Obtaining and Characterization of Some Ecologic Pigment Pastes for Finishing Natural Leathers and Furs

OLGA NICULESCU[1,2]*, MINODORA LECA[1], TEODORA STAICU[1], ZENOVIA MOLDOVAN[1], CIPRIAN CHELARU[2], DANIELA MARIANA BERECHET[2]

[1] University of Bucharest, Faculty of Chemistry, 36-46 Mihail Kogalniceanu Blvd., 050107, Bucharest, Romania

[2] National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute Bucharest, 93 Ion Minulescu Str., 031215, Bucharest, Romania

The quality of pigment pastes used in the production of finishing films for semi-processed leather and fur influences some of the physico-mechanical, technological, aesthetic and ecological properties which provide finished products with use value and commercial aspect. Prohibitions on the use of salts of heavy metals, ethoxylated alkyl phenols, formaldehyde and other toxic crosslinking agents in pigment pastes have raised concerns for finding alternatives for the industry of finishing ancillaries. Pigment pastes were obtained based on black iron oxide, polymeric binder, lauryl alcohol ethoxylated with 7 moles of ethylene oxide (biodegradable), waxes and plasticizers for finishing natural nappalan leather and fur. The acrylic polymer replaces protein binders used in the compositions of pigment pastes, thus eliminating cross-linking with formaldehyde, which is toxic. Pigment pastes obtained were characterized by physical-chemical, microscopic, spectral and rheological analyses. They have the appearance of viscous and homogeneous fluids, exhibiting stability over time and characteristics of concentrated paste. FT-IR spectrum shows characteristic bands of the acrylic binder used. Studied pigment pastes have a more or less pronounced pseudoplastic behaviour; under the action of shear stress they reduce their viscosity, and have weak thixotropy. Pigment pastes were used in combination with film forming polymers (acrylic and polyurethane) for natural nappalan leather and fur finishing.

Keywords: inorganic pigments, acrylic polymer, leather and fur finishing, rheology

Pigments are inorganic or organic chemical compounds which constitute the coloring base of coating dyes. In order to be used for nappalan leather and fur finishing, pigments must have certain characteristics, among which the most important are: fastness to light, to weathering and high temperatures, bright colour, high coating power, high dispersion rate, compatibility with the other components of the coating dye [1-6].

Environmental and toxicity concerns have led to new alternatives for the industry of ancillary finishing materials. [7-9]

This paper presents the development of pigment pastes based on black iron oxide, polymeric binder, biodegradable lauryl alcohol ethoxylated with 7 moles of ethylene oxide, waxes and plasticizers, for finishing natural nappalan leather and fur and their characterization by physico-chemical, microscopic, spectral and rheological analyses.

Experimental part

Materials and methods

Black iron oxide based on iron tetroxide *(SC Nubiola SRL, Romania*), contained in Fe_3O_4 – 94%, density – 4.6 $\pm$ 0.8 g/cm^3, water absorption 32% g/g, particle size 0.60.1 µm.

Acrylic binder – Bindex Brillant (France), white homogenous emulsion, dry substance – 30.24 %, density – 1.965 g/cm^3, *p*H – 6.5, Hoppler viscosity– 4000 cP.

Ricin oil (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 moles of ethylene oxide (Bucharest) density – 0.95 g/cm^3 at 40^{0}C, *p*H (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%, *p*H (10% solution) – 7.0.

Black pigment paste (PPNF), viscous and homogenous fluid, dry substance – 30.67%, *p*H (10% solution) – 6.5-8.0, ash – 23.42%;

The wax mixture was prepared in an equipment consisting of a reaction vessel with 3L capacity and a heating system (electric bath with temperature control).

The 3-necked reaction vessel, made of high-temperature resistant glass, is equipped with a propeller stirrer to homogenize the reaction mass, a thermometer for temperature control and condenser connected to the water source to maintain the temperature constant during the preparation process.

Obtaining pigment pastes

Black iron oxide pigment, which is not toxic, was used to prepare pastes.

A macromolecular compound from the class of acrylates was tested as polymeric binder. The acrylic polymer replaces protein binders which were used in the compositions of pigment pastes, thus eliminating crosslinking with formaldehyde, which is toxic.

In order to improve pigment dispersion, a non-ionic tensioactive agent was used – lauryl alcohol ethoxylate with seven moles of ethylene oxide, which facilitates the dispersion of hydrophobic pigment in the hydrophilic chain. Dispersion and wetting agents also stabilize the disperse system formed.

* email: o_niculescu@yahoo.com; Tel.: 0213235060

Table 1
TECHNOLOGICAL VARIANTS OF OBTAINING PIGMENT PASTES FROM BLACK IRON OXIDE

Amount (%)/ Materials	PPNF 1	PPNF 2	PPNF 3
Black iron oxide	25	30	35
Acrylic binder	30	35	40
Lauryl alcohol ethoxylate	8	9	10
Castor oil	8	9	10
AGE 7 wax emulsion	2	2	2
Water	27	12	3

Wax emulsion and castor oil were used as plasticizer in the preparation of pigment pastes.

Development of pigment pastes involves the following operations:

- mixing the powder pigment with vegetable oil emulsion and non-ionic emulsifier;
- mixing the intermediate product with the acrylic binder and with the other components (wax emulsion, non-ionic emulsifier, water).

In order to ensure optimum stirring during the technological process, components introduced in the mixing vessel must not exceed 50-70% of its capacity.

The following components were added in the mixing vessel:

- 25-35% inorganic pigment – black iron oxide;
- 8-10% vegetable oil (castor oil) emulsified with 0.8-1.0% fully biodegradable non-ionic emulsifier – lauryl alcohol polyehtoxylate with seven moles, reported to the amount of oil;
- 30-40% acrylic resin in which the pigment is dispersed;
- 2 % wax emulsion;
- 8-10% non-ionic emulsifier, the same used for the castor oil.

The disperse system is subjected to mechanical stirring with a stirrer at 60-80 rpm speed, at a temperature of 25-30^{0}C, for 3-4 h.

The resulting product, to which the dispersing agent was added, is a paste containing 30-42% dry substance and *p*H 6-6.5, which is neutralized to *p*H 7 [10-12].

Using this work procedure, black iron oxide pastes were obtained in the technological variants presented in table 1.

Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were run with a Jasco instrument (model 4200), in the following conditions: wavenumber 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° [13, 14].

Table 2
PHYSICO-CHEMICAL CHARACTERISTICS OF STUDIED PIGMENT PASTES

Characteristic/Pigment paste	PPNF 1	PPNF 2	PPNF 3
Dry substance,%	30.67	31.34	32.45
pH	6.5-8	6.5-8	6.5-8
Ash, %	23.42	25.04	25.22

Rheological behaviour was determined using Haake VT 550 rotational viscometer, equipped with MV1 sensor system for average viscosities and RheoWin Thermo Fischer Scientific software [15, 16].

Optical microscopy images were captured using a Leica stereomicroscope S8AP0 model with optic fiber cold light source, L2, with three levels of intensity. Magnification was 20X. [17].

Results and discussions

Characterization of pigment pastes by physico-chemical analyses

Physico-chemical characteristics of tested pigment pastes are presented in table 2.

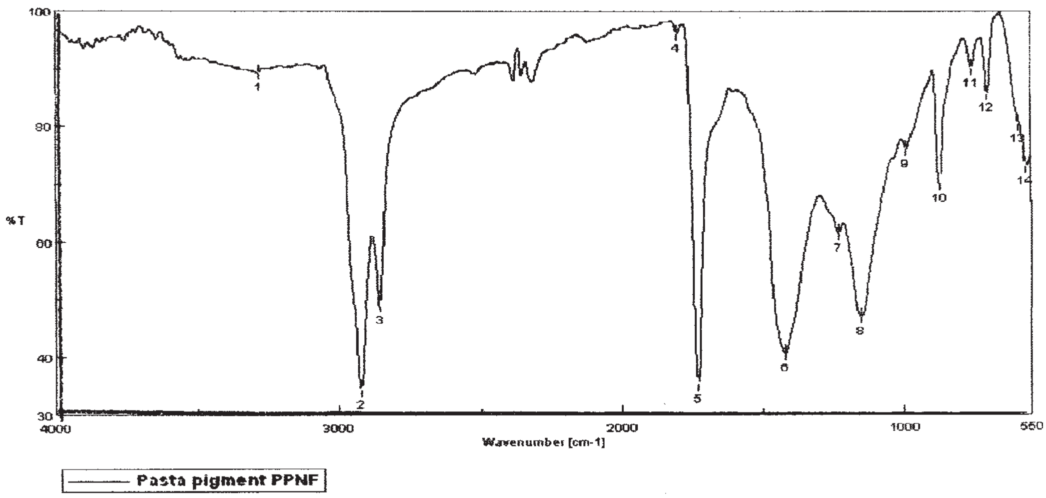
Dry substance percentages indicate that the formulated pigment pastes have the characteristics of concentrated pastes.

Pastes obtained are stable over time, without sediments of phase separation.

Characterization of pigment pastes by FT-IR

PPNF 1 black iron oxide paste dried on the glass plate, and the resulting film was analysed by FT-IR. The FT-IR spectrum obtained for the paste is presented in figure 1.

The FT-IR spectrum recorded for the film obtained from PPNF 1 pigment paste exhibits bands characteristic to acrylic polymers: between 3000 and 2800, 1500 and 1300 and at about 760 cm^{-1}, which can be attributed to asymmetric and symmetric stretching vibrations and deformation vibrations of methyl and methylene groups, an intense band at around 1730 cm^{-1} due to stretching of carbonyl groups in the ester and at 1200-1000 cm^{-1} attributed to ether groups.



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3280.71	89.3915	2	2923.94	34.4407	3	2854.52	49.0835
4	1796.75	96.302	5	1729.26	35.4471	6	1421.67	40.7933
7	1232.68	61.4822	8	1152.65	47.1593	9	988.726	76.2822
10	872.054	70.2263	11	759.239	90.3339	12	703.313	85.8217
13	592.426	80.6556	14	569.285	73.2414			

Fig. 1. FT-IR spectrum of black iron oxide paste film PPNF1

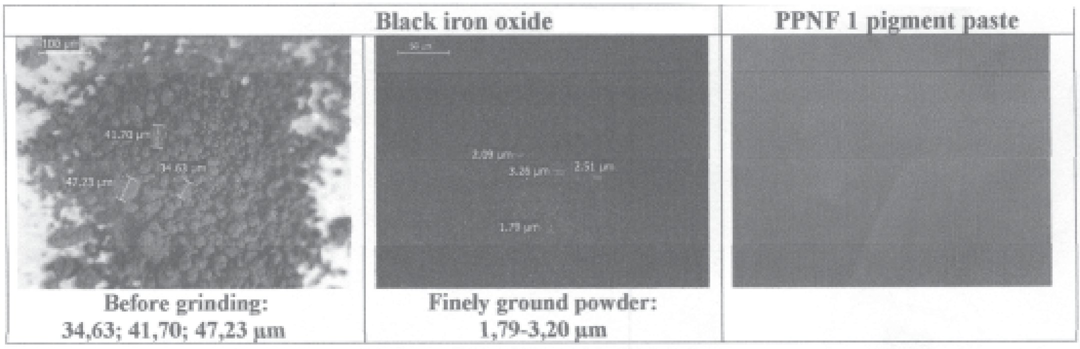


Fig. 2. Optical images at 20X and particle sizes of pigment powders and PPNF 1 pigment paste

Characterization of iron oxide powder and pigment paste by optical microscopy

Figure 2 illustrates optical images of pigment powders and particle sizes, before and after grinding, as well as the image of PPNF 1 pigment paste.

Images indicate an acircular geometry of particles, with agglomerate sizes ranging between 34.63 and 47.23 µm for the initial powder and between 1.79 and 3.20 µm for the finely ground powder.

The colour of PPNF pigment paste based on black iron oxide is comparable to that of imported pigment pastes.

Rheological behaviour of pigment pastes

Frequency dependence of storage modulus (G') and loss modulus (G") for suspensions can be described by power-low relationships as follows [18, 19]:

$$G'(\omega) = K_1\omega^{n_1} \quad (1)$$

$$G''(\omega) = K_2\omega^{n_2} \quad (2)$$

where K_1, K_2, n_1, and n_2 are the fitting parameters. At low frequencies, for a classic liquid like behaviour, n_1 equals 2 and n_2 = 1. As the elastic part of the fluid become more important, n_1 decreases until G' no longer depends on frequency. Equations (1) and (2) were used to determine the crossover frequency, where G" = G'.

Another important rheological parameter is the complex viscosity defined by the following equation:

$$|\eta^*| = \frac{1}{\omega}\left[(G')^2 + (G'')^2\right]^{1/2} \quad (3)$$

For a more elastic behaviour, due to the independence of both moduli on frequency, the $|h^*| \sim w^{-1}$, and for a more viscous behavior the complex viscosity is almost independent on frequency.

Samples PPNF

Mechanical spectra of samples PPNF1-3 are presented in figure 3. The fitting parameters and the determination coefficients are listed in table 3 for all samples. It can be seen that the values of K_1 are larger than those of K_2 for all samples, indicating a solid like behaviour, with G' > G" at low frequencies. For sample PPNF1 a crossover frequency is observed at approximately 10 rad/s, above this frequency the sample being more viscous than elastic. As the solid content of the sample increases, both K_1 and K_2 increase, while n_1 and n_2 decrease. The fact that n diminished indicates that the frequency dependence of the viscoelastic parameters becomes weaker with increasing concentration. Nevertheless, the values for n_1 remains higher than 0, so the samples are not chemically crosslinked gel.

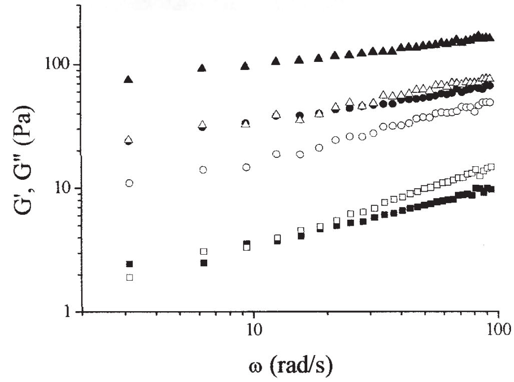


Fig. 3. Frequency dependencies of G' (closed symbols) and G" (open symbols) for PPNF1 (square), PPNF2 (circle), and PPNF3 (triangle)

Frequency dependences of complex viscosity for samples PPN1-PPNF3 are presented in figure 4. Experimental data can be fitted by linear equations having negative slopes. As the slope value approaches 0 the viscous behaviour prevailed upon the elastic one. Conversely, if the slope tends to -1 the elastic behavior become predominant. The complex viscosity at 1 rad/s (0.16 Hz) was obtained from 0 intercept and was used to compare the viscosities of prepared samples. The values of slopes and complex viscosities at 1 rad/s are listed in table 4. As expected viscosity at 1 rad/s increases with the solid content. As the samples concentration increases the elastic behaviour becomes more pronounced as indicated also by moduli dependences on frequency.

Table 3

CALCULATED POWER LOW PARAMETERS OF G' AND G" FOR ALL PIGMENT PASTES

Sample	K_1 (Pas$^{-n_1}$)	n_1	R	K_2 (Pas$^{-n_2}$)	n_2	R
PPNF1	1.23±0.02	0.46±0.01	0.99211	0.88±0.02	0.62±0.01	0.99618
PPNF2	17.23±0.01	0.30±0.01	0.99469	5.56±0.02	0.48±0.01	0.99232
PPNF3	57.80±0.01	0.23±0.01	0.99377	15.36±0.02	0.36±0.01	0.98683

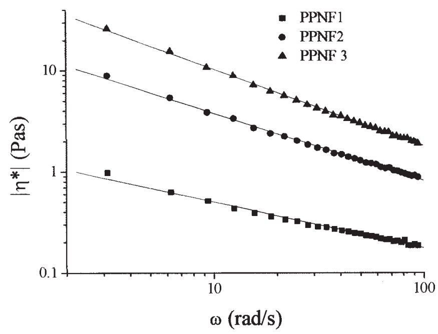


Fig. 4. Complex viscosity as a function of frequency for samples PPNF

Sample	$\|\eta^*\|_{1rad/s}$ (Pas)	Slope	R
PPNF1	1.44±0.01	-0.453±0.009	-0.99441
PPNF2	17.82±0.01	-0.664±0.006	-0.99877
PPNF3	60.19±0.01	-0.757±0.005	-0.99936

Table 4
COMPLEX VISCOSITY AT 1 RAD/S AND THE SLOPE VALUES OBTAINED FROM LINEARLY FITTING THE EXPERIMENTAL DATA IN A LOGHARITMIC PLOT

Conclusions

- Pigment pastes have the appearance of viscous and homogenous fluids, and dry substance percentages indicate that they have the characteristics of concentrated pastes.

- The obtained pastes are stable over time, without sedimentation of phase separation.

- The obtained finishing films, organoleptically analyzed by deposition on glass plate, correspond in terms of appearance, deposition uniformity and coating power to working technological characteristics and are comparable with reference samples (imported pastes).

- FT-IR spectra of the film obtained from PPNF 1 pigment paste show the characteristic bands of the acrylic binder used.

- The developed pigment pastes are compatible with the other auxiliaries used in the composition of disperse systems for natural nappalan leather and fur finishing.

- As the samples concentration increases the elastic behavior becomes more pronounced as indicated also by moduli dependences on frequency.

Obtaining and characterization of an ecologic wax emulsion were studied in [20].

References

1. LANGE, J., „Leather Finishing", Leather library vol. V, Umschau, Frankfurt, 1982.
2. HEIDEMANN, E., „Fundamentals of Leather Manufacturing", Eduard Roether KG Druckerei und Verlag, Darmstadt, 1994.
3. CHIRITA, Gh., CHIRITA, M., Tratat de chimia şi tehnologia pieilor şi blănurilor, vol. I şi II, Ed. Gh. Asachi, Iaşi 1999.
4. URBAN, D., TAKAMURA, K., Polymer Dispersion and Their Industrial Application, Wiley-VCH Verlag GmbH & Co.KGaA, Viena, 2002.
5. *** TRIDERMA, Germany – Leather finishing auxiliaries, 2010.
6. *** VECO, Italy – Leather finishing auxiliaries, 2010.
7. FLORIO, J. J., MILLER, D. J.,Handbook of coatings additives, 2nd New Edition, Marcel Dekker Inc., New York, 2004, 216-269
8. *** OSPAR Commission- Hazardous Substances Series-Nonylphenol/Nonylphenoletoxylates, 2004.
9.*** Patent Library of the European Community (http://www.epo.org).
10. *** PATENT, COARA, G., POLYMERIC BINDER AND ITS OBTAINING PROCESS, 00122205/ 2009.
11.*** PATENT APPLICATION, NICULESCU, O., MANTA, A., "INORGANIC PIGMENT PASTES FOR NATURAL LEATHER FINISHING", OSIM A/00533/ 2013.
12. *** Patent Application, NICULESCU, O., MACOVESCU, G., COARA, G., TONEA, S. „Film-forming composition and finishing process for Nappalan sheepskins", OSIM A/00923/2010.
13. HYO-SOOK JOO, YOUNG-JUN PARK, HYUN-SUNG DO, HYUN-JOONG KIM, SI-YONG SONG, KIL-YEONG CHOI, The curing performance of UV-curable semi-interpenetrating polymer network structured acrylic pressure-sensitive adhesives, J. Adhesion Sci. Technol., Vol. 21, No. 7, pp. 575–588 (2007).
14. SHI, YING; ZHAN, XIAOLI; LUO, ZHENHUAN; ZHANG, QINGHUA; CHEN, FENGQIU, Quantitative IR characterization of urea groups in waterborne polyurethanes, Journal of Polymer Science Part A: Polymer Chemistry, 46, (2008), 2433 - 2444.
15. NICULESCU, O., LECA, M., Estimation of performances of some aqueous pigment dispersions for leather finishing, Rev.Chim. (Bucharest), **58,** no. 3, 2007, 276-282.
16. B.I. NELSON, J.M. DEALY, Rheological Measurement: Dynamic Mechanical Analysis Using Complex Waveforms. London, Chapman & Hall, 1998.
17. *** Optical microscopy handbook, Leica, 2007.
18. B.E. MEZA, R.A. VERDINI, A.C. RUBIOLO, "Viscoelastic behaviour of heat-treated whey protein concentrate suspensions", Food Hydrocolloids **23**, 661-666 (2009).
19. K.-W. SONG, H.-Y. KUK, G.-S. CHANG, "Rheology of concentrated xanthan gum solutions: Oscillatory shear flow behavior", Korea-Australia Rheology Journal **18**, 67-81 (2006)
20. NICULESCU, O., LECA, M., MOLDOVAN, Z., CHELARU, C., GURAU, D., BERECHET, D.M., Obtaining and characterization of an ecologic wax emulsion for finishing natural leathers and furs, Rev. Chim. (Bucharest), **66**, no. 8, 2015, p. 1173

Manuscript received: 29.04.2014