.48	0.74	1.18
	IL	0.46	0.35	0.36	0.59

After irradiation and thermal treatment, samples P1(N)-P3(N) have positive values for brightness ($\Delta L^* > 0$), i.e. they have lighter (brighter) colours than samples P1(P)-P3(P), that has a negative value for brightness ($\Delta L^* < 0$), indicating the positive influence of polyurethane dressing on fastness to light of leathers compared to the nitrocellulose dressing, on the colour.

CONCLUSIONS

- The leathers with special effect finish (contrasting antique and cracked effect), can be used for artistic and luxury bookbinding, archival bookbinding and restoration purposes.
- Thermal and artificial light ageing change colorimetric characteristics (CIE $L^*a^*b^*$) compared to those of unaged samples, depending on the ageing method, leather assortment and type of final dressing. The highest values for fastness to light after artificial light ageing were those of leathers finished with polyurethane dressing and the lowest, those finished with nitrocellulose dressing.

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