NEW PIGMENT PASTE FOR LEATHER FINISHING

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Environmental problems that the leather industry faces today regarding leather finishing include restrictions on the use of heavy metals in pigment pastes, ethoxylated alkylphenols, formaldehyde and other toxic crosslinking agents. Environmental and toxicity related concerns have led to new alternatives for leather finishing auxiliaries. The quality of pigment pastes used, playing a major role in obtaining leather finishing film, influences some physical-mechanical, technological, aesthetic and ecological properties, which, cumulated, confer value of use and commercial appearance to various leather items: footwear, garments, bags and upholstery. This paper presents a study on the physical-chemical characterization and ATR-FTIR spectroscopy of a new pigment paste and leather finishing composition made using the new pigment paste, acrylic binder and biodegradable non-ionogenic emulsifier (which replaces nonylphenol ethoxylate). The finishing film obtained using the new finishing composition shows higher thermal stability compared to those currently used, as evidenced by differential thermal analysis (DTA).

Keywords: leather, finishing, pigment paste

INTRODUCTION

Leather finishing is done using disperse systems which contain the following auxiliaries: pigments, binders, dyes, natural and synthetic waxes, preservatives, plasticizers, thickening agents, fillers, odoriferous substances, penetrating agents, solvents (Lange, 1982; Heideman, 1994).

The quality of pigment pastes used, playing a major role in obtaining leather finishing film, influences some physical-mechanical, technological, aesthetic and ecological properties, which, cumulated, confer value of use and commercial appearance to various leather items: footwear, garments, bags and upholstery (Chirita and Chirita, 1999; Urban, 2002). 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.

In leather finishing operations there are restrictions regarding the use of heavy metals in pigment pastes, ethoxylated alkylphenols, formaldehyde and other toxic crosslinking agents (OSPAR, 2004; Triderma, 2010; Veco, 2010).

Environmental and toxicity related concerns have led to new alternatives for leather finishing auxiliaries (Niculescu and Leca, 2007).

The paper presents the characterization of a new pigment paste by physical-chemical analyses and ATR-FTIR spectroscopy, compared to pigment paste used in industrial production. The paper also presents the development of a finishing composition made using the new pigment paste and characterization by differential thermal analysis (DTA) of films obtained on glass from the finishing composition, compared to coating films obtained according to current leather finishing processes. For the new finishing composition the following chemicals were used: non-ionic tensioactive agent – lauryl alcohol ethoxylated with seven moles of ethylene oxide, which replaces nonylphenol ethoxylated with 9 moles of ethylene oxide, which is used usually in leather finishing. Its utilization in industrial production was forbidden by the Directive 76/769/EL/2003, as a consequence of assessment of its ecotoxicity which shows a 30% biodegradability only.

EXPERIMENTAL

Materials

Black iron oxide (Pebeo, France), content of Fe_2O_3 – 94%, bulk density – 0.8-1.2 g/cm^3, water absorption – 32% g/g, particle size – 0.6±0.1μm.

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.

Castor oil (S.C. Happynatura SRL, Bucharest), total fatty matters – 64%, viscosity Ford cup 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 moles of 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 used as handle modifier (made from beeswax, lanolin and triethanolamine monostearate and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide: dry substance – 12%, pH (10% solution) – 7.0 (Niculescu *et al.*, 2013).

Roda-cryl 87, marked AC87, (Triderma, 2010), acrylic binder for ground coat, dry substance – 38.92%, pH (10% solution) – 6.0, Ford cup viscosity Φ4 – 14.5, density – 1.036 g/cm^3.

Black pigment paste (Roda Casicolor Black), viscous and homogenous fluid, dry substance – 22.45%, pH (10% solution) – 6.5-8.0, ash – 12.24%.

Methods

Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were run with a Jasco instrument 4200 model, in the following conditions: wave number range – 4000-600 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}; filter – 30 kHz; angle of incident radiation – 45°.

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

Obtaining the New Pigment Paste

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

Materials used for obtaining of new black pigment paste are:

- black iron oxide pigment, which is not toxic;
- acrylic polymer, which replaces protein binders used in the compositions of pigment pastes, thus eliminating crosslinking with formaldehyde, which is toxic;

- non-ionic tensioactive agent was used – lauryl alcohol ethoxylated with seven moles of ethylene oxide; for blank pigment paste nonylphenol ethoxylated with 9 moles of ethylene oxide was used as 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 used as plasticizer.

Table 1. The composition of new pigment pastes

New pigment paste composition	Quantities
Black iron oxide, (%)	30
Polyacrylic binder, %	40
Ethoxylated lauric alcohol, %	9
Castor oil, %	9
Wax emulsion, %	3
Water, %	9

Obtaining the Finishing Film on Glass Plate

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

RESULTS AND DISCUSSION

Characterization of Pigment Pastes

New pigment pastes were characterized by physical-chemical analyses and ATR-FTIR spectroscopy.

Physical-chemical characteristics are presented in the Table 2.

Table 2. Physical-chemical characteristics of pigment pastes

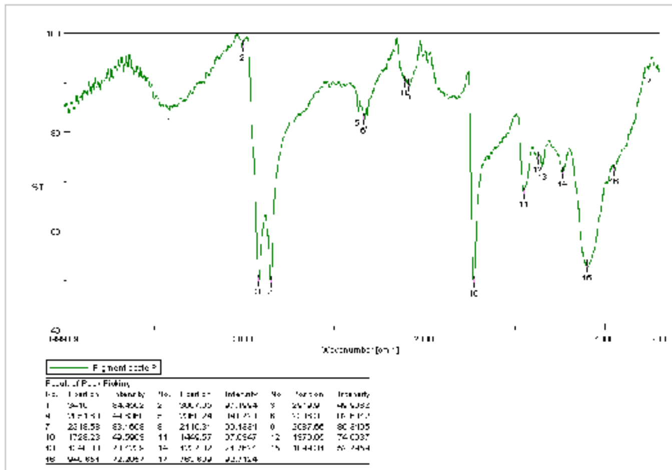
Characteristics / samples	New pigment paste	Blank Roda Casicolor Black
Dry substance, %	30.67	22.45
pH 10% solution	6.8	6.5-8
Ash, %	23.42	12.24

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.

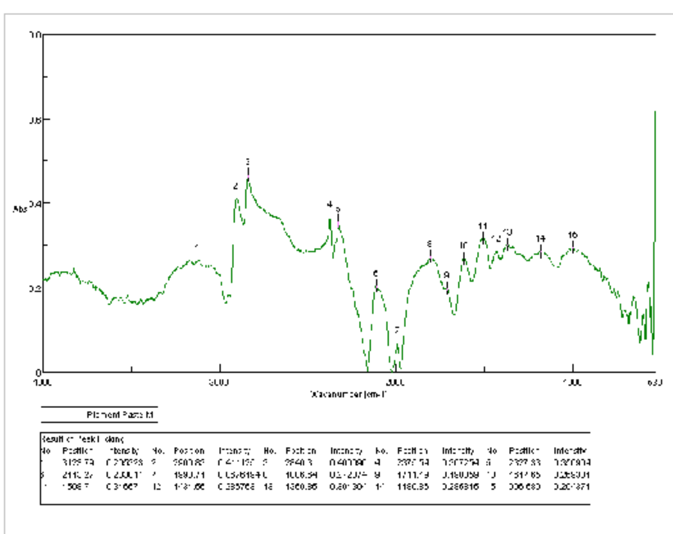
Rheological behavior of ecological pigment paste has been presented before (Niculescu *et al.*, 2014).

Characterization of Pigment Pastes by FT-IR

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



a) New pigment paste



b) Roda Casicolor Black pigment paste (blank)

Figure 1. ATR-FTIR spectrum for pigment pastes

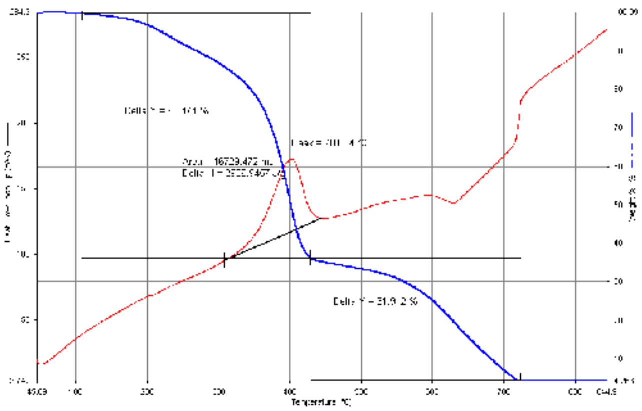
The ATR-FTIR spectrum from Figure 1 presents all the bands characteristic to acrylic polymers: in the range 3200-3500 cm^{-1}, a broad weak band assigned to carboxyl OH group, which usually overlaps the -NH band attributed to amide group. At 2919-

2851 cm^{-1}, 1449 cm^{-1} assigned to stretching and deformation vibrations of CH_3 and CH_2 groups. An intense band around 1728 cm^{-1} due to stretching of C=O groups from esters, and at 1099 given by ether groups. Both pigment pastes (new and blank) contain all the bands characteristic to acrylic polymers.

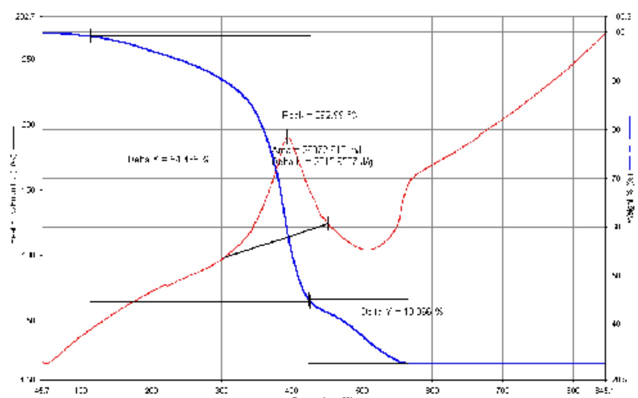
Characterization of Finishing Films

The finishing films obtained by deposition on glass plate of finishing compositions containing new pigment paste (Figure 2a) and Roda Casicolor Black pigment paste (Figure 2b) were characterized by DTA.

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 a), and b) for the finishing film used in industrial leather production.



a) Finishing film containing new pigment paste



b) Finishing film containing Roda Casicolor Black pigment paste (blank)

Figure 2. TG and DTA diagram for the finishing film obtained on the glass plate

Latent heat graphs show that the decomposition temperature for finishing film containing new pigment paste is 401.04°C and for finishing film with Roda Casicolor Black pigment paste (blank) is 394.79°C.

For finishing film containing new pigment paste, the temperature interval for mass loss is 110-725°C and mass loss is 63.474% in the temperature interval 110-430°C and 31.912% in the temperature interval 430-725°C. Total degradation of the finishing film occurs at the temperature of 725°C.

For finishing film containing Roda Casicolor Black pigment paste (blank) the temperature interval for mass loss is 118-565°C and mass loss is 54.435% in the temperature interval 118-425°C and 13.066% in the interval of 425-565°C. Total degradation of the finishing film occurs at the temperature of 565°C.

The specific thermal degradation parameters show that finishing film containing new pigment paste has an increased thermal stability compared with classic finishing film.

CONCLUSIONS

The new pigment paste has better characteristics than classic pigment paste used in leather finishing. Finishing film obtained with finishing composition containing new pigment paste is more stable at temperature as observed by DTA.

The research will continue with finishing tests on leather and test of biodegradability of the finishing composition /film in order to determine environmental impact.

Acknowledgements

This work was supported by ANCS from National budget Fund in the framework of "Nucleu" Program CERTEXPEL under the project code PN 09 10 04 10/2014.

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