MATERIALS FOR SURFACE DESIGN AND FINISHING FOR CONTEMPORARY FOOTWEAR – PART 1

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The leather industry creates a product that is both natural and long lasting. Leather is unique in its ability to combine beauty, comfort and practicality. Finishing, the last operation in natural leather processing, determines the appearance and value of the finished product, and has the purpose of embellishment, providing lustre and pleasant feel, covering flaws and forming a surface layer that protects leather during wear while improving resistance to external factors. The quality of the pigment pastes used in the composition of the leather surface finishing films influences some of the physical-mechanical, technological and aesthetic properties of the finished products. The materials for finishing – pigment pastes with aesthetic effect – were obtained based on dioxide-titanium, metal pigment-aluminum, polymeric binder, lauryl alcohol ethoxylated with 7 moles of ethylene oxide, waxes and plasticizers and were characterized by physical-chemical, microscopical, spectral and rheological analyses. Pigment pastes with metallic effect were used in combination with film forming acrylic and polyurethane polymers, with high resistance to light and aging for finishing natural leathers, with applications in creative industries (modern footwear).

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

INTRODUCTION

The leather industry creates a product that is both natural and long lasting. Leather is unique in its ability to combine beauty, comfort and practicality. Well-made leather lasts a long time and unlike most man-made or synthetic materials it gets better with age, acquiring a depth of patina and wear pattern that is individual to the user. Investing in quality leather products is investing for the future.

Finishing, the last operation in natural leather processing, determines the appearance and value of finished product, and has the purpose of embellishment, providing lustre and pleasant feel, covering flaws and forming a surface layer that protects leather during wear while improving resistance to external factors (Lange, 1982; Heidemann, 1994). Pigments used in leather finishing must have certain characteristics, among which the most important are: fastness to light, resistance to weathering and high temperatures, high coating power, high dispersion degree, compatibility with the other components of coating dyes (Chiriţă and Chiriţă, 1999).

In leather finishing operations there are restrictions regarding the use of heavy metals, ethoxylated alkylphenols, formaldehyde and other toxic crosslinking agents in pigment pastes (ETAD, 2004; SG, 2006; Directive 2010/75/EU).

Ecological and Toxicological Association of Dyes and Organic Pigment Manufactures (ETAD) has set limits for heavy metal content in water-soluble dyes (for copper the permissible limit is 250 ppm). SG, "The Test Mark for Low Pollutant Leather Products", includes the limits for heavy metal content in leather products (for copper the permissible limit is 60.0 ppm). Environmental and toxicity concerns have led to new alternatives for finishing ancillary industry (Niculescu *et al*., 2015a; Niculescu *et al*., 2015b; Niculescu and Manta, 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

https://doi.org/10.24264/icams-2022.V.5

well-known and coordinated, can be spectacular and sustainable at the same time (Pop *et al*., 2019).

Pigments are organic or inorganic chemical compounds which constitute the dye base for coatings. In order to obtain special finishing effects, when preparing pigment pastes, certain filling substances can be used (graphite, metallic aluminum powders for silver effects, or copper alloys for golden effects) (US Patent, 2005; EP Patent, 2014; 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, printed, pressed, waxed, etc.

Recipes are proposed to obtain stable pastes with aqueous dispersion medium using the components: dioxide-titanium white, 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), completely biodegradable non-ionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide – as dispersing agent, metal pigment-aluminum for silver effects, and bronze powder for golden effects. Pigment pastes were used in combination with film forming polymers (acrylic and polyurethane) with resistance to light and aging for finishing natural leather for shoes (especially for women), with applications in creative industries.

EXPERIMENTAL

Materials

- Metal Pigment-Aluminum for silver effect (Messerini SRL, Italy).
- Bronze Powder-Rich Gold for golden effect (Messerini SRL, Italy).
- Dioxide-titanium white (Europlastic SRL, Bucharest).
- 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, France), total fatty matters – 99%, Ford cup viscosity Φ 6 – 23 s, saponification index – 290 mg KOH/g, acidity index – 3 mg KOH/g, iodine index – 138g 100/g oil.
- Castor 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 – lauryl alcohol ethoxylated with 7 mols ethylene oxide (SC Elton Corporation SA, Bucharest), density at 40°C – 0.950 g/cm^3, pH (10%) solution – 7-8.
- Wax emulsion AGE 7 (ICPI), dry substance – 12%, pH (10% solution) – 7.0.
- Pigment pastes (PPS with silver effect and PPG with golden effect), viscous and homogenous fluid, dry substance – 30-35%, pH (10% solution) – 7.0-8.0, ash – 25-30%.
- Finishing auxiliaries from Triderma, Germany (Triderma, 2020).

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: aperture setting – 7.1 mm; scanning speed – 2 mm/s; number of scans – 30; resolution – 4 cm^{-1}.

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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 and 100X.

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

RESULTS AND DISCUSSION

Obtaining Pigment Pastes

The pigment pastes with special effect based on dioxide-titanium white and metal pigment-aluminum, for silver effect (PPS), or bronze powder, for golden effect (PPG), were obtained by means of the following operations:

- mixing powder pigment with vegetable oil emulsion (poppy seed oil) and non-ionic emulsifier;
    - 15-20% dioxide-titanium white, 10% metal pigment-aluminum or 10% bronze powder, 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 rpm), at 25-30°C, for 3-4 h.

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

Table 1. The composition of new pigment pastes (PPS, PPG and M1, M2)

New pigment paste composition	Quantity (%) - PPS	Quantity (%) - PPG	Quantity (%) - M1	Quantity (%) - M2
Dioxide-titanium white	15-20	15-20	15-20	15-20
Metal pigment-aluminum	10	-	10	-
Bronze powder	-	10	-	10
Polyacrylic binder	35-40	35-40	35-40	35-40
Ethoxylated lauric alcohol	8-10	8-10	8-10	8-10
Poppy oil	8-10	8-10	-	-
Castor oil	-	-	8-10	8-10
Wax emulsion	1-2	1-2	1-2	1-2
Water	8-23	8-23	8-23	8-23

Obtaining the Finishing Film on Glass Plate

Finishing compositions were prepared containing: 100 g/L pigment pastes (PPS or PPG); 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 air drying.

Characterization of Pigment Pastes by Physical-Chemical Analyses

Physical-chemical characteristics are presented in Table 2.

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Table 2. Physical-chemical characteristics of pigment pastes

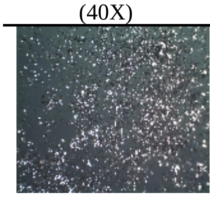
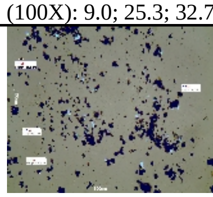
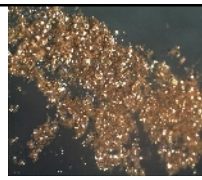
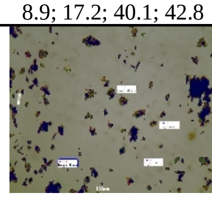
Characteristics/ samples	Pigment paste (PPS)	Pigment paste (PPG)
Dry substance, %	32.48-34.65	31.88-34.16
pH 10% solution	7.0-8.0	7.0-8.0
Ash, %	25.67-27.45	27.35-29.24

The pigment pastes (PPS, PPG) are viscous and homogeneous fluids and dry substance content indicates that they are concentrated pastes.

Analysis of Pigment Pastes by Optical Microscopy

Table 3 illustrates optical images of metal pigment-aluminum and bronze powder.

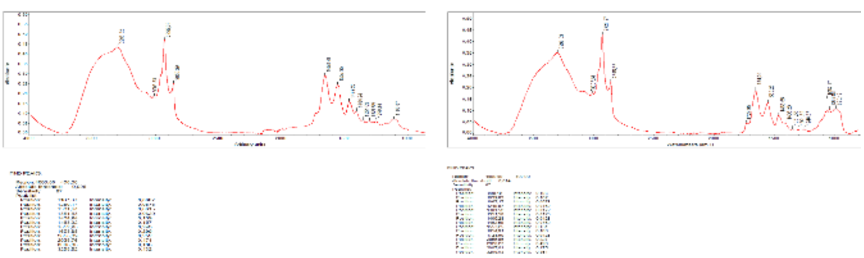
Table 3. Optical images at 40X and 100X of the particle sizes of pigment powders (µm)

Particles of metal pigment-aluminum (40X)	Particle sizes of metal pigment-aluminum (100X): 9.0; 25.3; 32.7	Particles of bronze powder (40X)	Particle sizes of bronze powder 100X): 8.9; 17.2; 40.1; 42.8
			

Images indicate an acircular geometry of particles, with agglomerate sizes ranging between 8.9 and 42.8 µm for the initial powder.

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.



a) b)

Figure 1. ATR-FTIR spectra for pigment pastes PPS (a) and PPG (b)

The spectra of films obtained from the pigment pastes show characteristic bands of acrylic polymers: between 2925 and 2855, 1552 and 1463 cm^{-1} assigned to asymmetric and symmetric stretching and deformation vibrations of CH_3 and CH_2 groups, an intense

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band at ≈1653 cm^{-1} typical for acrylates (the stretch of the ester carbonyl groups) and 1200-1000 cm^{-1} assigned to ether groups.

Rheological Behaviour of Pigment Pastes

The data of the rheological measurements are presented in Table 4.

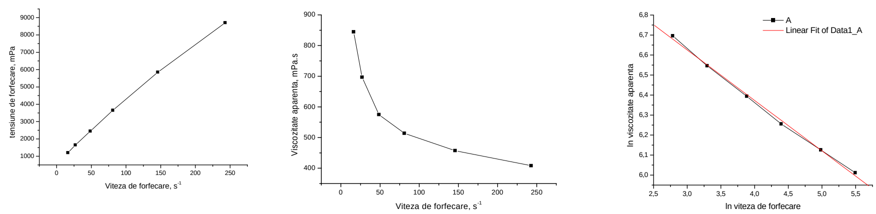
Table 4. Rheological data for pigment paste PPS

$\dot{\gamma}$, s^{-1}	α	τ, mPa	η, mPa.s	ln η	ln $\dot{\gamma}$
16.2	1150	13110	809.2593	6.696119	2.785011
27	1650	18810	696.6667	6.546307	3.295837
48.6	2550	29070	598.1481	6.393838	3.883624
81	3700	42180	520.7407	6.255252	4.394449
145.8	5850	66690	457.4074	6.125574	4.982236
243	8700	99180	408.1481	6.01163	5.493061

Rheograms obtained for pigment pastes PPS are shown in Figure 2. The representation of the shear stress-shear rate curve for this paste (Fig. 2.a.) leads to the rheogram in Fig. 2.b., which shows a slightly pseudoplastic behavior. The PPS pigment paste does not exhibit time-dependent rheological behavior. The apparent viscosity decreases with increasing shear rates, suddenly between 16 and 49 s^{-1} and much slower for higher shear rates (Fig.2.b.). Linearization of the data from Fig.2.b. leads to the following equation of the line obtained by linear regression (Schramm, 2000):

$\ln \eta^* = 7.38253 - 0.25233 \ln \dot{\gamma}$, with a coefficient of r = 0.9986 (1)

A viscosity value η_0 of 1607 mPa.s or 1.607 Pa.s results from the equation of the straight line (Fig. 2.c.).



a) b) c)

Figure 2. Rheograms obtained for pigment paste PPS

Pigment paste PPS has a slightly pseudoplastic behaviour, therefore, under the action of shear stress, it decreases its viscosity.

CONCLUSIONS

• Pigment pastes are concentrated pastes with pH of 1/10 solution of 7.0-8.0, with good coating power.

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• The spectra of films obtained from the pigment pastes show characteristic bands of acrylic polymers.

• Pigment pastes have a slightly pseudoplastic behaviour (under the action of shear stress, their viscosity decreases).

• The composition for natural leathers with special finishing effects, contains ecological components (titanium dioxide, acrylic resin, wax emulsion, vegetable oil and biodegradable non-ionic emulsifier, metal pigment-aluminum for silver effect or bronze powder for golden effect) and can be used for the surface finishing of natural leathers (white and pastel), in the composition of film-forming aqueous dispersions applied on the surface of natural leather for shoes (especially for women), to improve the organoleptic and aesthetic properties (related to fashion).

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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