COLORIMETRIC CHARACTERIZATION OF LEATHER ASSORTMENTS FINISHED WITH ECOLOGIC MATERIALS

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Leather is finished by coating the dermal substrate with disperse finishing systems containing: pigments, binders, natural and synthetic waxes, preservatives, plasticizers, thickeners, fillers, odorizers, penetrating agents, solvents. To prepare the pigment pastes, black iron oxide pigments were used – admitted by the legislation in force, Bindex BRILLANT acrylic binder as carrier resin – also having protective colloid properties, lauryl alcohol ethoxylated with 7 moles of ethylene oxide – fully biodegradable – as a dispersing agent and stabilizer and natural oils as plasticizers: castor oil, flax oil or poppy seed oil. The pigment pastes to be used in the final dressing for the dry finishing of natural leather. In this paper, a finishing composition, technology for leather assortments and characterization by CIE L*a*b* colorimetric method are presented. After thermal and artificial light aging, the colorimetric characteristics (CIE L*a*b*) change, depending on the temperature of the heat treatment and UV light, leather assortment, and type of final dressing. The highest resistance to light after aging under the influence of artificial light has the leathers finished with polyurethane or acrylic dressing in comparison with those finished with nitrocellulose dressing.

Keywords: leather, finishing, pigment pastes, colorimetric method

INTRODUCTION

Leather is finished by coating the dermal substrate with disperse finishing systems containing: pigments, binders, natural and synthetic waxes, preservatives, plasticizers, thickeners, fillers, odorizers, penetrating agents, solvents (Lange, 1982; Heidemann, 1994; Chirita and Chirita, 1999).

Environmental and toxicity concerns have led to new alternatives for the industry of ancillary finishing materials (Niculescu *et al.*, 2013; Niculescu *et al*., 2015; Florescu *et al*., 2009).

Flax and poppy seed oils, used as plasticizers, increase the films' resistance to aging over time (Lăzărescu, 2009; Istudor, 2011).

The paper presents the physical-chemical characterisation of newly obtained pigment pastes, developing a finishing composition using the pigment pastes for the basecoat and final dressing (polyurethane, acrylic or nitrocellulose) and CIE L*a*b* colorimetric method characterisation of cattle leather finished and aged using various methods (Tarlea and Ilie, 2006; Tarlea and Ilie, 2008; Niculescu and Leca, 2005).

EXPERIMENTAL

Materials

Bovine Leather chrome tanned, retanned, fatliquored and dyed (black), 1.2-1.4 mm thick from INCDTP-ICPI, Romania.

Finishing auxiliaries from (Triderma, Germany, 2012; Florescu *et al*., 2009).

Black pigment paste -PN - obtained by a process described in (Niculescu and Manta, 2013; Niculescu *et al*., 2015).

The product was used as handle modifier containing black iron oxide based on iron tetroxide (Fe_3O_4 – 94%), acrylic binder, castor, flax or poppy seed oils, stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide with the following characteristics: dry substance – 30.22-31.34, pH (10% solution) – 6.8-7.1, ash – 23.90-25.04%;

Feeling agent -Wax-AGE 7- obtained by o process described in (Niculescu *et al*., 2013). The product was used as handle modifier containing beeswax, lanolin and triethanolamine monostearate and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide with the following characteristics: dry substance – 18.96, pH (10% solution) – 7.3, Ford cup viscosity Φ4 – 27 s, kinematic viscosity, cSt – 10.48, density – 0.975 g/cm^3.

Methods

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). In the CIE L*a*b* space used in colorimetric analysis by reflection, the tint (represented by fundamental colours – red, green, yellow and blue), brightness or clarity (represented by the chromatic stimulus varying from black to white) and saturation (purity of colour) are expressed according to three coordinates: L*, a* and b*. On the X axis, a* parameter has values between red (a* > 0) and green (a* < 0) stimuli, on the Y axis, b* parameter varies between yellow (b* > 0) and blue (b* < 0) stimuli, and L* parameter, on polar Z axis, represents brightness (grey axis), varying between white and black. (DIN 6174, 1976; Jawahar *et al*., 2013; X-Rite, 2007).

The colour difference parameters of the analyzed (P) and reference (R) samples are expressed by the following equations:

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

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

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

Based on these equations, the following parameters can be calculated:

- chromatic shifting, through the relation:

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

- saturation or purity difference, using the relation:

$$\Delta C^* = [a^{*2}_P + b^{*2}_P]^{1/2} - [b^{*2}_R + L^{*2}_R]^{1/2} \quad (5)$$

- tint difference, through the relation:

$$\Delta H^* = [\Delta E^{*2} - \Delta L^{*2} - \Delta C^{*2}]^{1/2} \quad (6)$$

Obtaining New Pigment Pastes

The receipts and methodology for obtaining the pigment pastes are described in (Niculescu and Manta, 2013; Niculescu *et al*., 2015) and composition is presented in Table 1.

Materials used for obtaining of new black pigment paste are: black iron oxide pigment, acrylic polymer, non-ionic tensioactive agent, wax emulsion made from beeswax, lanolin and triethanolamine monostearate and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide, castor oil, flax and poppy seed oils, used as plasticizers.

Table 1. The composition of new pigment pastes

Quantities	New pigment paste - PN 1	New pigment paste - PN 2	New pigment paste - PN 3
Black iron oxide, (%)	30	30	30
Polyacrylic binder, %	40	40	40
Ethoxylated lauric alcohol, %	9	9	9
Castor oil, %	9	-	-
Flax oil, %	-	9	-
Poppy seed oil, %	-	-	9
Wax emulsion, %	3	3	3
Water, %	9	9	9

The framework technology for dry finishing of bovine leather into natural grain box assortments, black, is presented in Table 2.

Table 2. Technology for dry finishing of bovine leather into black natural grain box assortments

Operation	Dispersion composition/application method
Application of dispersion I (basecoat)	100 g/L pigment paste (PN 1, PN 2 or PN 3) 30 g/L aqueous wax emulsion 300 g/L aqueous acrylic dispersion, or 150 g/L aqueous acrylic dispersion and 150 g/L aqueous polyurethane dispersion, or 200 g/L aqueous acrylic dispersion and 100 g/L aqueous polyurethane dispersion 70 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 I	By spraying (2-3 passes dispersion I)
Application of final dressing (fixing)	Emulsion/dispersion with the following composition: 700 g/L aqueous nitrocellulose, acrylic or polyurethane emulsion 20 g/L aqueous wax emulsion for handle 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.

Application of the final dressing (fixing films deposited onto the dermis) was performed in three variants: FN – nitrocellulose, FA – acrylic and FP – polyurethane, presented in Table 3.

Table 3. Technological variants for fixing bovine leather into natural grain box assortments

Components of final dressing (g/L)/Variant	FN	FA	FP
Roda lac 93	700	-	-
Medacril EFP34	-	700	-
Roda pur 5011	-	-	700
Wax emulsion AGE 7	20	20	20
Water	280	280	280

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 for 7 days;
- IL – leather aged with artificial light (Xenotest) for 7 days.

RESULTS AND DISCUSSION

Characterization of Pigment Pastes

New pigment pastes were characterized by physical-chemical analyses. Physical-chemical characteristics are presented in Table 4.

Table 4. Physical-chemical characteristics of pigment pastes

Characteristics/samples	New pigment paste - PN 1	New pigment paste - PN 2	New pigment paste - PN 3
Dry substance, %	31.34	30.84	30.22
pH 10% solution	6.8	7.0	7.1
Ash, %	25.04	24.65	23.90

The new pigment paste are viscous and homogeneous fluids and dry substance indicate that they are more concentrated pastes. They are stable over time, without sediments of phase separation and have the characteristics of concentrated pastes.

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 assortments (variants PN1-PN3 for finishing with using the pigment pastes for base coat and variants FN, FA and FP for final dressing) non-aged and aged using the methods IT1, IT2, IL, plus those aged in artificial light (UV) for 7 days–IUV obtained using the prepared pigment pastes are given in Table 5.

Table 5. Values of colorimetric parameters for finished unaged black natural grain box leather samples

Sample	Technological variant	CIE L*	CIE *	CIE b*	CIE C*	CIE H*
P 1	PN1, FN	25.05	0.23	-0.60	0.65	290.55
P 2	PN2, FN	24.65	0.20	-0.69	0.71	286.47
P 3	PN3, FN	25.47	0.23	-0.51	0.55	294.24
P 4	PN1, FA	25.14	0.16	-0.65	0.67	283.97
P 5	PN2, FA	24.48	0.17	-0.69	0.71	284.08
P 6	PN3, FA	25.16	0.17	-0.64	0.66	285.2
P 7	PN1, FP	24.94	0.21	-0.57	0.61	290.67
P 8	PN2, FP	24.70	0.21	-0.70	0.73	286.32
P 9	PN3, FP	25.25	0.13	-0.54	0.56	284.01

Variation of colorimetric parameters for finished natural grain box leather samples P1-P9 aged using IT1, IT2, IL and IUV methods is shown in Table 6.

Table 6. Variation of colorimetric parameters for finished aged black natural grain box leather samples using IT1, IT2, IL and IUV methods

Sample	Method	ΔL*	Δa*	Δb*	ΔE*
P 1	IT1	0.54	0.29	0.05	0.61
	IT2	0.83	-0.1	0.26	0.88
	IL	0.89	-0.09	0.02	0.40
	IUV	0.87	-0.09	0.1	0.88
P 2	IT1	0.48	-0.05	-0.02	0.48
	IT2	0.61	-0.1	-0.23	0.66
	IL	0.86	-0.09	0.13	0.87
	IUV	0.53	-0.03	-0.16	1.24
P 3	IT1	0.24	0.1	-0.11	0.28
	IT2	0.29	-0.1	0.1	0.32
	IL	0.69	-0.15	0.09	0.72
	IUV	0.52	-0.07	0,05	0.09
P 4	IT1	0.28	-0.04	-0.06	0.19
	IT2	0.5	-0.09	0.09	0.52
	IL	0.44	-0.04	0.09	0.45
	IUV	0.43	0.12	0.23	0.77
P 5	IT1	0.18	-0.04	0	0.09
	IT2	0.37	-0.18	0.21	0.32
	IL	0.33	0	0.01	0.33
	IUV	0.21	-0,07	0.12	0.17
P 6	IT1	0.14	-0.07	0.8	0.87
	IT2	0.16	-0.19	0.32	0.52
	IL	0.29	-0.04	0.02	0.39
	IUV	0.13	-0.04	0.06	0.15
P 7	IT1	0.1	-0.04	-0.05	0.12
	IT2	0.18	-0.19	0.35	0.44
	IL	0.2	0.03	0	0.40
	IUV	0.11	-0.11	0.01	0.22
P 8	IT1	0.1	-0.13	0.02	0.17
	IT2	0.14	-0.14	0.08	0.21
	IL	-0.01	0.01	0.04	0.04
	IUV	-0.01	-0.17	0.4	0.43
P 9	IT1	0.02	0.01	-0.05	0.05
	IT2	0.05	0.01	0.02	0.05
	IL	-0.38	-0.05	0.19	0.43
	IUV	-1.02	0.04	-0.16	1.03

The samples finished using black pigment pastes (P1-P9) containing the plasticizers: castor oil (P1, P4 and P7), flax oil (P2, P5 and P8) or poppy seed oil (P3, P6 and P9) and nitrocellulose (P1-P3), acrylic (P4-P6) or polyurethane (P7-P9) dressing. Samples P2 and P3 aged using IT1, IT2, IL and IUV methods have lower values of ΔL* parameter compared to P1 and are darker, which indicates a positive influence of the acrylic and polyurethane dressing on fastness to light of leathers finished compared to nitrocellulose dressing. Samples P5 and P6 aged using IT1, IT2, IL and IUV methods have lower values of ΔL* parameter compared to P4 and are darker, which indicates a positive influence of the acrylic and polyurethane dressing on fastness to light of leathers finished. Samples P8 and P9 aged using IT1 and IT2 methods have lower values of ΔL* parameter compared to P7 and are darker, which indicates a positive influence of the acrylic and polyurethane dressing on fastness to light of leathers finished compared to nitrocellulose dressing.

Samples P8 and P9 aged using IL and IUV methods have negative values for brightness ($\Delta L^*<0$), i.e. are darker compared to sample P7. Samples P4-P9 aged using IL and IUV methods have ΔL^* lower than P1-P3, and therefore are darker. Leather samples finished with acrylic and polyurethane dressing and aged using the specified methods have lower ΔL^* values and change their colour less compared to those finished with nitrocellulose dressing. The lower values of ΔL^* also indicate the positive influence of plasticizer poppy seed oil used on resistance to ageing.

CONCLUSIONS

- 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 or acrylic dressing and the lowest, those finished with nitrocellulose dressing.
- Flax and poppy seed oils, used as plasticizers, improve resistance to ageing of coating.

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