Rheological Behaviour of Ecologic Pigment Pastes for Natural Leather and Fur Finishing

OLGA NICULESCU[1,2]*, MINODORA LECA[1], TEODORA STAICU[1], MARIAN MICUTZ[1], ZENOVIA MOLDOVAN[1]
[1] University of Bucharest-Faculty of Chemistry, 36-46 Mihail Kogalniceanu Str., 050107, Bucharest, Romania
[2] National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute, 93 Ion Minulescu Str., Bucharest, Romania

Physico-mechanical, technological, functional, and especially aesthetic properties depend to a great extent on the quality of pigment pastes used to generate the grain layer of semi-processed nappalan fur and leather. Cumulated properties give value of use and appearance to the manufactured products: footwear, clothing, handbags, etc. Environmental protection has required restrictions on the use of heavy metals salts (Cr, Cd, Pb, Co, Hg, Ni) in pigment pastes, of ethoxylated alkylphenols as stabilization agents, of formaldehyde as crosslinker for the usual protein binders or on other toxic crosslinking agents, resulting in new alternatives for the industry of auxiliary finishing materials. Pigment pastes were prepared using a polyacrylic binder, red and yellow iron oxide pigments, lauric alcohol ethoxylated with 7moles of ethylene oxide (100% biodegradable) as stabilizing agent and castor oil as plasticizer. Acrylic polymer substitutes the protein binders, which eliminates crosslinking with formaldehyde. Pigment pastes were characterized by stationary and dynamic rheological behaviour. They have type-dependent pseudoplastic behaviour of thixotropic type, which increase with pigment concentration for both pigments. The same behaviour was obtained for the elastic component of viscoelasticity. Pastes containing yellow iron pigment are more pseudoplastic and thixotropic than the corresponding ones containing red iron oxide.

Keywords: ecological pigment pastes, polyacrylic binder, finishing of leather and fur, rheological behaviour

The quality of pigment pastes used in obtaining of finishing films impart some physical-mechanical, technological, aesthetical and ecological properties to the semi-finished leather and fur. Cumulated, they give value of use and commercial appearance to the manufactured products: footwear, clothing, handbags, etc.

Pigments are inorganic or organic compounds constituting the colouring base of covering paints. To be used for finishing of nappalan leather and fur, pigments have to present some characteristics, the most important being: resistance to light, atmospheric agents and temperature, brilliant colour, great covering power, great degree of dispersion, compatibility with the other components of the paint. [1-4]

Each type of pigment paste contains characteristic amounts of pigments and other components. Proportion of components in commercial pigment pastes is a „firm secret". [5,6]

Stationary rheological studies are very important when the flow characteristics of a material determines either its processability, performance, and/or consumer acceptance, helping to drive the technology for better quality, consistency, acceptance, and growth. [7]

In addition to pseudoplastic flow behaviour, higher elastic properties are required in aqueous systems, which can be achieved by using a suitable combination of additives. Thus the balance between ingredients – binder, pigments, solvents, dispersants and surfactants – is very important in order to develop coating rheology systems [8].

Environmental and toxicity restrictions have generated new alternatives for the industry of auxiliary finishing materials. [9]

The paper presents obtaining of some ecological pigment pastes based on red and yellow iron oxides and polyacrylic binder, their characterization by rheological behaviour and characterization of the obtained finished leather and fur by optical microscopy.

In [10] was presented the obtaining of some ecologic pigment pastes.

Experimental part

Materials and methods

Red iron oxide (Pebeo, France), content of Fe_2O_3 – 96%, bulk density – 0.7-1.1 g/cm^3, water absorption – 35% g/g, particle size – 0.6 ± 0.1μm.

Yellow iron oxide (Pebeo, France), content of Fe_2O_3 – 85%, bulk density – 0.8-1.2 g/cm^3, water absorption – 80% 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, *p*H – 6.5, Hoppler viscosity – 4.000 cP.

Castor oil (S.C. Happynatura SRL, Bucharest), total fatty matters – 64%, viscosity Ford coupe 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, *p*H (10%) solution – 7-8.

Brown-reddish prepared pigment paste (A) – homogenous viscous fluid, dry substance –43-64%, *p*H (10% solution) – 6.5-8.0, ash – 56-62%;

Yellow-ochre prepared pigment paste (B), homogenous viscous fluid, dry substance – 47-54%, *p*H (10% solution – 6.5-8.0, ash –44-48%.

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

Quantity (%)/material	A1	A2	A3	B1	B2	B3
Red iron oxide	25	30	35	-	-	-
Yellow iron oxide	-	-	-	25	30	35
Polyacrylic binder	30	35	40	30	35	40
Ethoxilated lauric alcohol	8	9	10	8	9	10
Castor oil	8	9	10	8	9	10
Water	29	17	5	29	17	5

Table 1
TECHNOLOGICAL VARIANTS FOR OBTAINING PIGMENT PASTES BASED ON RED (A) AND YELLOW (B) IRON OXIDE

Characteristic/paste	A1	A2	A3	B1	B2	B3
Dry substance, %	43.83	52.63	60.16	47.14	55.82	64.85
pH	6.5-8.0	6.5-8.0	6.5-8.0	6.5-8.0	6.5-8.0	6.5-8.0
Ash, %	56.45	59.58	66.57	57.19	61.43	68.65

Table 2
PHYSICO-CHEMICAL CHARACTERISTICS OF THE PREPARED PIGMENT PASTES

Technological variants used to obtain the pigment pastes are given in table 1.

Shear rheological measurements were made at 25±0.1°C using a rotational viscometer Hake VT 550 equipped with MV1 sensor system for medium viscosity and RheoWin 4 Thermo Fischer Scientific software. Shear rates ranged between 0.1 and 200 s^{-1}.

Dynamic rheological behaviour was determined at room temperature using a Micro Fourier Transform Rheometer MRF 2100, GBC Scientific, with parallel plate geometry under squeeze flow conditions. Applying the Fourier transform to the displacement and force signals, both storage and loss modulus at a large number of discrete frequencies can be obtained [11]. To remain into the linear viscoelastic domain, the gap between the upper and bottom plates of the rheometer was 0.3 mm and the displacement amplitude was 0.03μm.

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; apperture 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°.

Results and discussions

The binder is a very important ingredient, it affecting almost all the properties of a coating: adhesion and related properties like resistance to blistering, cracking and peeling, resistance to scrubbing, chalking and fading, as well as application properties like flow, leveling and film build, and gloss development. Bindex Brillant was selected as binder due to its properties: resistance to light, absence of yellowing, high capacity to disperse pigments and its function of protective colloid. The polyacrylic polymer replaces the usual protein binders that require crosslinking with formaldehyde, which is toxic. [12, 13] It has the FT-IR spectrum presented in figure 1.

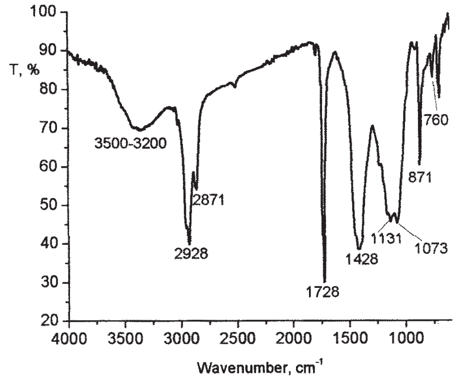


Fig. 1. FT-IR spectrum of acrylic binder Bindex Brillant used to obtain pigment pastes

The FT-IR 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 2928-2871 cm^{-1}, 1428 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 1131 and 1073 cm^{-1} given by ether groups; două benzi la 870 and 760 cm^{-1}, atribuite vibraţiilor legăturilor sp^2 din grupări alchenice trisubstituite.

Iron oxides pigments, which is not toxic, was used to prepare pastes [14].

To improve the dispersion of pigments and stability of pastes a non-ionic surfactant – wholly biodegradable lauric alcohol ethoxylated with 7 mol of ethylene oxide – was used.

Increasing of film elasticity was done using castor oil as plasticizer.

Physico-chemical characteristics of the prepared pigment pastes are given in table 2.

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 knowledge of stationary rheological properties of coatings are very important for their application on substrate, behaviour at the application site, processing, handling, process design and product development [15]. They give information on the consistency of coatings, their capacity to flow, type of flowing as well as on their dynamic viscosity, spreadability and dependence of rheological behaviour on time [15].

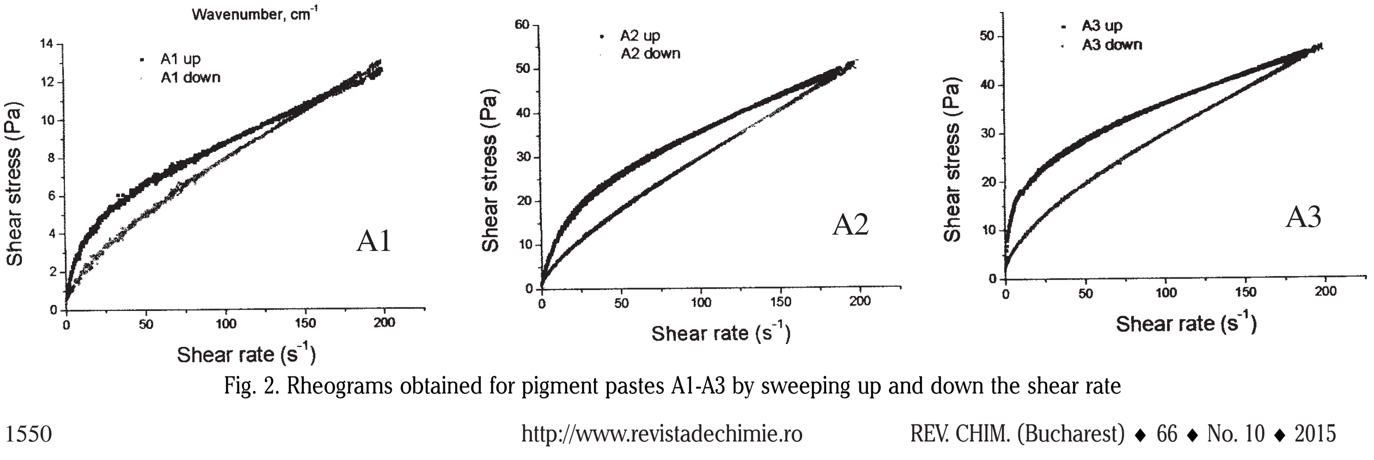


Fig. 2. Rheograms obtained for pigment pastes A1-A3 by sweeping up and down the shear rate

System	η_0 (Pa.s)	η_∞ (Pa.s)	1/C (s^{-1})	m
A1 up	1.20 ± 0.01	0.030 ± 0.001	2.86 ± 0.05	0.83 ± 0.01
A1 down	1.80 ± 0.30	0.036 ± 0.002	0.13 ± 0.06	0.56 ± 0.02
A2 up	4.16 ± 0.05	0.040 ± 0.010	2.12 ± 0.09	0.64 ± 0.01
A2 down	6.40 ± 0.50	0.159 ± 0.003	0.07 ± 0.02	0.52 ± 0.01
A3 up	13.50 ± 0.10	0.112 ± 0.004	1.06 ± 0.02	0.87 ± 0.01
A3 down	16.00 ± 1.00	0.134 ± 0.002	0.05 ± 0.01	0.61 ±0.01
B1 up	25.5 ± 0.10	~ 0	0.86 ± 0.01	0.91 ± 0.01
B1 down	19.6 ± 0.5	0.114 ± 0.001	0.07 ± 0.004	0.72 ± 0.002
B2 up	37.5 ± 0.40	0.100 ± 0.010	1.37 ± 0.03	0.97 ± 0.06
B2 down	27.0 ± 1.0	0.240 ± 0.002	0.09 ± 0.01	0.73 ± 0.004

Table 3
PARAMETERS OF CROSS MODEL CALCULATED FROM EXPERIMENTAL DATA MEASURED FOR PIGMENT PASTES A1-A3 AND B1-B2

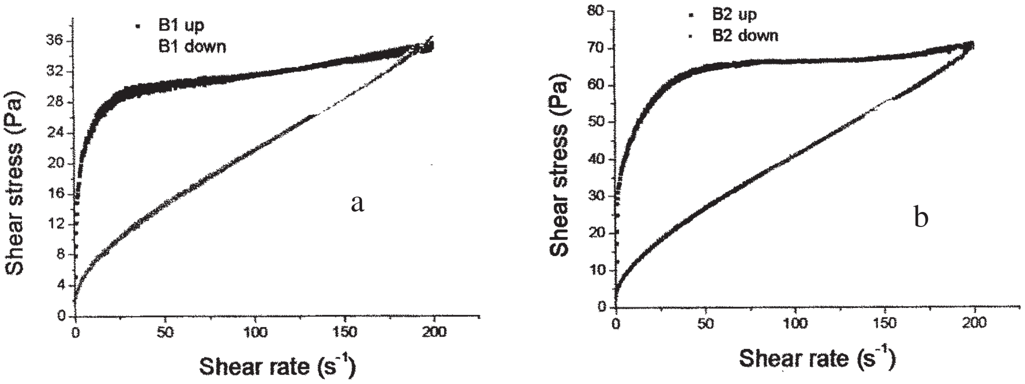


Fig. 3. Rheograms obtained for pigment pastes B1 and B2 by sweeping up and down the shear rate

The rheograms obtained for pigment pastes A1-A3 containing red iron oxide by measurements performed by sweeping up then down the shear rates with constant shear acceleration are shown in figure 2a-c.

The rheograms show that the pastes A1-A3 have pseudoplastic-type behaviour, the flowing starts at low sher stresses – yield stress ranges between about 2 and 5 Pa, and present thixotropic hysteresis loops.

The rheograms were modelled with the four parameters Cross model, [16] frequently used during the last time for pseudoplastic systems:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (C\dot{\gamma})^m} \qquad (1)$$

where η_0 and η_∞ are the limiting values of the apparent viscosity at low and high shear rates (when viscosity approaches asymptotically a finite constant level), respectively, C – fitting parameter having dimension of time, called Cross time constant and m – dimensionless fitting parameter representing the degree of dependence of viscosity on shear rate, called Cross rate constant. The reciprocal of C indicates the value of shear rate at which the pseudoplastic behaviour appears. The Cross model has the advantage of offering information on viscosity of system over the entire shear rate range.

The parameters obtained modelling the rheograms from figure 2, both up and down, with Cross model are given in table 3.

The table shows that the viscosities at zero, η_0, and high shear rates,η_∞, increase when the pigment concentration is raised, both when shear rates increase and decrease. Concomitantly the differences between h„ obtained from rheograms recorded increasing shear rates are very small, proving that the more concentrated pastes cand be applied almost as easily as the diluted one. On the contrary the Cross time constants decrease, which indicates that the more concentrated the paste the lower the value of shear rate at which the pseudoplastic behaviour appears, as expected for polymeric disperse systems.

As the deformation applied during the application of thixotropic systems increases their fluidity, facilitating their spreading, while the recovery of the initial viscosity after application prevents the paste from dripping, thixotropy is desired in paste formulations.

The figure 2 emphasizes also that the area of hysteresis loops increases when the concentration of pigment in the paste becomes higher. The area indicating the energy required to break down the thixotropic structure, [17] represent a measure of thixotropy. Though it depends on the parameters defining the hysteresis loop – [18] maximum shear rate and length of time of increasing/decreasing shear rates – and is only a qualitative measure of thixotropy, it is very useful for demonstrating the thixotropic behaviour [19].

As a quantitative measure of thixotropy the relative hysteresis area was proposed, defined as percentage of the ratio of the hysteresis aria to the area beneath the ascending shear curve, called also coefficient of thixotropic breakdown [20] The coefficient of thixotropic breakdown were calculated according to the relation [21]

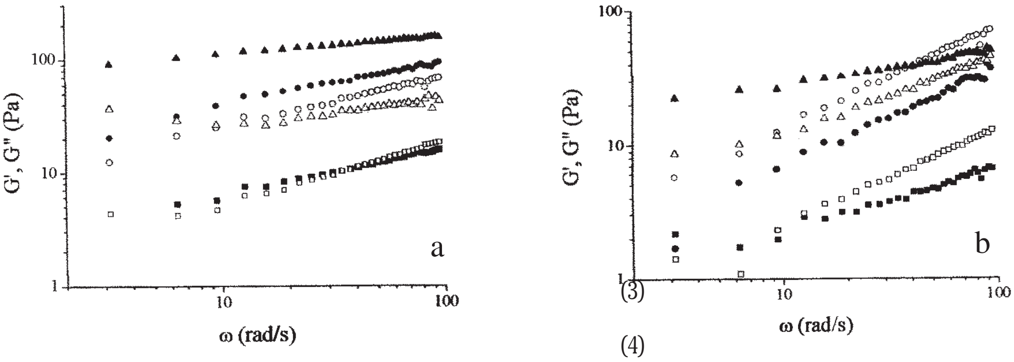
$$A_r = \frac{A_{up} - A_{down}}{A_{up}} x100 \qquad (2)$$

were A_r is the relative area, A_{up} – area obtained by sweeping up the shear rates and A_{down} –area resulted by sweeping they down.

The calculated coefficients of thixotropic breakdown of pigment pastes A1-A3 have the values 9.9, 15.4 and 17.3 respectively. They become higher with increasing pigment concentration, indicating enhancing of thixotropy when the concentration of pigment increases. At the same time the values for the last two pastes are pretty close.

In the case of B series of paste, containing the same amounts of yellow iron oxide, the shear rheological measurements were done only for pastes B1 and B2, B3 being too viscous to be subjected to such measurements. The rheograms are presented in figure 3a,b.

The two rheograms indicate that the pigment pastes B1 and B2 are more viscous than those containing the same amounts of red iron oxide, present more prominent pseudoplastic behaviour and their hysteresis loops are much larger, which demonstrates that they are more



(3)

(4)

Fig. 4. Dependence of G' (closed symbols) and G" (open symbols) on frequency for pigment pastes:
a – A1 (□), A2 (o), and A3 (Δ);
b – B1 (□), B2 (o), and B3(Δ)

Table 4
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
A1	2.41±0.02	0.42±0.01	0.99608	1.37±0.02	0.57±0.01	0.99770
A2	15.52±0.02	0.40±0.01	0.98943	8.69±0.02	0.46±0.01	0.99202
A3	77.60±0.03	0.16±0.02	0.99686	21.11±0.04	0.15±0.02	0.75685
B1	0.73±0.02	0.48±0.01	0.98807	0.45±0.04	0.73±0.02	0.98579
B2	1.03±0.03	0.79±0.02	0.98779	2.38±0.02	0.75±0.01	0.99722
B3	15.57±0.01	0.26±0.01	0.98948	3.69±0.02	0.54±0.01	0.99096

thixotropic. Indeed, the calculated viscosities at zero and high shear rates, given in table 3, are higher than those of pastes A1 and A2 (21 times in the first case and 9 times in the second) and the coefficients of thixotropic breakdown have much higher values: 31.1 and 37.7%, respectively (3.15 and 2.45 times higher than A1 and A2).

The Cross time constants have lower values, which shows that the shear rates at which the pseudoplastic behaviour appears for the pastes containing yellow iron oxide are lower than for those containing the same amount of red iron oxide, as expected for more pseudoplastic systems. At the same time, the shear rates at which the viscosity approaches asymptotically a finite constant level, η_∞, have low values, which reveals that the pastes belonging to this series can be applied as easy as series A.

If the viscosities at zero shear rate of pigment pastes B1 and B2 are much higher than those of pastes A1 and A2, viscosities at high shear rates are comparable (Table 3), which demonstrates once more the higher thixotropy of pigment pastes B1 and B2.

The higher viscosity of pigment pastes containing yellow iron oxide can be explained by the difference of structure of the two oxides: yellow iron oxide is a hydrated iron (III) oxide, while red iron oxide is an anhydrous one. Consequently the yellow iron oxide has the capacity to form a higher number of hydrogen bonds with the components of the paste.

The yield stresses, which reflect the resistance of the fluid structures to deformation or breakdown, are a little bit higher for B series of pigment pastes.

Establishing of contribution of elasticity and viscosity to the viscoelastic behaviour of dispersions can be obtained from rheological dynamic measurements.

Dynamic rheological measurements were performed in the range of 0.5-15 Hz (angular frequency 1-100 rad/s) at room temperature.

For suspensions the frequency dependence of storage (G') and loss (G") moduli can be described by power-low relationships [22, 23]:

$$G'(\omega) = K_1\omega^{n_1} \quad (3)$$

$$G''(\omega) = K_2\omega^{n_2} \quad (4)$$

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 becomes more important, n_1 decreases until G' no longer depends on frequency. The two equations were used to determine the crossover frequency, where G" = G'.

The mechanical spectra of samples A1-A3 are presented in figure 4 a.

Sample A1 has almost equal values for storage and loss moduli, that is the contribution of elasticity and viscosity is practically the same. However at low frequencies it is a little more elastic than viscous, the crossover frequency having the value about 40 rad/s. As the solid content of the sample increases the paste becomes more elastic than viscous, that is it behaves as a solid-like fluid. The most elastic pigment paste is A3.

The fitting parameters and correlation coefficients for pigment pastes A1-A3 are given in table 4, together with those for B1-B3.

It can be seen from the table that the values of K_1 are higher than those of K_2 for all the samples, which suggests a solid-like behaviour. Also, at low frequencies G' > G" even for sample A1. The diminishing of n values with increasing solid content shows that viscoelastic parameters depend less on frequency when pigment concentration increases. The values n_1 higher than 0 indicates that the samples are not chemically crosslinked gels, as expected.

The dependences of storage and loss moduli on frequency for the pastes containing yellow iron oxide pigment are given in figure 4b.

The figure emphasizes that the samples B1-B3 have quite different rheological behaviour: B1 presents a theoretical crossover frequency at about 7 rad/s, with prevalent viscous behaviour which increases with frequency more than the elastic contribution above the crossover point. B2 has $K_2 > K_1$ and G" > G' over the entire frequency range, indicating a preponderant viscous behaviour irrespective of frequency. B3 is more elastic than viscous at low frequencies and shows a theoretical crossover frequency of 164 rad/s (not shown in fig. 4b). For paste B2 n_1 and n_2 have very close values and close to unity, which also indicates a preponderant liquid-like behaviour. For B3 both values are lower, which indicates a rather solid-like fluid. Consequently B1 and B2 are more or less viscoelastic, while B3 is preponderantly elastic, especially at low frequencies. Increasing samples concentration both K_1 and K_2 increase, as expected, the solid like behaviour becoming more prominent.

Conclusions

The pastes containing red and yellow iron oxides as pigments have pseudoplastic time-dependent rheological behaviour of thixotropic type.

The rheograms, modelled with Cross model, show that the pigment pastes containing red iron oxide have lower zero shear rates viscosities, lower values of shear rate at which the pseudoplastic behaviour manifests and lower dependence of viscosity on shear rate compared with the pastes containing the same percentages of yellow iron oxide. Consequently the first are less pseudoplastic and less thixotropic, differences given by the structure of the two iron oxides. Pseudoplasticity and thixotropy increase with pigment concentration for both pastes.

The two pastes having the lowest pigment concentration are viscoelastic fluids and present a crossover point, A1 at a higher frequency and B1 at a lower one, above which the viscous component increases more than the elastic one with frequency. Increasing of pigment concentration enhances elasticity. If the elastic and viscous components of pastes A2, B2 and A3 increase in the same measure with frequency, for B3 the viscous component increases more and presents a crossover point at 164 rad/s.

Though in the rest state the pastes belonging to B series are more viscous, given the very close viscosities at high shear rates they can be applied almost so easy as A series.

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. K. G. H. SILVA, R. R. SANTIAGO, K. S. SILVA, K. C. H. SILVA and E. S. T. EGITO, "Rheological Properties of Sesame Oil Emulsions", Eur. Cells Mat., 2010, 20, Suppl. 3, 238-244 .

8. J.J. FLORIO, D.J. MILLER, Handbook of coatings additives, 2nd New Edition, Marcel Dekker Inc., New York, 2004, 216-269.

9. *** OSPAR Commission- Hazardous Substances Series-nonylphenol/ Nonylphenoletoxylates, 2004.

10. NICULESCU, O., LECA, M., STAICU, T., MOLDOVAN, Z., CHELARU, C., BERECHET, D.M., Obtaining and Characterization of Some Ecologic Pigment Pastes for Finishing Natural Leather and Furs, Rev. Chim. (Bucharest), **66**, no. 9, 2015, p. 1278

11. B.I. NELSON, J.M. DEALY, Rheological Measurement: Dynamic Mechanical Analysis Using Complex Waveforms. London, Chapman & Hall, 1998.

12. Patent Library of the European Community (http://www.epo.org).

13.PATENT APPLICATION, NICULESCU, O., MANTA, A., "INORGANIC PIGMENT PASTES FOR NATURAL LEATHER FINISHING", OSIM A/00533/ 2013.

14. *** www.pictorshop.ro/article-maimeri-polycolor-raw-sienna-607-8050.html

15. M. MICUTZ, T. STAICU, L. LACATUSU, G. OPREA, M. LECA, „Behaviour of some dispersions, for long lasting protection of copper-aluminium contacts in power transmission equipment", Rev. Roum. Chim., 2012, 57, 829-836.

16. M. M. CROSS, „ Rheology of non-newtonian fluids: A new flow equation for pseudoplastic systems", J. Colloid Sci., 1965, 20, 417–437.

17.G. SCHRAMM, "A Practical Approach to Rheology and Rheometry",2nd edition, Gebrueder HAAKE GmbH, Karlsruhe, 2000.

18. E. ARMELIN, M. MARTI, E. RUDE, J. LABANDA, J. LORENS, C. ALEMAN, „A simple model to describe the thixotropic behavior of paints", Prog. Org. Coat., 2006, 57, 229-235.

19.T. DAPCEVIC, P. DOKIR, M. HADNADEV and V. KRSTONOSIC, „Determining the yield stress of food products – importance and shortcomings", Food Proc. Quality Safety, 2008, 35, 33-39.

20.P. DOKIR, V. SOVILJ, I. SEFER, G. RASULIC, "THIXOTROPY EVALUATION BY THE PARAMETERS OF FLOW EQUATION", ACTA PERIODICA TECHNOLOGICA, 1998-1999, 29-30, 67-79.

21. A. TARREGA, L. DURAN, E. COSTELL, „Flow behaviour of semi-solid dairy desserts. Effect of temperature", Int. Dairy J., 2004, 14, 345-353.

22. B.E. MEZA, R.A. VERDINI, A.C. ROBIOLO, "Viscoelastic behaviour of heat-treated whey protein concentrate suspensions", Food Hydrocolloids **23**, 661-666 (2009).

23. K.-W. SONG, H.-Y. KUK, G.-S. CHANG, "Rheology of concentrated xanthan gum solutions: Oscillatory shear flow behavior", Korea-Australia Rheology J. **18**, 67-81 (2006)

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