ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

LEATHER FINISHING PRODUCTS WITH APPLICATIONS IN CREATIVE INDUSTRIES AND CULTURAL HERITAGE

NICULESCU Olga

National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute, Ion Minulescu Street, no. 93, Sector 3, Bucharest, Romania, icpi@icpi.ro

Corresponding author: Niculescu Olga, E-mail: o_niculescu@yahoo.com

Abstract: *From prehistoric times to the present day, pigments have been used in cave paintings, decorations, clothing, writing, fine arts and more. Blue is the color most often considered the symbol of spirituality.*
Cobalt blue is a mixed oxide of cobalt and aluminum and one of the most important blue pigments used in painting. It was used a lot by Van Gogh and Renoir. Heritage objects from museums, libraries and archives are sensitive to the quality of the microclimatic conditions in storage and exhibition areas. Inadequate environmental conditions may alter the aesthetic, use and material quality of art works and reduce their lifetime. The quality of pigment pastes used in the production of finishing films for semi-processed leather influences some of the physico-mechanical, technological, aesthetic properties of the finished products. Pigment pastes were obtained based on cobalt blue oxide, polymeric binder, lauryl alcohol ethoxylated with 7 moles of ethylene oxide (biodegradable), waxes and plasticizers and were characterized by physical-chemical, microscopic, rheological and thermal analyses. Pigment pastes were used in combination with film forming polymers (acrylic and polyurethane) with high resistance to light and aging for finishing natural leather with applications in creative industries (bookbinding, office items, paintings on leather) and cultural heritage.

Key words: *natural leather, pigment pastes, creative industries, cultural heritage*

1. INTRODUCTION

Pigments are organic or inorganic chemical compounds which constitute the dye base for coatings. Pigments used in leather finishing must have certain characteristics, among which the most important are: fastness to light, resistance to weathering and high temperatures, bright and vivid color, high coating power, high dispersion degree, compatibility with the other components of coating dyes. (1)

In leather finishing operations there are restrictions regarding the use of heavy metals in pigment pastes, ethoxylated alkylphenols, formaldehyde and other toxic crosslinking agents. (2)

Ecological and Toxicological Association of Dyes and Organic Pigment Manufactures (ETAD) has set limits for heavy metal content in water-soluble dyes (for cobalt the permissible limit is 500 ppm). (3) SG, “The Test Mark for Low Pollutant Leather Products”, includes the limits for heavy metal content in leather products (for cobalt the permissible limit is 4.0 ppm). (4)

Recipes are proposed to obtain stable pastes with aqueous dispersion medium using the components: cobalt blue oxide, acrylic resin as dispersion medium for pigments, light and ageing resistant vegetable oils as plasticizers (poppy seed oil), natural and artificial wax emulsions (beeswax, lanolin and stearin, the last obtained by splitting of natural fats) and completely biodegradable non-ionic emulsifier - lauryl alcohol ethoxylated with 7 moles of ethylene oxide – as dispersing agent. Pigment pastes were used in combination with film forming polymers (acrylic and polyurethane) with high resistance to light and aging for finishing natural leather with applications in creative industries (bookbinding, office items, paintings on leather, albums) and cultural heritage.(5-8)

2. EXPERIMENTAL

2.1. Materials

• Cobalt blue (Pebeo, France), is a mixed oxide of cobalt and aluminum ($CoO \cdot Al_2O_3$) - 95%, particle size – 3 ± 120μm.

• Acrylic binder Bindex Brillant (Pebeo, France), homogenous emulsion, dry substance – 30,24 %, density – 1.965 g/cm^3, pH – 6.5, Hoppler viscosity – 4.000 cP.

• Poppy oil (Pebeo, Franţa), total fatty matters – 99%, viscosity Ford coupe Φ 6 – 23 s, saponification index – 290 mg KOH/g, acidity index – 3 mg KOH/g, iodine index – 138g 100/g oil.

• Ricin oil (SC Happynatura SRL, Bucharest), total fats – 64%, Ford cup viscosity Φ 6 – 57 s, saponification index – 14 mg KOH/g, acidity index– 9 mg KOH/g, iodine index – 92g 100/g oil.

• Nonionic emulsifier – lauric alcohol etoxilated with 7 mols ethylene oxide (SC Elton Corporation SA, Bucharest), density at 40^{0}C – 0.950 g/cm^3, pH (10%) solution – 7-8.

• Wax emulsion AGE 7 (ICPI), dry substance – 12%, pH (10% solution) – 7.0.

• Blue pigment paste, viscous and homogenous fluid, dry substance – 30-32%, pH (10% solution) – 6.5-8.0, ash – 23-25%.

• Roda-cryl 87 (Triderma, Germany), acrylic binder for ground coat (marked AC87), dry substance – 38.92%, pH (10% solution) – 6.0, Ford cup viscosity Φ4 – 14.5, density – 1.036 g/cm^3.

• 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.

• The nappa bovine leathers, mineral tanned and wet finished by retanning, fatliquoring and dyeing (1.0-1.2 mm thick, dyed blue) (INCDTP – Division ICPI Bucharest, Romania).
`

2.2. Methods

• 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}.

• Simultaneous Thermal Analysis of TG with DTA mode (ΔT) and DSC (mW) were run with a Perkin-Elmer instrument (model STA 6000); themperature: 25-950^{0}C, heating rate 10° C/min.

• 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.

• Rheological behaviour was determined using Haake VT 550 rotational viscometer, equipped with MV1 sensor system for average viscosities and RheoWin Thermo Fischer software.

• Physical-mechanical characteristics of finished leather assortments were determined according to the following standards: fastness to light (1-8 ranking) – SR EN ISO 105-B02:2003; dry and wet abrasion (1-5 ranking) – SR EN ISO 11640:2002.

• Finished leathers were artificially aged and tested according to ISO 17228/2006 standard.

2.3. Obtaining of pigment pastes

The pigment pastes based on cobalt blue oxide (PBC) were obtained by the following operations:
- mixing powder pigment with vegetable oil emulsion (poppy seed oil) and non-ionic emulsifier;
▪ 25-30% cobalt blue oxid, 8-10% vegetable oil emulsified with 0.8-1.0% non-ionic emulsifier – polyehtoxylated lauryl alcohol (reported to the amount of oil);
- mixing the intermediate product with the acrylic binder (Bindex Acrylic), AGE 7 wax emulsion (made from beeswax, lanolin and triethanolamine monostearate), lauryl alcohol ethoxylate with 7 moles of ethylene oxide and water;
▪ 35-40% acrylic resin in which the pigment is dispersed, 1-2% wax emulsion, 8-10% fully biodegradable non-ionic emulsifier and water;
▪ The disperse system is subjected to mechanical stirring (60-80 rot/min), at 25-30^{0}C, for 3-4 h.

The composition of new pigment pastes are given in Table 1.

Table 1. *The composition of new pigment pastes (PBC and M)*

New pigment paste composition	Quantity (%)- PBC	Quantity (%)- PBC-M
Cobalt blue oxide	25-30	25-30
Polyacrylic binder	35-40	35-40
Ethoxilated lauric alcohol	8-10	8-10
Poppy oil	8-10	-
Ricin oil	-	8-10
Wax emulsion	1-2	1-2
Water	8-23	8-23

2.4. Obtaining the Finishing Film on Glass Plate

Finishing compositions were prepared containing: 100 g/L new pigment paste (PBC) ; 30 g/L wax emulsion (AGE 7); 300 g/L acrylic binder (AC87); 570 g/L water. With these dispersions, finishing films were obtained by deposition on glass plate and dried on air.

2.5. Framework technology for dry finishing of bovine leathers

Framework technology for dry finishing of bovine leathers, with blue pigment paste is presented in Table 2.

Table 2. *Framework technology for dry finishing of bovine leathers*

Operation	Composition of dispersion/Method of application
Applying base coat	50-100 g/L pigment paste, 30 g/L wax emulsion, 300 g/L acrylic dispersion, 570-620 g/L water. Application by spraying (2 applications)
Intermediate pressing	In hydraulic press using mirror plate; parameters: T=50-60oC; P=50-100 atm.
Applying base coat	Spraying (2-3 applications)
Applying top coat (fixing)	Emulsion/dispersion with the following composition: 700 g/L aqueous polyurethane dispersion (PU5011) or nitrocellulose emulsion (LAC93), 300 g/L water. Application by spraying (2 applications)
Final pressing	In hydraulic press using mirror plate, parameters: T=70-80oC; P=50-100 atm.

The samples vere marked: PBC –FP (witch contains poppy oil/ fixing with polyurethane dispersion, PBC –FN (witch contains poppy oil/ fixing with nitrocellulose emulsion), PBC-M-FP (witch contains ricin oil/ fixing with polyurethane dispersion) and PBC-M-FN (witch contains ricin oil/ fixing with nitrocellulose emulsion).

2.6. Testing artificially aged finished Leather

Mechanical characteristics of finished natural grain Nappa leather assortments in the same variants but artificially aged were determined. The following abbreviations were used:

- IT1 – leather aged at 50^0C for 7 days;
- IL – leather aged with artificial light (Xenotest) for 7 days.

3. RESULTS

3.1. Characterization of Pigment Pastes by physical-chemical analyses

Physical-chemical characteristics are presented in the Table 3.

Table 3. *Physical-chemical characteristics of pigment pastes*

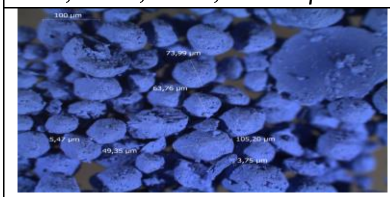
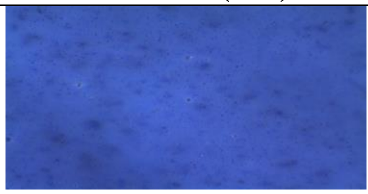
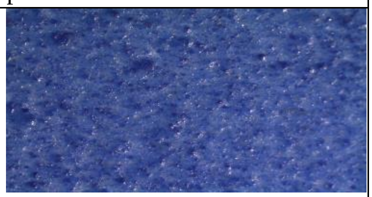
Characteristics /samples	Pigment paste - PBC	Pigment paste - PBC-M
Dry substance, %	30.67-31.87	30.12-31.75
pH 10% solution	6.5-6.8	6.5-6.8
Ash, %	23.42-25.25	23.80-24.86

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

3.2. Analysis of pigment pastes and leather finished with pigment paste by optical microscopy

Table 4 illustrates optical images of blue cobalt oxide powder and particle sizes, of pigment paste based on blue cobalt oxide (PBC), as well as the image of leather finished with pigment paste.

Table 4. *Optical images at 20X of the particle sizes of pigment powders, the pigment paste (PBC) and the leather finished with pigment paste*

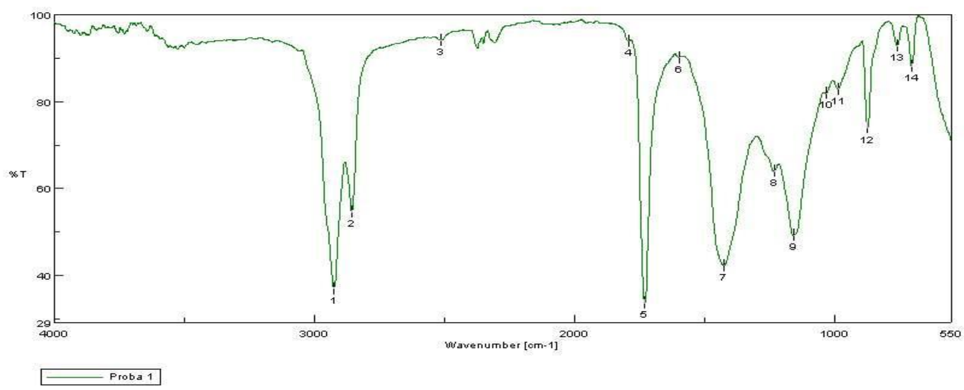
Particle sizes of pigment powders: 3.75; 49.35; 73.99; 105.20 µm	Pigment paste based on blue cobalt oxide (PBC)	Leather finished with pigment paste based on blue cobalt oxide
		

Images indicate an acircular geometry of particles, with agglomerate sizes ranging between 3.75 and 105.20 µm for the initial powder.

The resulting shades can be used to paint leather in a modern style.

3.3. Characterization of Pigment Pastes by FT-IR

The new pigment pastes, dried on the glass plate, were analyzed by ATR-FTIR and spectra are shown in Figure 1.



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2925.87	36.9384	2	2856.45	54.5909	3	2514.14	94.0677	4	1793.86	93.8816
5	1730.22	33.5551	6	1599.09	90.1275	7	1426.49	42.2713	8	1233.64	63.8946
9	1158.43	49.1357	10	1034.04	81.8443	11	987.762	82.8167	12	873.982	73.8955
13	760.203	92.7642	14	704.277	88.1099						

Figure 1. *ATR-FTIR spectrum for pigment pastes (PBC)*

The spectra of films obtained from the pigment pastes show characteristic bands of acrylic polymers: between 2925 and 2856, 1500 and 1426 and approximately 760 cm^{-1} assigned to asymmetric and symmetric stretching and deformation vibrations of CH_3 and CH_2 groups, an intense band at $\approx$1730 cm^{-1} typical for acrylates (the stretch of the ester carbonyl groups) and 1200-1000 cm^{-1} assigned to ether groups.

3.4. Characterization of coating films by thermal analysis

Figure 2 a and b presents TG and DTA curves for finishing films obtained by depositing on glass and drying, for the new pigment paste (PBC).

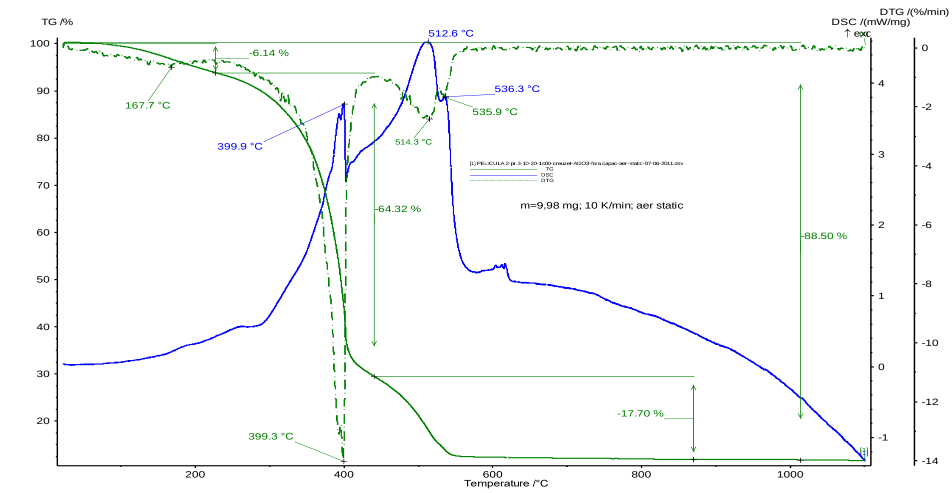


Figure 2. *TG and DTA diagram for the finishing film for the PBC*

For finishing film containing new pigment paste, the temperature interval for mass loss is 0-514°C. Mass loss is 6.14% in the temperature interval 0-167.7°C, 64.32% in the temperature interval 167.7- 399.3°C, and in the temperature interval 399.3-514.3°C, mass loss is 17.70%. Total degradation of the finishing film (88.50 %) occurs at the temperature of 514°C.

The specific thermal degradation parameters show that finishing film containing new pigment paste (PBC) has a very good thermal stability.

3.5. Rheological behaviour of pigment pastes

Rheograms obtained for pigment pastes PBC, containing blue cobalt oxide, when increasing (sus) and decreasing (jos) shear rates are shown in Figure 3.

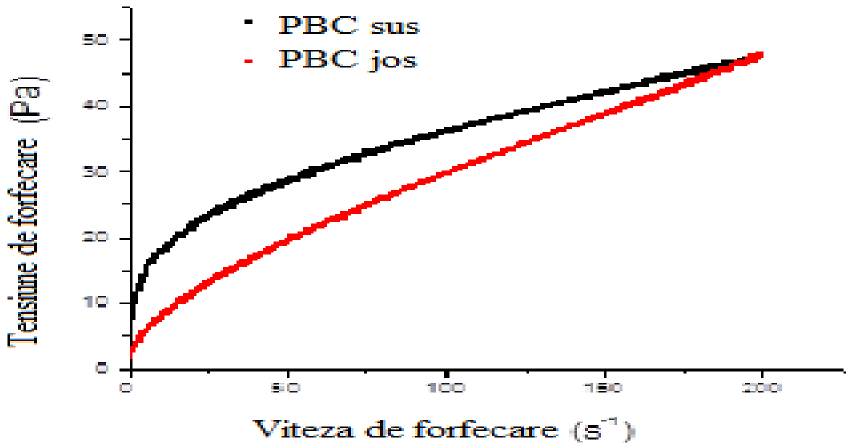


Figure 3. *Rheograms of pastes PBC when increasing (sus) and decreasing (jos) shear rates*

Parameters obtained by modelling rheograms in Figure 3 using the Cross model, both whenincreasing and decreasing shear rates, are presented in Table 5.

Table 5. *Parameters obtained by modelling rheograms in figure 3 with the Cross model*

System	η_0 (Pa.s)	η_∞ (Pa.s)	1/C (s^{-1})	m
PBC up	4.18 ± 0.05	0.040 ± 0.010	2.14 ± 0.08	0.65 ± 0.01
PBC down	6.42 ± 0,50	0.158 ± 0.002	0.08 ± 0.03	0.53 ± 0.01

They were modeled with Cross four parameters model, which has the advantage of providing information on system viscosity for the entire shear rates range, where η_0 and η_∞ are the limit values of the apparent viscosity at low and high shear rates, respectively, when the viscosity asymptotically approaches a constant value, C – adjustable parameter with dimension of time called Cross time constant and m – dimensionless adjustable parameter representing the dependence of viscosity on shear rate, called Cross velocity constant. The value indicates 1/C the shear rate at which pseudoplastic behavior begins. (9)

Rheograms show that the pastes have a pseudoplastic behaviour, flow starting at lower shear stress of 2-5 Pa.s. Rheograms obtained by increasing and decreasing shear rates do not overlap, but show a hysteresis loop, that is the pastes (PBC) are thixotropic.

Thixotropic behavior is desirable, fluidity increasing under the action of shear stress, facilitating the application and restoring original viscosity after application prevent dripping.

Hysteresis loop area is a measure of thixotropy. (10)

3.6. Characterization by mechanical methods of finished leathers

After the application of artificial aging treatments, the physical-mechanical characteristics were determined, using the same standards as for the non-aged ones. Variation of the physical-mechanical characteristics for finished natural grain napa leather samples marked: PBC-FP, PBC-FN, PBC-M- FP, PBC-M-FN, aged using IT1 and IL methods (M) is shown in Table 6.

Table 6: *Physical-mechanical characteristics of bovine hides into natural grain nappa*

Samples	M	PBC-FP	PBC-FN	PBC-M- FP	PBC- M-FN	SR EN ISO
Tear Resistance (N/mm^2)	IT1	44.5	44.1	43.8	42.7	SR EN ISO 3377:2012
Resistance to dry friction (mark)	IT1	5/4	5/3-4	5/3	5/2	SR EN ISO 11640:2002
Resistance to wet friction (mark)	IT1	4/4-5	4/4	4/3	4/2	SR EN ISO 11640:2002
Fastness to light (1-8 ranking)	IL	8	7-8	7-8	7	SR EN ISO 105-B02:2003

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

4. CONCLUSION

• Pigment pastes are concentrated pastes with pH of 1/10 solution of 6.5-8.0, with good coating power, more or less pseudoplastic and thixotropic rheological behavior and contributions of elastic and viscous components dependent on pigment and binder used. The spectra of films obtained from the pigment pastes show characteristic bands of acrylic polymers.

• The specific thermal degradation parameters show that finishing film containing new pigment paste has a very good thermal stability.

• The highest resistance to light after aging under the influence of artificial light has the leathers finished with polyurethane dressing in comparison with those finished with nitrocellulose dressing. Poppy seed oil, used as plasticizer, improve resistance to yellowing of coating films.

• Pigment pastes were used in combination with film forming polymers (acrylic and polyurethane) with high resistance to light and aging for finishing natural leather with applications in creative industries (bookbinding, office items, albums, paintings on leather) and cultural heritage.

ACKNOWLEDGEMENTS

This research was funded by the Romanian Ministry of Research and Digitalization, CCCDI - UEFISCDI, Nucleus Program, TEX-PEL-VISION 2022, 4N/8.02.2019, project number PN 19 17 01 02_ CREATIV_PIEL, and PNCDI III - Program 1 – Development of the national RD system, Subprogram 1.2-Institutional Performance-RDI excellence funding projects, Contract no. 4PFE/ 2022.

REFERENCES

[1] Gh. Chiriţă, M., Chiriţă, (1999), Chemistry and technology of leather (in Romanian), vol. I and II, Gh. Asachi Press, Iaşi.

[2] Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control).

[3] Ecological and Toxicological Association of Dyes and Organic Pigment Manufactures (ETAD).

[4] SG, “The Test Mark for Low Pollutant Leather Products”.

[5] O., Niculescu, A., Manta, Patent RO A/00533/2019, Inorganic pigment pastes for natural leather finishing.

[6] O., Niculescu, Z., Moldovan, M., Leca, C., Chelaru, Alexandrescu, L., Aboul-Enein, H. Y., Characteristics of natural leather finished with some ecofriendly mixtures of polymeric aqueous dispersions, J. Polymer Eng., 2015, 35(6), p.463-470.

[7] O., Niculescu, C., Gaidau, E., Badea, L., Miu, D., Gurau, D., Simion, (2020), *Special effect finish for bookbinding leather*, Proceedings of ICAMS 2020, p. 231-236.

[8] M., Lucretia, V., Bratulescu, C., Gaidau, V., Bocu, O., Niculescu, Natural leather for the patrimony book binding and the procedure for its development, Patent RO A/ 122098/2008.

[9] Cross, M.M., Rheology of non-newtonian fluids: A new flow equation for pseudoplastic systems, J. Colloid Sci., 1965, 20, 417.

[10] Schramm, G., A Practical Approach to Rheology and Rheometry,2nd ed., Gebrueder HAAKE GmbH, Karlsruhe, 2000.