UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY

SUMMARY OF DOCTORAL THESIS

FILM-FORMING DISPERSE SYSTEMS USED IN FINISHING OF NATURAL LEATHER

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INTRODUCTION

Finishing - the last operation in natural leather processing determines, to a large extent, the appearance and value of finished product. It as purpose the embellishment, providing of lustre and pleasant feel, covering of flaws and forming of a surface layer that protects leather during wear and improves resistance to external factors.

The demanded effects are: contrasting, antique, cracked, crumpled, pleated, polished, printed, glossy, matte, shimmer, silky touch, waxy, aniline, semi-aniline, hydrophobic, varied color range or imitation of other animal skin patterns, obtained from pressed bovine skins imitating that of reptile (crocodile, python, iguana), ostrich or kangaroo if they are properly finished using materials that provide the desired aesthetic characteristics.

Almost all types of large (cattle) and small hides (sheep, goats, reptiles, fish, etc.) can be finished into assortments for footwear, garments, leather goods, furniture and car upholstery, bookbinding etc.

Finishing is done using disperse systems containing as auxiliaries: pigments, binders, natural and synthetic waxes, preservatives, plasticizers, thickeners, fillers, odorizers, penetrating agents, solvents.

Finishing is carried out by a number of technologies that impart different characteristics.

Current problems of the leather finishing industry include prohibition of heavy metal salts (chromium, cadmium, lead, cobalt, mercury, nickel) in pigment pastes, of ethoxylated alkylphenols as wax dispersing agents, of formaldehyde and other toxic crosslinking agents. Environmental and toxicity concerns have lead to new alternatives for finishing ancillary industry.

Silicone polymers, amide derivatives of C_{12}–C_{18} fatty acids, products obtained by esterification of fatty acids with fatty alcohols and polymeric compounds, products based on a mixture of C_{10} – C_{18} fatty acids obtained by paraffin oxidation, etc. are used for the manufacture of wax products.

The surface of finished leather and products may be contaminated by fungi and bacteria in some phases of leather processing, that may cause damage by degrading the grain layer (stains, mattifying, etc.), reduce mechanical resistance and produce illness caused by mold spores or bacteria and pathogenic fungi that may lead to developing certain types of mycosis. To prevent the emergence and development of microorganisms, biocides are used in various stages of leather processing, which improve resistance to biological attack and prevent damage of mechanical and chemical properties of leather. Biocides used in the leather industry, based on beta-naphthol, benzothiazole and sulfone derivatives, organic sulfur compounds, etc.) are toxic to humans and environment, some of these being prohibited by the directives in force (pentachlorophenol, polyhalogenated phenolic compounds). The current research aims at replacing totally or partially the potentially toxic biocides with environmentally friendly materials.

Damage due to external factors and insects may also occur during the use or storage of finished leather and fur items, effects that can be controlled or corrected by finishing and maintenance treatment. Essential oils, known for their particular scent and therapeutic qualities, are highly concentrated in biologically active compounds with different properties: antiseptic, antibacterial, immunostimulatory etc. They can be used both for perfuming leather and fur, and for protection against damages caused by fungi, bacteria and insects.

■ **The aim of the thesis** is the obtaining and characterization of some ecologic film-forming disperse systems to be used as auxiliaries in various stages of natural leather finishing: pigment pastes, wax emulsions, bactericidal, fungicidal and fragrance products; the establishment of leather finishing technologies (cattle, sheep, goats) in different types of assortments using the developed auxiliary materials in disperse finishing systems and to characterize the obtained film-coated leather assortments.

■ **The objectives of the experimental part** are:

- Obtaining and characterization of pigment pastes for natural leather finishing.
- Obtaining and characterization of wax emulsions for natural leather finishing.
- Obtaining and characterization of bactericide and fungicide products for natural leather finishing.
- Obtaining and characterization of products for fragrance of natural leather.
- Establishing of natural leather finishing technologies (cattle, sheep, goats) into natural grain box or Nappa assortments using the developed auxiliary materials in disperse finishing systems.
- Characterization of film-coated leather assortments.

4. MATERIALS AND METHODS

4.1. Materials

4.1.1. Materials for preparation of pigment pastes

- Red iron oxide (Pebeo, France), Fe_2O_3 content – 96%, bulk density – 0.7-1.1 g/cm^3, water absorption – 35%, g/g, particle size – 0.1 ± 0.6 µm.
- Yellow iron oxide (Pebeo, France), Fe_2O_3 content – 85%, density – 4.1 g/cm^3, water absorption – 80% g/g, particle size 0.1 ± 0.6 µm.
- Black iron oxide (Nubiola, Romania), Fe_3O_4 content – 94%, density – 4.6 g/cm^3, water absorption 32% g/g, particle size 0.1 ± 0.6 µm.
- Castor oil (Happynatura, 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 – 92 g/100 g oil.
- Flax oil (Pebeo, France), total fats – 98%, Ford cup viscosity Φ 6 – 26 s, saponification index – 245 mg KOH/g, acidity index – 3 mg KOH/g, iodine index – 131 g/100 g oil.
- Poppy seed oil (Pebeo, France), total fats – 99%, Ford cup viscosity Φ 6 – 23 s, saponification index – 290 mg KOH/g, acidity index – 3 mg KOH/g, iodine index – 138 g/100 g oil.
- Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (Elton, Bucharest), melting point -15^{0}C, ignition point over 170^{0}C, density – 0.97 g/cm^3 at 40^{0}C, pH – 5-7, viscosity – 25 mPa x s.
- Acrylic binder – Bindex Brillant (Pebeo, France), white homogenous emulsion, dry substance – 30.24 %, density – 1.085 g/cm^3, pH – 6.5, Ford cup viscosity Φ4 – 18 s, Hoppler viscosity – 6.89 cP.
- Wax emulsion, AGE 7, made from beeswax, lanolin and triethanolamine monostearate and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide, dry substance – 16%, pH (10% solution) – 7.0.

4.1.2. Materials for preparation of wax emulsions

- Beeswax (Happynatura, Bucharest), solid with specific odour, yellow colour, melting point 62-65°C.
- Lanolin (Medchim, Bucharest), solid greasy compound with specific odour, light yellow colour, melting point 38-42°C.
- Strearin (Sterochemical, Bucharest), solid with specific grease odour, white, melting point 69-70°C.
- Triethanolamine (Stera Chemicals, Bucharest) – colourless liquid, melting point – 20-21^{0}C, boiling point – 277-279^{0}C, density – 1.124 g/cm^3, refractive index – 1.4852.
- Nonionic emulsifier (Elton Corporation, Bucharest), C_{12-14} fatty alcohol ethoxylated with 7 moles of ethylene oxide, with the properties specified in section 4.1.1.
- pH regulator –10% aqueous solution of potassium hidroxide.

4.1.3. Materials for preparation of bactericidal and antifungal products

- Beeswax (Happynatura, Bucharest), with properties specified in section 4.1.2.
- Lanolin (Medchim, Bucharest), with properties specified in section 4.1.2.
- Nonionic emulsifier (Elton Corporation, Bucharest), C_{12-14} fatty alcohol ethoxylated with 7 moles of ethylene oxide, with properties specified in section 4.1.1.
- Ethanol (Chemical Company, Germany), density – 0.789 g/cm^3 at 20^{0}C, boiling point – 78^{0}C, melting point –114^{0}C, water solubility – in any proportion.
- Coriander essential oil (Solaris Plant, Bucharest), containing 74.17% linalool, 10.23% limonene, 7.86% α-pinene, 3.72% camphor etc.
- Cedar essential oil (Solaris Plant, Bucharest), containing 37.25% thujopsene, 20.03% cedrene, 20.79% cedrenol, cuparene, etc.

4.1.4. Materials for preparation of fragrance products

- Lavender essential oil (Solaris Plant, Bucharest), containing 36.57% linalool, 35.60% linalyl acetate, 7.67% α-terpineol, camphor, carbitol, cineol, etc.
- Orange essential oil (Solaris Plant, Bucharest), containing 94.7% limonene.
- Ethanol (Chemical Company, Germany), with properties specified in section 4.1.3.

- Polyethylene glycol 600 (Merck, Germany), density – 1.13 g/cm^3 at 20^{0}C, ignition point – 270^{0}C, pH (10% solution) – 4-7; melting point – 17-22^{0}C, hygroscopic, flammability temperature – 380^{0}C.
- Hexadecyl-trimethyl ammonium bromide (Merck, Germany), water solubility – 3g/L, pH (10% solution) – 5-7, melting point – 237-243^{0}C, hygroscopic.
- Fully biodegradable nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide, with properties specified in section 4.1.1.

4.2. Methods of analysis

Methods of analysis specific to each class of materials were used.

- **Pigment pastes** were characterized by dry substance, pH, relative viscosity, coating power, thermal resistance, rheological behaviour, FT-IR, thermal analysis, and optical microscopy.
- **Waxes were characterized** by dry substance, pH, rheological behaviour, FT-IR and optical microscopy.
- **Oil characterization** involved determining of fat amount, pH, relative viscosity, iodine index, acidity and saponification indices.
- **Binders were characterized** by mechanical strength of resulted films (elongation, tensile and tear strength), FT-IR spectrometry, optical and scanning electron microscopy.
- **Essential oils were characterized** by FT-IR and GC coupled with MS (GC-MS).
- **Characterization of film-coated leather** included: mechanical strength (tensile, tear, wet and dry friction, elongation, pressing, light and UV radiation), optical and SEM microscopy, FT-IR, colorimetry (CIE LAB) and biological analysis.

5. OBTAINING OF SOME ECOLOGIC AUXILIARY MATERIALS TO BE USED AS DISPERSE SYSTEMS FOR LEATHER FINISHING

The prepared materials belong to the following classes of auxiliaries used for preparation of aqueous dispersions used in natural leather finishing: pigment pastes, wax emulsions, antibacterial, antifungal and fragrance products.

5.1. Obtaining pigment pastes

The literature indicates inorganic pigment pastes based on casein or collagen, which require the fixation of the final coating layer with formaldehyde or acrylic binder and castor oil, as plasticizer. [48-52]

Recipes are proposed to obtain stable pastes with aqueous dispersion medium using ecologic components: iron oxides (red, yellow, and black), acrylic resin as dispersion medium for pigments, light and ageing resistant vegetable oils as plasticizers, 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.

The selected acrylic binder is light resistant and has protective colloid properties. The protein binders were removed from the pigment pastes and thus cross-linking with the toxic formaldehyde.

Polyethoxylated nonylphenol, the most efficient stabilizing agent of aqueous dispersions, is prohibited for industrial products because it is non-biodegradable. It has been replaced by a completely biodegradable stabilizing agent - lauryl alcohol ethoxylated with 7 moles of ethylene oxide.

Flax and poppy seed oils, used as plasticizers, increase the films' resistance to yellowing over time.

5.1.1.1. Characterization of components used in obtaining pigment pastes

Optical images of pigment powders were obtained using a Leica stereomicroscope S8AP0 with optic fiber cold light source, L2, with three levels of intensity. [228] They indicate an acicular geometry of particles, with agglomerate sizes ranging between 3.75 and 89.50 µm and finely ground powder between 0.1 and 0.6 µm.

5.1.2.2. Obtaining pigment pastes

- Inorganic **pigment pastes** based on iron oxides (reddish brown – PPRF, ochre yellow – PPGF and black – PPNF) were obtained by the following **operations**:

♦ mixing powder pigment with vegetable oil emulsion (castor, flax, poppy seed oil) and non-ionic emulsifier

▪ 25-35% inorganic pigment, 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, 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.

Using this procedure, reddish brown, ochre yellow and black pigment pastes were obtained, in the technological variants presented in table 5.4 for red iron oxide.

Table 5.4. Technological variants of pigment pastes based on red iron oxide

Amount (%)/materials	A1	A2	A3	A4	A5	A6	A7	A8	A9
Red iron oxide	25	25	25	30	30	30	35	35	35
Acrylic binder	35	35	35	37.5	37.5	37.5	40	40	40
Lauryl alcohol ethoxylate	8	8	8	9	9	9	10	10	10
Castor oil	8	-	-	9	-	-	10	-	
Flax oil	-	8	-	-	9	-	-	10	-
Poppy seed oil	-	-	8	-	-	9	-	-	10
Wax emulsion	1	1	1	1,5	1,5	1,5	2	2	2
Water	23	23	23	13	13	13	3	3	3

♦ Similar variants were prepared using yellow and black iron oxide (marked B1-B9, and C1-C9, respectively).

5.2. Obtaining wax emulsions for leather finishing

To improve the physical properties of finished leather and obtain fatty, waxy or silky finishing, handle modifiers (waxes and oils emulsions) are used for. [231]

The obtained ecologic wax emulsions may be used in surface finishing of natural bovine, sheep, and goat leather, in the final dressing composition (nitrocellulose, acrylic, polyurethane), or in finishing suede, buffo or nubuck leather, to achieve a waxy feel and better resistance of finishing films to scratches and water.

The resulting emulsion offers long-term protection, can be applied easily and contains only natural ingredients. It may be also used in finishing footwear, garments, furniture and car upholstery, etc. with metallic ornaments, as it does not contain nitrate or sulfate ions which may initiate metal oxidation.

● **The wax emulsion** was obtained by emulsification of 15-20% wax mixture and 10% polyoxyethylene lauryl alcohol relative to the amount of wax in water, under mechanical stirring (300-500 rot/min), at 60-80^{0}C.

♦ The O/W emulsion obtained (marked **AGE 7**) was cooled under stirring to room temperature.

♦ The wax mixture contains: triethanolamine monostearate, lanolin and beeswax in a ratio of 7/3/1.

♦ Triethanolamine monostearate was obtained by esterification of stearin with triethanolamine, fatty acid/amino alcohol mass ratio = 1.0/0.8-1.0; operating parameters: 120-140^{o}C, stirring – 60-80 rot/min, time – 4 h.

♦ The wax mixture was obtained by liquefaction of lanolin (at 50-60^{o}C) and beeswax 3/1 (la 80-90^{0}C) in a water bath; the two fluid waxes were cooled at 60^{0}C.

5.3. Obtaining antifungal and antibacterial products based on natural oils and waxes

Research aims the replacement of potentially toxic biocides with ecologic materials – essential oils extracted from plants. [151-154] Complex mixtures of aliphatic and aromatic hydrocarbons, aldehydes, alcohols, esters, etc., they have antioxidant, antibacterial, antifungal and fragrance properties.

5.3.1. Components used to obtain antifungal and antibacterial products

Coriander and cedar essential oils, known for their properties, [162] were used as antifungal and antibacterial products.

The composition of essential oils depending on environmental factors: intensity and duration of light, altitude, season, soil and nutrients, [242, 243] the used oils were analyzed by gas chromatography coupled with mass spectrometry - GC-MS, [244 -246] and the chromatograms are shown in figures 5.1 and 5.2.

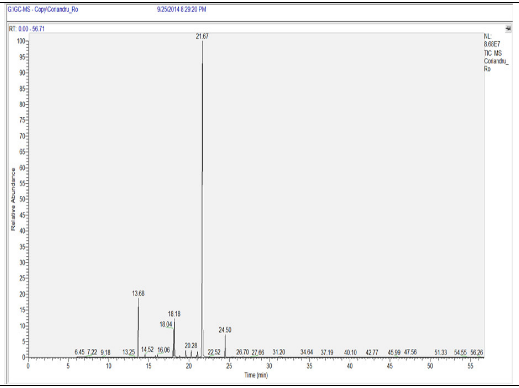


Figure 5.1. Chromatogram of coriander oil

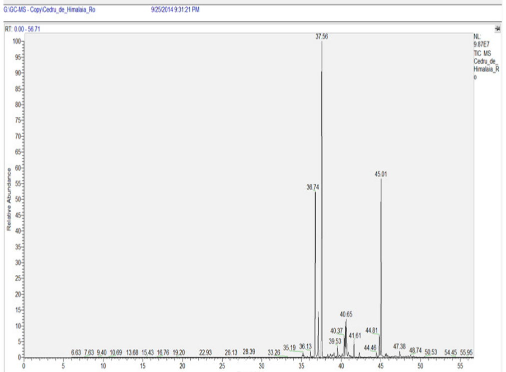


Figure 5.2. Chromatogram of cedar oil

♦ **The main compounds in the coriander essential oil** are: linalool – 74.17%, α-pinene – 7.86% and camphor – 3.72%, with antibacterial and antifungal properties.

♦ **Cedar essential oil** contains: thujopsene – 37.25% and cuparene – 9.47% with antibacterial and antifungal properties, cedrenol – 20.79% and cedrene – 20.03% with antimicrobial properties as main components.

5.3.2. Obtaining antifungal and antibacterial products

● **The antifungal product based on coriander essential oil (AF-C-1)** was obtained from 80 % coriander essential oil, 10 % wax emulsion, 5-10 % ethanol and 5-10% ethoxylated lauryl alcohol

♦ The wax emulsion was obtained from: 15-20% wax mixture 1/3, 10% ethoxylated lauryl alcohol reported to the amount of wax emulsified and water under stirring (300-500 rot/min), at 60-80^{0}C.

♦ The wax mixture was obtained by beeswax and lanolin (1:3) liquefied by heating at 80-90^{0}C and stirring for 40-60 min (60-80 rot/min).

● **Antifungal product based on cedar essential oil (AF-C-2)** was obtained by the same method, using 80 % essential oil, 10 % wax emulsion, 5-10 % ethanol and 5-10 % ethoxylated lauryl alcohol.

5.4. Obtaining fragrance products based on essential oils

Fragrance compounds in the lavender essential oil are: linalool – 36.57%, linalyl acetate – 35.60% and terpineol – 7.67%, while the orange essential oil contains mainly limonene (94.7%) and small amounts of pinene, linalool and linalyl acetate, like lavender oil.

● **Fragrance products for leather** were obtained at 30-35^{0}C in a glass flask, under mechanical stirring for 15-20 min. An ultrasound bath (Elmasonic S 15 H) was also used, at 25^{0}C for 10 min.

♦ Components: 10-30% lavender essential oil, 10-30% orange essential oil, 20% ethyl alcohol, 10% lauryl alcohol ethoxylated with 7 moles of ethylene oxide, 9-10% polyethylene glycol 600, 1% hexadecyl-trimethyl ammonium bromide (cationic emulsifier) and 0-39% deionized water.

♦ The resulted products were marked P- LP-1-3.

6. CHARACTERIZATION OF DISPERSE SYSTEMS USED IN LEATHER FINISHING

6.1. Characterization by Physical-Chemical Analyses

6.1.1. Physical-chemical characteristics of pigment pastes

The obtained pigment pastes have the following characteristics: dry substance – 40-45%, pH (1/10 solution) – 6.5-8.0, uniform spread on glass surface and comparability with reference samples.

6.1.3. Physical-chemical characteristics of wax emulsions

The resulted wax emulsions (1-AGE 7 and 2-AGE 7) are white homogenous fluids containing 12-19% dry substance, pH–7.0-7.3, Ford cup viscosity Φ4 –12-27 s and density – 0.951-0.975 g/cm^3.

6.1.4. Physical-chemical characteristics of antifungal and antibacterial products based on natural oils and waxes

The prepared products, AF-C-1 and AF-C-2, are yellowish white fluids, homogenous, with 11-18% dry substance, pH – 3.8-4.5, density – 0.805-0.820 g/cm^3.

6.1.5. Physical-chemical characteristics of fragrance products based on essential oils

Products P-LP-1, P-LP-2 and P-LP-3 are homogenous yellowish white fluids with with 19-26% dry substance, pH – 5.2-6.2, density – 0.844-0.863 g/cm^3, total nitrogen – 0.39-0.57%.

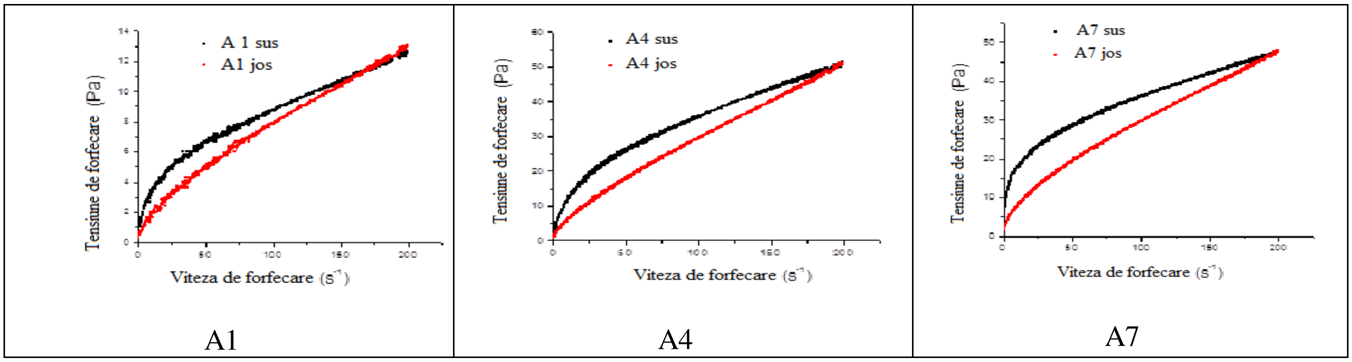
6.3. Rheological behaviour of some of the aqueous leather finishing systems

6.3.1. Rheological behaviour of pigment pastes

Pigment pastes for leather finishing are yield for rheological determinations. [280, 281]

6.3.1.1. Stationary rheological behaviour

Rheograms obtained for **pigment pastes A1**, **A4** and **A7**, containing red iron oxide, when increasing (sus) and decreasing (jos) shear rates are shown in figure 6.9a-c.



A1 A4 A7

Figure 6.9.a-c. Rheograms of pastes A1, A4 and A7 when increasing (sus) and decreasing (jos) shear rates

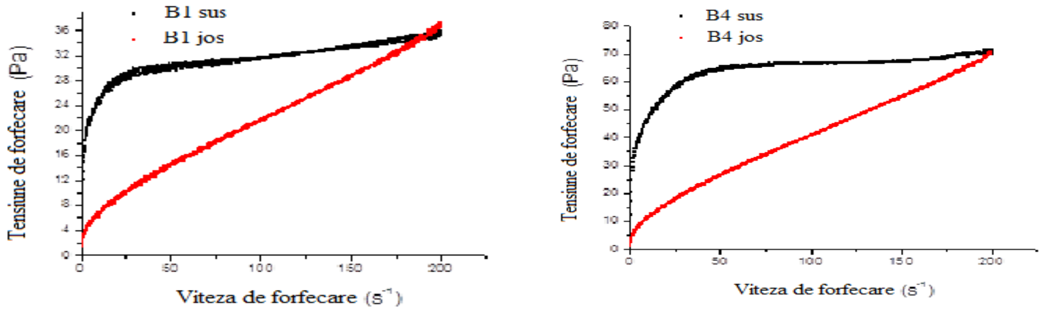
Rheograms show that the three pastes have a pseudoplastic behaviour, flow starting at lower shear stress of 2-5 Pa.s. Rheograms obtained by increasing and decreasing shear rates do not overlap, but show a hysteresis loop, that is the three pastes are thixotropic. They were modeled with Cross four parameters model, [287] which has the advantage of providing information on system viscosity for the entire shear rates range:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (C\dot{\gamma})^m} \tag{6.2}$$

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.

Rheograms obtained for pigment pastes B1 and B4 containing yellow iron oxide, when increasing and decreasing shear rates are shown in Figure 6.10a, b.

They also have time-dependent thixotropic pseudoplastic behavior. Hysteresis loops have larger areas than the previous ones, so their thixotropy is much higher.



B1

B4

Figure 6.10.a, b. Rheograms of pigment pastes B1 and B4 when increasing and decreasing shear rates

Parameters obtained by modelling rheograms in Figures 6.9 and 6.10 using the Cross model, both when increasing and decreasing shear rates, are presented in Table 6.8.

Table 6.8. Parameters obtained by modelling rheograms in figures 6.9. and 6.10 with the Cross model

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
A4 up	4.16 ± 0.05	0.040 ± 0.010	2.12 ± 0.09	0.64 ± 0.01
A4 down	6.40 ± 0,50	0.159 ± 0.003	0.07 ± 0.02	0.52 ± 0.01
A7 up	13.50 ± 0.10	0.112 ± 0.004	1.06 ± 0.02	0.87 ± 0.01
A7 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 ± 0.50	0.114 ± 0.001	0.07 ± 0.04	0.72 ± 0.02
B4 up	37.5 ± 0.40	0.100 ± 0.010	1.37 ± 0.03	0.97 ± 0.06
B4 down	27.0 ± 1.00	0.240 ± 0.002	0.09 ± 0.01	0.73 ± 0.04

The table shows that the viscosity at zero shear rate, η_0, and at high shear rate, η_∞, grows by increasing the pigment concentration both when raising and lowering shear rates. At the same time, the differences between η_∞ values obtained from rheograms recorded when increasing shear rates are very low, proving that the more concentrated pastes can be applied almost as easily as the diluted ones.

Cross time constants decrease with increasing pigment concentration, indicating that the more concentrated the paste, the lower the shear rate, as expected for polymer disperse systems. Thixotropic behavior is desirable, fluidity increasing under the action of shear stress, facilitating the application and restoring original viscosity after application prevent dripping.

Figures 6.9. and 6.10. also emphasize that areas of hysteresis loops increase by raising the pigment concentration, i.e. pastes become highly thixotropic.

Hysteresis loop area is a measure of thixotropy. [288]

Conclusions

▪ Reddish brown pigment pastes – PPRF-A1, PPRF-A4 and PPRF-A7 – have pseudoplastic and thixotropic behavior, while the control paste – Casicolor Brown – is not thixotropic.

▪ Ochre yellow pigment pastes PPGF-B1 and PPGF-B4 behave pseudoplastic and thixotropic, just like the control Casicolor Ochre, but thixotropy of the prepared ones is much stronger, therefore easier to apply.

▪ B1 and B4 pastes are more viscous than those containing the same amount of red iron oxide, are more pseudoplastic and hysteresis loops are much larger, which demonstrates that they are more thixotropic.

▪ Although viscosities of B1 and B4 pastes at zero shear rate are much higher than those of A1 and A4, the ones at high shear rates are comparable, due to the more pronounced thixotropy of B1 and B4.

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

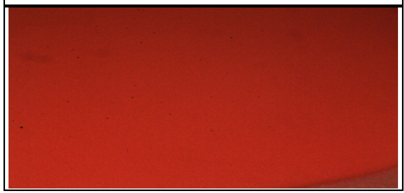
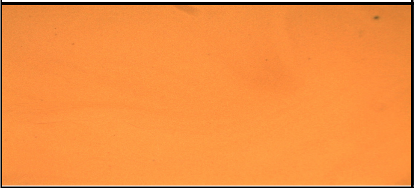
- Black pigment pastes have pseudoplastic and thixotropic behavior, while the control – Casicolor Black – behaves poorly pseudoplastic.

6.4. Microscopic analysis of finishing auxiliaries

6.4.1. Analysis of pigment pastes by optical microscopy

Optical microscopy images for pigment pastes were captured using Leica stereomicroscope, as in the case of the previous ones, and are presented in table 6.13.

Table 6.13. 20X Optical images of prepared pigment pastes

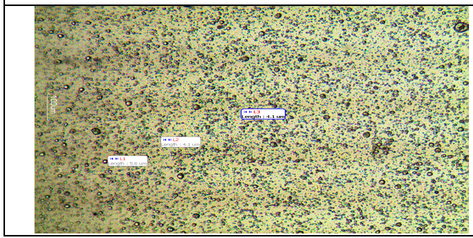
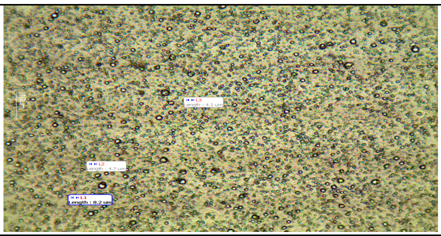
Red iron oxide (PPRF)	Yellow iron oxide (PPGF)	Black iron oxide (PPNF)
		

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

6.4.2. Analysis of wax emulsions by optical microscopy

Optical images of wax emulsions were obtained using the same stereomicroscope (table 6.16).

Table 6.16. Optical images of prepared wax emulsions at 100X

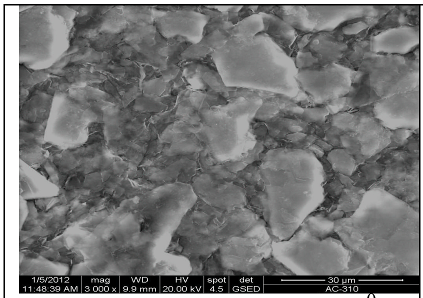
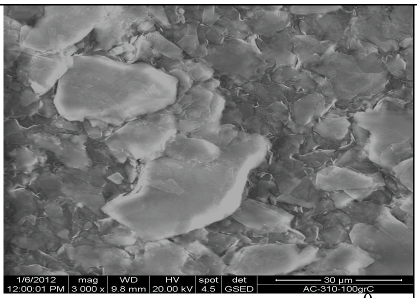
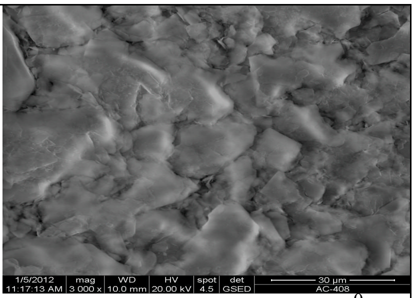
Wax emulsion 1-AGE 7	Wax emulsion 2-AGE 7
	

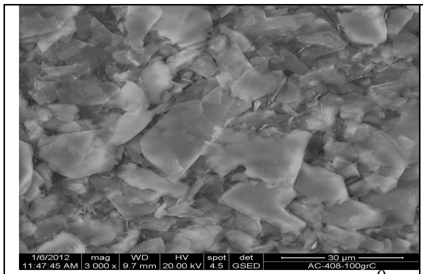
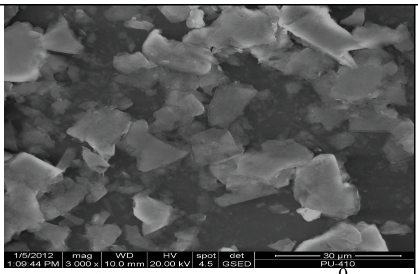
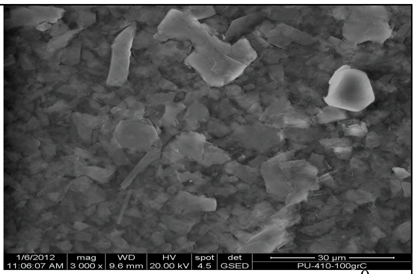
Emulsions are of O/W type and particle size is 4-8 μm.

6.4.3. Analysis of binder films by scanning electron microscopy

The films obtained from the acrylic and polyurethane binders used were analyzed by SEM at 25 and 100°C (pressing temperature for finished leather). Surface topography of films obtained from evaporation of dispersion medium was observed directly using an ESEM QUANTA 200 microscope equipped with GSED detector, [298] at 20 kV. 3000X images are given in Table 6.17.

Table 6.17. SEM images of acrylic and polyurethane binder films used in leather finishing at specified temperatures and magnifications

		
Vecosol AC 310-3000 X, 25^{0}C	Vecosol AC 310-3000 X, 100^{0}C	Vecosol AC 408-3000 X, 25^{0}C

		
Vecosol AC 408-3000 X, 100^{0}C	Vecosol PU 410-3000 X, 25^{0}C	Vecosol PU 410-3000 X, 100^{0}C

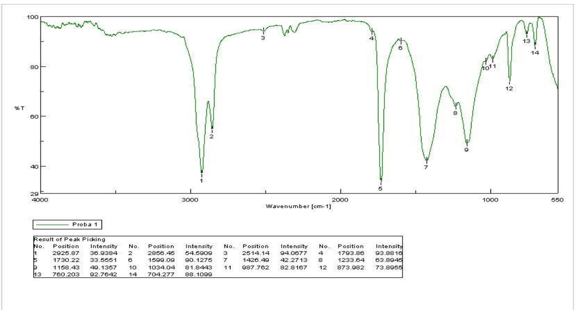
Conclusions

- SEM images show that the increase in temperature from 25 to 100°C lead to changes in the appearance of coating films obtained from acrylic and polyurethane aqueous dispersions for leather surface finishing. This is due to the cross-linking of the film-forming substances by heating and it proves that pressing causes cross-linking, leading to increased resistance of finished leather.

6.5. Characterization of finishing auxiliaries by FT-IR

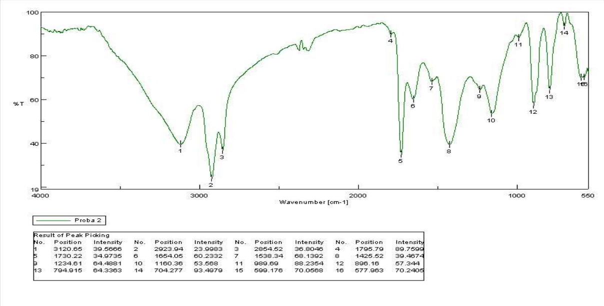
6.5.1. Characterization of pigment pastes

The films resulted from drying pigment pastes, variants A1, B1 and C1 in Table 5.4, and three with similar colours produced by Triderma Germany: Casicolor Brown, Ochre and Black on glass slides were analyzed by FT-IR, [299, 300] and the spectra are shown in Figures 6.22, 6.24 and 6.26.



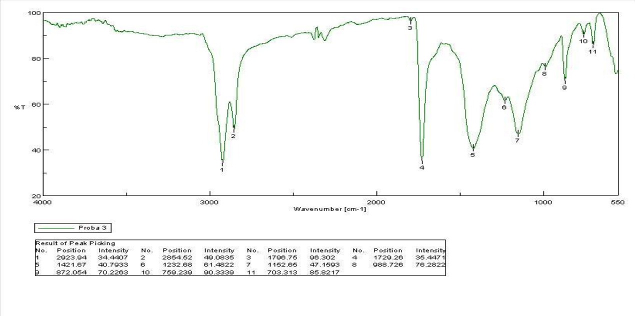
```
Result of Peak Picking
No.  Position  Intensity  No.  Position  Intensity  No.  Position  Intensity  No.  Position  Intensity
1    2925.87   36.9384    2    2856.45   54.5909    3    2514.14   94.0677    4    1793.86   93.8816
5    1730.22   33.5551    6    1599.09   90.1275    7    1426.49   42.2713    8    1233.64   63.8945
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 6.22. FT-IR spectrum of the pigment paste film based on red iron oxide, PPRF-A1



```
Result of Peak Picking
No.  Position  Intensity  No.  Position  Intensity  No.  Position  Intensity  No.  Position  Intensity
1    3120.65   39.5666    2    2923.94   23.9983    3    2854.52   36.8046    4    1795.79   89.7599
5    1730.22   34.9735    6    1654.05   60.2332    7    1538.34   68.1392    8    1425.52   39.4674
9    1234.61   64.4881    10   1160.36   53.568     11   989.69    88.2354    12   896.16    57.344
13   794.915   64.3363    14   704.277   93.4979    15   599.176   70.0568    16   577.963   70.2405
```

Figure 6.24. FT-IR spectrum of the pigment paste film based on yellow iron oxide, PPGF-B1



```
Result of Peak Picking
No.  Position  Intensity  No.  Position  Intensity  No.  Position  Intensity  No.  Position  Intensity
1    2923.94   34.4407    2    2854.52   49.0835    3    1796.75   96.302     4    1729.26   35.4471
5    1421.67   40.7933    6    1232.68   61.4822    7    1152.65   47.1593    8    988.726   76.2822
9    872.054   70.2263    10   759.239   90.3339    11   703.313   85.8217
```

Figure 6.26. FT-IR spectrum of the pigment paste film based on black iron oxide, PPNF-C1

The spectra of films obtained from the pigment pastes show characteristic bands of acrylic polymers: [301] 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 ≈1730 cm^{-1} typical for acrylates (the stretch of the ester carbonyl groups) and 1200-1000 cm^{-1} assigned to ether groups.

Films based on red and black iron oxide have the same bands, but the one based on yellow oxide presents additional bands (Figure 6.24): a relatively large band at 3120 cm^{-1}, a weak one at 896 cm^{-1} and a very weak one at 1538 cm^{-1}. In addition, the bands between 900 and 750 cm^{-1} are shifted to higher wave numbers and intensities increase, reaching average values. Given that the only difference between the three pastes consists in the iron oxides used and that yellow iron oxide is an iron (III) oxide-hydroxide, these bands can be attributed only to bonds established between oxide and polymer.

Conclusions

- FT-IR spectra of the films obtained from the pigment pastes show characteristic bands for the acrylic binder used. The spectrum of the film obtained from the paste containing the yellow iron oxide shows that the oxide bonds with the acrylic binder.
- FT-IR spectra of films prepared from Casicolor Brown R and Casicolor Ochre pastes demonstrate that the binder used is also acrylic.
- FT-IR spectrum of the film obtained from the Casicolor Black paste is completely different, which means that the binder is different.

6.5.2. Characterization of waxes

AGE 7 wax emulsion and the component waxes were dried on glass slides and the resulting films analyzed by FT-IR, [299] using the same device as for the pigment pastes.

6.5.2.1. Characterization of materials used and wax emulsion

FT-IR spectra of the following components: beeswax, lanolin, triethanolamine monostearate, and film obtained after evaporation of the dispersion medium from the wax emulsion 2-AGE 7 are shown in figure 6.28.

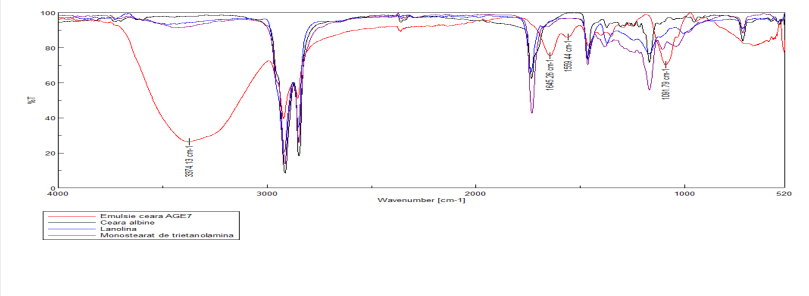


Figure 6.28. FT-IR spectra of component waxes and the film obtained from 2-AGE 7 wax emulsion

The figure shows that the beeswax and lanolin have common bands: two intense bands at about 2920, and 2850 cm^{-1}, respectively, assigned to the asymmetric and symmetric stretching vibrations of methylene and methyl groups, a weak band at about 1730 cm^{-1} due to the stretch of C=O bond of ester groups, a weaker band at 1470 cm^{-1} and a very weak one at 720 cm^{-1} specific to compounds containing long aliphatic chains, slightly more intense for beeswax, and the band at about 1170 cm^{-1} attributed to C-O-C bonds, also more intense for beeswax. The triethanolamine monostearate has all these bands, given by the stearyl radical, and a medium intensity band at 1169.5 cm^{-1} due to the tertiary amine group of triethanolamine (C-N stretch). The spectrum of the film obtained by evaporating the emulsion derived from three waxes stabilized with lauryl alcohol ethoxylate contains all characteristic bands of the components, at which the intense band at 3374 cm^{-1} due to hydrogen bonds formed by water left in the film can be added, the relatively weak one at 1645 cm^{-1} – present in stearate and attributed to C=O stretch of hydrogen bonds coupled with C-N stretching vibration, the very weak one at 1559 cm^{-1} which may be due to the COO^- stretch in the 33% neutralized stearic acid in triethanolamine monostearate, the weak one at 1092 cm^{-1}, present in triethanolamine monostearate as a very weak band, which may be due to the stretch of C-O-C bonds of the ether groups of the emulsifier.

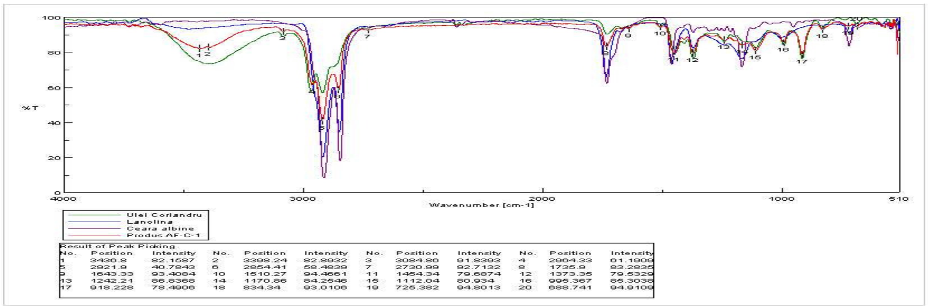
Conclusions

- The spectrum of the film obtained from the 2-AGE 7 wax emulsion contains all the bands of components and the broad band at about 3374 cm^{-1} due to hydrogen bonds formed by water left in the film.

6.5.2.2. Characterization of materials and products with antifungal and antibacterial properties

FT-IR spectra of the components of the antifungal product AF-C-1, containing coriander oil, beeswax and lanolin and of the films obtained thereof by evaporation are presented in figure 6.29.

The spectrum of the AF-C-1 contains all the bands of components: an intense band at about 2922 cm^{-1} and weaker ones at about 2964 and 2854 cm^{-1} assigned to asymmetrical and symmetrical stretching vibrations of methyl and methylene groups of coriander oil, beeswax and lanolin; a weak band around 1736 cm^{-1} due to



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3436.8	82.1587	2	3398.24	82.8932	3	3084.86	91.8393	4	2964.33	61.1909
5	2921.9	40.7843	6	2854.41	58.4839	7	2730.99	92.7132	8	1735.9	83.2835
9	1643.33	93.4084	10	1510.27	94.4661	11	1454.34	79.6874	12	1373.35	79.5329
13	1242.21	86.8368	14	1170.86	84.2546	15	1112.04	80.934	16	995.367	85.3038
17	918.228	78.4906	18	834.34	93.0106	19	725.382	94.8013	20	688.741	94.9109

Figure 6.29. Overlapping FT-IR spectra of coriander oil, waxes and film obtained from the antifungal and antibacterial product AF-C-1

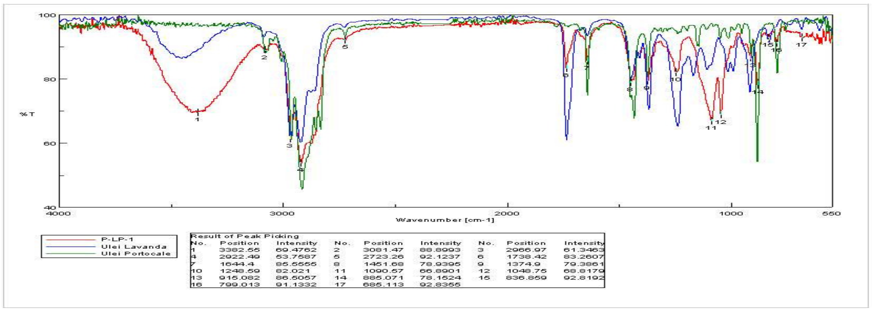
the stretching of the C = O bond of ester groups, two more intense bands at 1454 and 1373 cm^{-1} specific to compounds containing long aliphatic chains, and one at about 1112 cm^{-1} assigned to C-O-C bonds of ether.

Conclusions

▪ FT-IR spectra of films obtained by evaporation of dispersion medium from antifungal and antibacterial products AF-C-1 and AF-C-2 contain bands of all components, with intensities determined by their proportions.

6.5.3. Characterization of fragrance products

FT-IR spectra of lavender and orange oils and of the film obtained from the fragrance product P-LP-1 are presented overlapped in figure 6.31.



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3382.55	69.4762	2	3081.47	88.8993	3	2966.97	61.3463
4	2922.49	53.7587	5	2723.26	92.1237	6	1738.42	83.2607
7	1644.4	85.5555	8	1451.68	78.9395	9	1374.9	79.3861
10	1248.59	82.021	11	1090.57	66.8901	12	1048.75	68.8179
13	915.082	86.5057	14	885.071	78.1524	15	836.859	92.8192
16	799.013	91.1332	17	685.113	92.8355			

Figure 6.31. Spectra for essential oils and film obtained from the fragrance product, P-LP-1

Conclusions

▪ Spectra of fragrance product P-LP-1- P-LP -3 films contain bands of essential oils used more or less intense, depending on their proportions.

6.6. Characterization of coating films by thermal analysis

Auxiliary materials being used for film coating of leather or fur assortments, in order to determine the thermal stability of the films, pressed at 100°C, aqueous dispersions with the following composition were prepared: 10% PPRF-A6, PPGF-B6 or PPNF-C6 pigment paste, 3% AGE 7 wax emulsion, 30% acrylic dispersion and 57% water, as well as with Casicolor Brown, Ochre or Black paste. Thy were prepared by deposition on glass plates and air dried and marked as Sample 1-3 and Control 1-3, respectively.

TG and DTA curves of Sample 1 and Control 1 recorded using Perkin Elmer STA 6000 instrument within the temperature range 50-850°C in air, heating rate 10°C/min [302] are shown in Figures 6.37 and 6.38.

Sample films differ only by the iron oxide used in the preparation of pastes. However, pigment paste components used as control are unknown, as they constitute a trade secret. In the composition of the dispersions obtained using these pastes the known components are preponderant (pigment paste is only 10% of the composition of the dispersion films, and the total amount of acrylic dispersion and wax emulsion – containing organic compounds, that decompose thermally within the used temperature range is 3.3 times higher). In all the films the polymer from the acrylic dispersion is preponderant, it being introduced in a proportion of 30%.

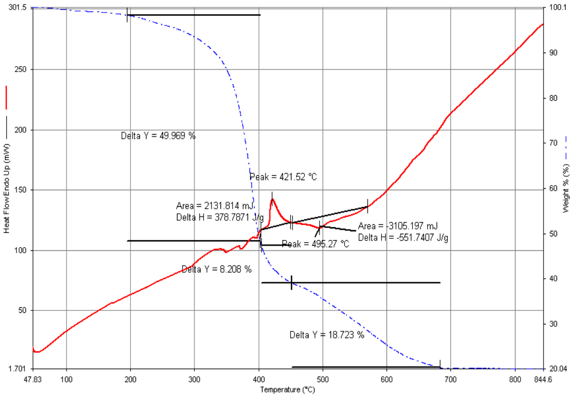


Figure 6.37. TG and DTA curves for Sample 1

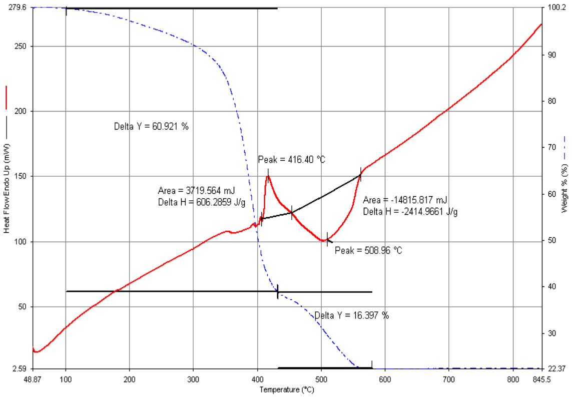


Figure 6.38. TG and DTA curves for Control 1

Up to 600-700°C water is removed from the film, and organic components decompose: the film-forming acrylic polymer (from the acrylic dispersion), the acrylic one from the pigment paste, the components of wax dispersion, the emulsion-stabilizing agent, the additives for dispersing pigments and plasticisers. If there is no interaction in the film between the mentioned components and pigments, TG and DTA curves of the three films should be alike. But the curves obtained for film Samples 1-3 show that the degradation of the three films does not occur identical: it occurs in three stages for Sample 1 and in two stages for the other two.

To emphazise the differences, Table 6.12 presents values of parameters describing thermal degradation: loss of mass, Δm%, of TG curves, and peak temperatures in DTG curves - T_{max}.

Table 6.12. Values of parameters obtained for thermal degradation of analyzed films

Characteristic/ Sample	Water desorption (denaturation)			Thermal-oxidative degradation	
	Δm	T_{max} (DTG)	T_{max} (DTA)	T_{max} (DTG)	T_{max} (DTA)
	%	°C	°C	°C	°C
Sample 1	76.90				
Stage I	49.969	200	350; 370; 390 – endo		
Stage II	8.208			400	421.52 – exo
Stage III	18.723			450	495.27 – endo
Control 1	77.32				
Stage I	60.921	100	360 – endo 416.40 – exo		
Stage II	16.397			430	508.96 – endo
Control 2	77.50				
Stage I	59.183	100	350 – exo 410 – endo 421.23 – exo		
Stage II	18.308			430	441.50 – endo
Control 2	79.70				
Stage I	57.28	140	384.11– exo		
Stage II	22.40			430	460 – exo 530 – endo
Sample 3	95.40				
Stage I	63.475	110	401.04 – exo		
Stage II	31.912			430	630 – endo
Control 3	67.50				
Stage I	54.435	120	392.99 – exo		
Stage II	13.066			430	510 – endo

Figure 6.37 shows that **Sample 1** degrades over three stages and has the following weight losses: 49.969% in the first stage, at temperatures between 200 and 400°C – due to the cleavage of the main chains of acrylic polymers, [303] 8.21% in the second one, in the range of 400-450°C, and 18.723% in the third stage at temperatures between 450 and 690°C; during the last two, functional groups are eliminated. The total loss is

76.9%, to which the elimination of water between 48 and 200°C, of about 2%, is added and the residue of 20.04%. The decomposition rate is maximum between 370 to 400°C. The three endothermic peaks at 350, 370 and 390°C are due to transitions taking place in the polymer film, and the exothermic one – to thermal oxidative degradation. **Sample 2** is basically free of water and degrades in two stages: chain cleavage between 100 and 430°C – 59.2% – nearly 10% higher than the previous one, and 18.3% in the second stage, occurring between 430 and 620°C. The total losses are 77.5% and residue is 22.5%. The maximum decomposition rate is 380 to 400°C. The wider temperature range in which chain breaking occurs can be explained by the interactions between polymers and yellow iron oxide by the hydroxyl groups they contain. The presence of endothermic and exothermic peaks has the same cause as for the previous film. **Sample 3** shows a weight loss of 63.474% in the first stage, between 110 and 430°C and of 31.912% in the second, in the temperature range 430-730°C; the total is 95.4%, and the residue – 4.263%. Thermal resistances are different: Sample 3 shows the highest resistance and Sample 2 the lowest, by over 100°C lower than for Sample 3, decomposition ceasing at 620°C.

Control films have different TG and DTA curves. **Control 1** decomposes in two stages, in the first one the weight loss is 60.921% and occurs between 100 and 430°C, and in the second one16.397%, occuring between 430 and 580°C, with a total loss of 77.32%. The residue is 22.37% and the film contains virtually no water. Maximum decomposition temperature is between 370 and 400°C, as for Sample 1. **Control 2** also breaks down in two steps: 140-430°C with a weight loss of 57.281%, and at 430-580°C with a loss of 22.397%, with a total of 79.7%; The residue is 18.3% and the water is absent. **Control 3** decomposes in two steps too: weight loss of 54.43% between 120 and 430°C and 13.1% between 430 and 580°C with a total of 67.5%. The residue is 23%, and the water loss of about 1% occurs in the range of 46-112°C.

Conclusions

▪ Parameters of thermal degradation show that films containing pigment pastes are more resistant than those obtained from control pastes; all films are resistant enough to protect finished leather.

7. LEATHER ASSORTMENTS OBTAINED USING THE PREPARED DISPERSE FINISHING SYSTEMS

7.1. Finishing technologies for bovine leather into natural grain box assortments using the prepared pigment pastes and handle modifier

● **The framework technology** for dry finishing of bovine leather into natural grain box assortments, black and coloured, is presented in table 7.2.

Table 7.2. Technology for dry finishing of bovine leather into black and coloured natural grain box assortments

Operation	Dispersion composition/application method
Application of dispersion I (basecoat)	100 g/L pigment paste 30 g/L aqueous wax emulsion 300 g/L aqueous acrylic dispersion, or 150 g/L aqueous acrylic dispersion and 150 g/L aqueous polyurethane dispersion, or 200 g/L aqueous acrylic dispersion and 100 g/L aqueous polyurethane dispersion 570 g/L water Application by spraying (2 passes dispersion I)
Itermediate pressing	In hydraulic press with the mirror or fog plate, parameters: - temperature – 50-60°C; pressure – 50-100 atm
Application of dispersion I	By spraying (2-3 passes dispersion I)
Application of final dressing (fixing)	Emulsion/dispersion with the following composition: 700 g/L aqueous nitrocellulose, acrylic or polyurethane emulsion 20 g/L aqueous wax emulsion for handle 280 g/L water Application by spraying (2 passes final dressing)
Final pressing	In hydraulic press with the mirror plate, parameters: - temperature – 70-80°C; pressure – 50-100 atm

● **Technological variants for finishing** bovine leather into natural grain box assortments, with reddish brown pigments, marked F1-F10, are presented in table 7.3.

Table 7.3. Technological variants for finishing bovine leather into natural grain box assortments with reddish brown pigments

Component/Amount (g/L)	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
PPRF-A4	100	100	-	-	-	-	-	-	-	-
PPRF-A5	-	-	100	100	-	-	-	-	-	-
PPRF-A6	-	-	-	-	100	100	-	-	-	-
Casicolor Brown R	-	-	-	-	-	-	100	100	100	100
Vecosol AC 310	150	150	150	150	150	150	150	150	100	-
Vecosol AC 408	150	-	150	-	150	-	150	-	100	-
Vecosol PU 410	-	150	-	150	-	150	-	150	100	-
Medacril EFP33	-	-	-	-	-	-	-	-	-	300
Roda wax Mono	30	30	30	30	30	30	30	30	30	30
Water	570	570	570	570	570	570	570	570	570	570

Similar variants were prepared using ochre yellow and black pigment pastes, and the resulting samples were marked F11-F20, and F21-F30, respectively.

● **Application of the final dressing** (fixing films deposited onto the dermis) was performed in three variants: FN –nitrocellulose, FA – acrylic and FP – polyurethane, presented in table 7.4.

Table 7.4. Technological variants for fixing bovine leather into natural grain box assortments

Components of final dressing (g/L)/Variant	FN	FA	FP
Roda lac 93	700	-	-
Medacril EFP34	-	700	-
Roda pur 5011	-	-	700
Wax emulsion 2-AGE 7	20	20	20
Water	280	280	280

The final dressing for most samples contains 20g/L 2-AGE 7 wax emulsion, amount comonly used to improve the final handle of coating films. Samples F9-F10 contains 20g/L silicone oil emulsion Roda Feel KTA (control) in the final dressing.

7.3. Finishing technologies for bovine leather into natural grain box and sheepskin nappa assortments using antifungal and antibacterial products

Testing of antifungal products based on coriander (AF-C-1) and cedar oil (AF-C-2) was carried out monitoring the manner in which mold growth is influenced by the treatment applied to the sample through the resistance to mold in simulated contamination conditions.

Framework technology for dry bovine leather finishing into reddish brown and black natural grain box assortments is presented in table 7.2 and that of sheepskins into black and reddish brown Nappa assortments in Table 7.6.

The final dressing was applied to the FP variant shown in Table 7.4. Finished leathers were further treated with final dressing whose composition includes AF-C-1 and AF-C-2 products in various proportions.

Technological variants for treating bovine hides into natural grain box and sheepskin Nappa assortments for samples treated with antifungal products have been marked AF1-AF40. Some of them are presented in Table 7.8.

Table 7.8. Technological variants for treating bovine hides into natural grain box and sheepskin Nappa assortments

Sample	Final dressing composition	Treated leather assortments
AF 1	1000 g/L product AF-C-1	Film-coated brown box leather
AF 7	1000 g/L product AF-C-1	Uncoated brown nappa (treated on velvet part)
AF 8	1000 g/L product AF-C-2	Film-coated brown box leather
AF 14	1000 g/L product AF-C-2	Uncoated brown nappa (treated on velvet part)
AF 17	400 g/L product AF-C-1	Film-coated brown box leather

	400 g/L product AF-C-2 200 g/L Roda pur 5011	
AF 18	400 g/L product AF-C-1 400 g/L product AF-C-2 200 g/L Roda pur 5011	Film-coated black box leather
AF 19	400 g/L product AF-C-1 400 g/L product AF-C-2 200 g/L Roda pur 5011	Uncoated black box leather (treated on velvet part)
AF 20	400 g/L product AF-C-1 400 g/L product AF-C-2 200 g/L Roda pur 5011	Uncoated brown nappa
AF 21	750 g/L product AF-C-1 250 g/L Roda pur 5011	Film-coated brown box leather
AF 22	750 g/L product AF-C-1 250 g/L Roda pur 5011	Film-coated black box leather
AF 23	750 g/L product AF-C-1 250 g/L Roda pur 5011	Uncoated black box leather (grain treated)
AF 26	650 g/L product AF-C-1 350 g/L Roda pur 5011	Uncoated brown box leather (grain treated)

Development of the *Aspergillus niger* strain on leather samples over time, i.e. macroscopic images of the samples treated with AF-C-1 and AF-C-2 products are presented in section 8.5.

7.4. Finishing technologies for sheepskins into natural grain nappa assortments using fragrance

Finished leather samples were further treated with final dressing containing products P-LP-1 – P-LP-3 in various proportions.

Some technological variants of treating sheepskins into Nappa assortments for clothing for samples PP1-PP15 (scented leather) are shown in Table 7.9.

Table 7.9. Technological variants of treating sheepskins into Nappa assortments

Sample	Final dressing composition
PP1	500 g/L Roda pur 5011 and 500 g/L product P-LP-1
PP4	200 g/L Roda pur 5011 and 800 g/L product P-LP-1
PP5	1000 g/L product P-LP-1
PP6	500 g/L Roda pur 5011 and 500 g/L product P-LP-2
PP9	200 g/L Roda pur 5011 and 800 g/L product P-LP-2
PP10	1000 g/L product P-LP-2
PP11	500 g/L Roda pur 5011 and 500 g/L product P-LP-3
PP14	200 g/L Roda pur 5011 and 800 g/L product P-LP-3
PP15	1000 g/L product P-LP-3

The fragrance strength of leather treated with P-LP-1 – P-LP-3 products is presented in subchapter 8.6.

8. CHARACTERIZATION OF LEATHER ASSORTMENTS FINISHED USING DISPERSE SYSTEMS

8.2. Characterization by mechanical methods

Physical-mechanical characteristics of finished leather assortments were determined according to the following standards: elongation at a load of 10 N/mm^2 (%) and tensile strength (N/mm^2) – SR EN ISO 3376:2012; tear strength (N/mm) – SR EN ISO 3377:2012; resistance to repeated bending, number of flexions – SR EN ISO 5402:2012; resistance to pressing (^{o}C) – STAS 7047:1998; fastness to light (1-8 ranking) – SR EN ISO 105-B02:2003; strength to dry and wet abrasion (1-5 ranking) – SR EN ISO 11640:2002.

8.2.1. Testing finished leathers

The use of reddish brown pigment pastes in the basecoat and 2-AGE 7 wax emulsion in the final nitrocellulose, polyacrylic or polyurethane dressing led to the results presented in table 8.3.

Table 8.3. Mechanical characteristics of natural grain box bovine leathers obtained using reddish brown pigment pastes and nitrocellulose, polyacrylic or polyurethane dressing

Sample/Characteristic	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
Nitrocellulose dressing										
Elongation at 10 N/mm^2 load, %	27	28	28	28	27	28	28	30	27	28
Tensile strength, N/mm^2	24.9	24.3	24.1	25.2	23.8	25.2	23.3	23.8	24.9	24.1
Tear strength, N/mm	42.7	43.8	45.3	46.7	46.5	48.8	43.3	44.9	42.7	42.4
Resistance to repeated bending, number	200.000	200.000	200.000	205.000	200.000	210.000	200.000	200.000	200.000	180.000
Dry and wet abrasion strength, rank	5/4 4/3	5/4 4/3-4	5/4 4/3	5/4 4/3-4	5/4-5 4/3	5/4-5 4/3-4	5/4 4/3	5/4 4/3	5/5 5/4-5	5/4-5 4/4
Polyacrylic dressing										
Elongation at 10 N/mm^2 load, %	28	28	27	28	27	28	28	30	28	27
Tensile strength, N/ mm^2	25.0	24.8	24.6	25.8	24.2	25.8	24.4	24.9	2.8	25.8
Tear strength, N/mm	44.5	44.1	45.8	47.2	47.4	49.1	43.5	45.4	42.2	42.0
Resistance to repeated bending, number	200.000	205.000	200.000	205.000	210.000	220.000	200.000	200.000	200.000	180.000
Dry and wet abrasion strength, rank	5/4 4/3	5/4 4/3-4	5/4 4/3-4	5/4 4/3-4	5/4-5 4/3-4	5/4-5 4/3-4	5/4-5 4/3-4	5/4-5 4/3-4	5/4-5 5/4	5/4-5 4/4
Polyurethane dressing										
Elongation at 10 N/mm^2 load, %	28	28	27	28	27	28	28	30	28	27
Tensile strength, N/mm^2	25.7	25.2	25.6	26.3	25.7	26.2	25.4	25.5	24.8	25.8
Tear strength, N/mm	50.4	51.9	52.2	52.5	53.5	54.1	50.2	50.7	47.4	47.4
Resistance to repeated bending, number	250.000	250.000	250.000	250.000	250.000	250.000	250.000	250.000	250.000	250.000
Dry and wet abrasion strength, rank	5/4 4/3-4	5/5 4/3-4	5/4 4/4	5/5 5/4	5/5 5/5	5/5 5/5	5/5 4/4	5/5 4/4-5	5/4-5 5/4	5/4-5 4/4

Conclusions

▪ Leather samples finished using the prepared pigment pastes and waxes – natural grain box and Nappa – fall within the limits set in standards regarding chemical and physical-mechanical analyses.

▪ Nappa leather is less resistant to bending than box leather; elongation at 10 N/mm^2 load for Nappa leather is higher than for box leather by about 60%, while tensile and tear strength values are lower than that for box leather; resistance to pressing and to wet and dry abrasion are similar for Nappa and Box assortments.

8.2.2. Testing artificially aged finished Leather

Finished leathers were artificially aged and tested according to ISO 17228/2006 standard. [315-320]

Mechanical characteristics of finished natural grain box and 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;
- IT2 – leather aged at for 7 days;
- IL – leather aged with artificial light (Xenotest) for 7 days.

Conclusions

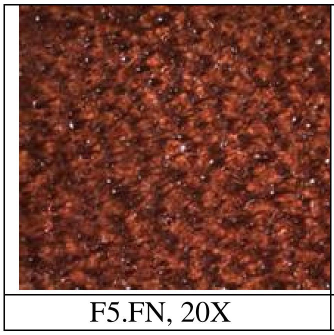
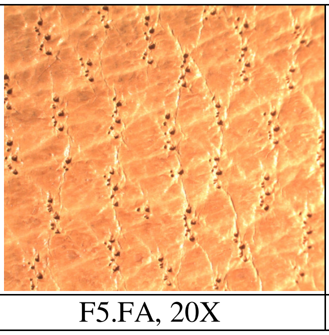
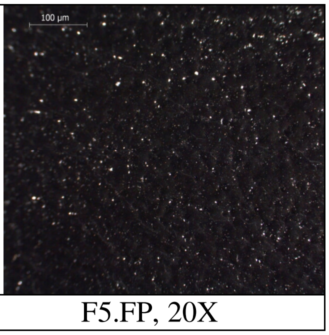
- Mechanical characteristics of thermally aged samples are inferior compared to those of unaged leathers and depend on temperature of the treatment, leather assortment and type of final dressing.
- Leather finished using the prepared pigment pastes and polyurethane or acrylic binder have the higher notes 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.

8.3. Microscopic analysis of leather assortments

8.3.1. Optical microscopy

Images shown in table 8.17 were obtained for natural grain box bovine leather and Nappa sheepskins finished using the three pigment pastes, 2-AGE 7 wax emulsion and the specified dressings.

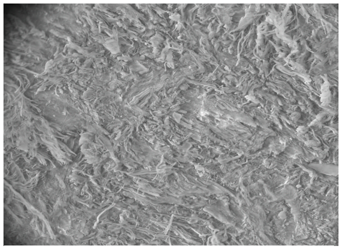
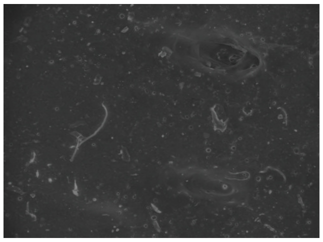
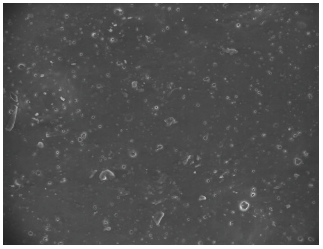
Table 8.17. Optical images of natural grain box bovine leather finished with specified pigment pastes and waxes

		
F5.FN, 20X	F5.FA, 20X	F5.FP, 20X

8.3.2. Electron microscopy analysis

Morphological study was performed by direct observation of surface topography of untreated crust reddish brown mineral tanned leather samples, wet finished by retanning, fatliquoring and deep dyeing (A) and treated with AC310+AC408+PU410+AC34 – F9.FA and with AC33+AC34 – F10.FA. SEM 3000X images obtained using the ESEM QUANTA 200 electron microscope are shown in table 8.18. [321]

Table 8.18. SEM 3000X images of untreated (A) and treated leather samples (F9.FA and F10.FA)

		
A	F9.FA	F10.FA

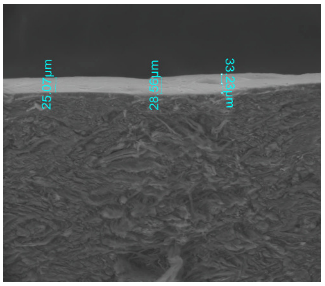
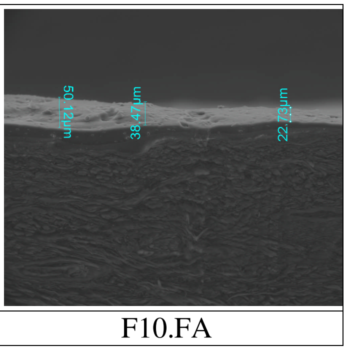
As the table shows, the surface of untreated leather is compact and wrinkled (A). On the contrary, surfaces of leather samples coated with the studied finishing agents are smooth and uniform, so the treatment seems to close leather pores. These evidences are more pronounced in microphotographs showing cross-sections of treated leather samples, presented in table 8.19.

The finishing agent was identified as the glossy area. Sample thickness is not constant, and the two samples have different thicknesses. Thus, values for F9.FA sample are higher than those for sample F10.

Conclusions

- Optical microscopy images for the bovine natural grain box leather finished with pigment pastes and waxes show the coating films uniformly set on the dermis.
- Electron microscopy images for the bovine natural grain box leather finished with pigment paste Roda Casicolor Brown R, acrylic binders or mixtures of acrylic and polyurethane binders in the basecoat and acrylic final dressing show smooth and uniform coating films.

Table 8.19. SEM images of treated leather samples F9.FA and F10.FA

	
F9.FA	F10.FA

8.4. FT-IR analysis of leather assortments

FT-IR spectroscopy was used to characterize acrylic, polyurethane and nitrocellulose polymer films used in the finishing process and untreated and coated leather samples. [322]

8.4.1. Characterization of Polyurethane and Acrylic Polymer Films

Acrylic polymers or acrylic and polyurethane polymer mixtures presented in chapter 7 were used as ecologic finishing agents to coat the surface of leathers.

Taking into account that the leather samples are treated with the finishing agent at 100°C (final pressing), films were kept for seven days at 100°C. Spectra were normalized by the corrected peak height at 2970 cm^{-1} which corresponds to $-CH_3$ stretching.

FT-IR spectra recorded for acrylic (AC33; AC34, AC310 and AC408), polyurethane (PU410) and nitrocellulose (EMAL) binder samples are presented in figure 8.25.

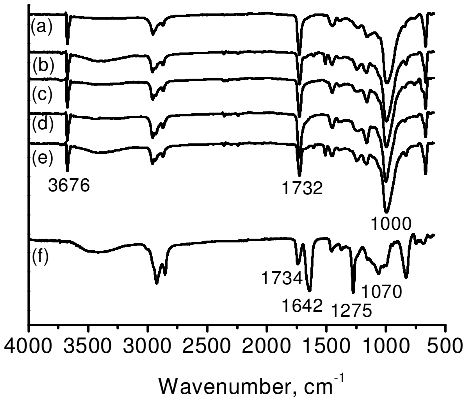


Fig. 8.25. FT-IR spectra for acrylic (a) AC33, (b) AC34, (c) AC310 and (d) AC408; polyurethane – (e) PU410 and nitrocellulose – (f) EMAL binder samples used in leather finishing

The most important bands for acrylic polymers in a-d spectra are: a medium sharp peak at 3670 cm^{-1} corresponding to stretching vibration of free -OH; a broad weak band in the range 3200-3500 cm^{-1} attributed to carboxyl OH group, which usually overlaps the -NH band attributed to amide group; sharp peaks at 2960 cm^{-1}, 2940 cm^{-1} and 2875 cm^{-1} associated with stretching vibrations of aliphatic CH link in $-CH_2$ and $-CH_3$, with asymmetric and symmetric CH_2 bending located at 1454 cm^{-1} and 1387 cm^{-1}; typical peaks of polyacrylate at 1730 cm^{-1} (corresponding to C=O stretching in saturated ester), and at 1240, 1145 and 1002 cm^{-1} attributed to C–O–C stretching vibrations in ester linkages; an intense peak at 1000 cm^{-1} given by the stretching vibration of C-OH in N-methylol groups of epoxy resin, a peak sited at 670 cm^{-1}, typical for alkene C-H bending (cis disubstituted) [323, 324]

The film obtained from polyurethane aqueous dispersion PU410 has the following bands: 3676 cm^{-1}, indicating the free O-H group (stretching); 3323 cm^{-1} attributed to N-H stretching; the group of NH vibrations is identified by the bands at 1541 cm^{-1}; the sharp peaks at 2938 and 2859 cm^{-1} are associated with $-CH_2$

stretching, while other modes of $-CH_2$ vibrations are identified by the bands at 1464, 1418, 1364, and 1294 cm^{-1}; the absorption peaks in the region 1750-1650 cm^{-1} are associated with the C=O vibrations in polyurethane. [325]

The spectrum of the film obtained from nitrocellulose emulsion – EMAL, figure 8.25f – has the following bands: at about 3460 cm^{-1} – broad band attributed to the–OH stretching vibration in intermolecular hydrogen bonds; a peak at 2920 cm^{-1} associated with the –CH stretching and another one at 1034 cm^{-1} corresponding to the C-O stretching; [326] a peak at 1275 cm^{-1} given by $C-NO_2$; a band at 1645 cm^{-1} due to O-N=O and another one at 1100 cm^{-1} given by the C-O link from ether.

8.4.2. Characterization of untreated and polymer treated leather samples

Figures 8.26 and 8.27 present the spectral characteristics of untreated leather samples (a), compared with those of finished leather using the variants F9 and F10 presented in table 7.3 and final dressing variants FN and FA in table 7.4 (basecoat treated with dispersions AC408, AC310 and PU410 or with AC33, and in the final coat with the acrylic AC34 or nitrocellulose dressing, for comparison).

Figure 8.26 (a) shows that the main spectral bands for untreated leather were identified in the following regions: 3660–3530 cm^{-1} (NH amide), 2922 and 2856 cm^{-1} ($-CH_3$ and $-CH_2-$), 1643 cm^{-1} (-OC-N), 1540 cm^{-1} (NH), 1446 cm^{-1} (C–H), 1239 cm^{-1} (NH-CO), 1076, and 1028 cm^{-1} (C-O).

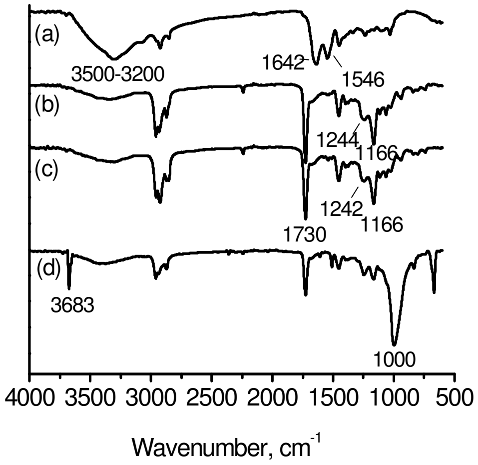


Fig. 8.26. FT-IR spectra of samples: (a) unfinished; (b) finished with AC408, AC310 and PU410 basecoat; (c) finished with AC33 basecoat; (d) final acrylic dressing AC 34

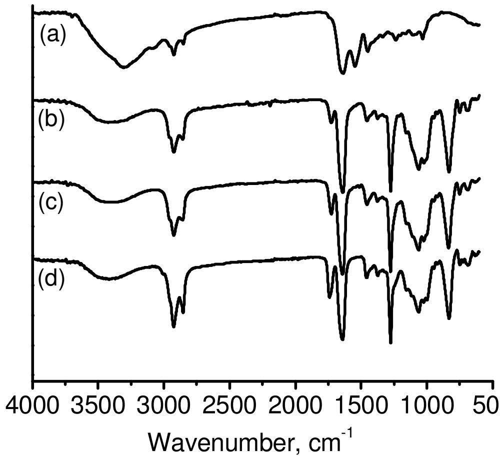


Fig. 8.27. FT-IR spectra of samples: (a) unfinished; (b) finished with AC408, AC310 and PU410 basecoat; (c) finished with AC33 basecoat; (d) final nitrocellulose dressing EMAL

Spectra of finished leather have the following characteristics compared to those of untreated samples:

- The intense band at 1642-1649 cm^{-1}, characteristic for C=O and –OC-N groups in the spectrum of untreated leather, are absent in the spectra of treated leather; the latter has a peak ar 1721-1725 cm^{-1} corresponding to C=O stretching in saturated ester in the polyurethane dressing.
- The two peaks at 1240 and 1165 cm^{-1}, attributed to the couplings of C-O and C-C stretches and to stretching vibration of C-O-C of acrylates, are find in the spectra of treated leather.
- The broad band in the region 3200-3500 cm^{-1}, assigned to hydroxyl and amide groups, is diminished in the case of the treated leather samples in comparison of the untreated sample. [327-330]

Differences between the IR spectra of treated and untreated leather may be considered as a proof for chemical bonds between dressing components and basecoat. Consequently the binder not only covers the leather surface, but it is bound to the basecoat, thus ensuring coating resistance. [331-333]

The polyurethane binder containing the prepared emulsion is also chemically bound to the basecoat. Thus, the band at 1640 cm^{-1} characteristic for C=O and –OC-N groups in the spectrum of the emulsion film is absent from the spectrum of finished leather samples. [334, 335]

Conclusions

▪ FT-IR spectra of leather samples finished both with acrylic and nitrocellulose binder do not have any of the bands characteristic for unfinished leather, which proves that the entire surface was coated by the films formed by the dressings used.

- The acrylic dressing is chemically bound to the basecoat, which causes an increased adherence compared to the nitrocellulose one.

8.5. Biological Characterization of Obtained Leather Assortments

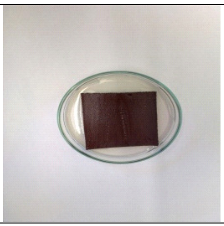
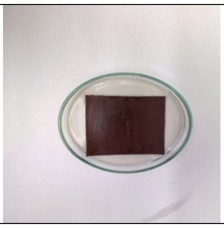
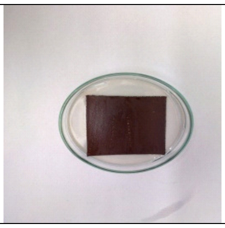
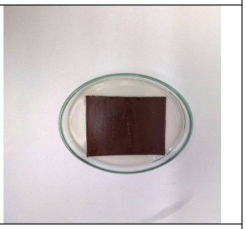
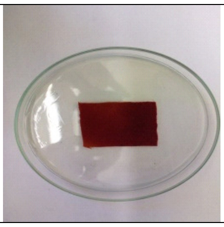
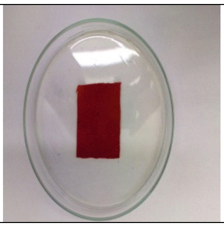
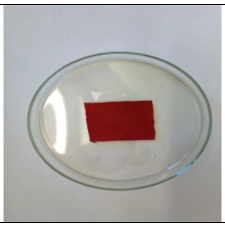
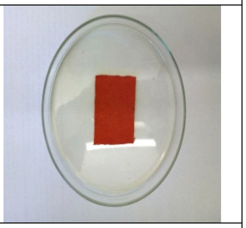
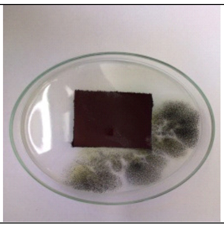
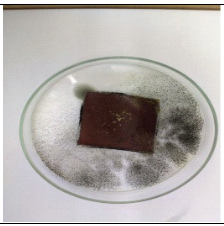
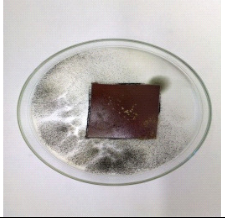
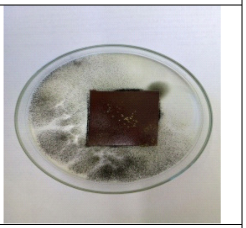
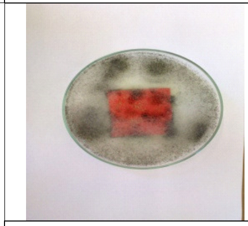
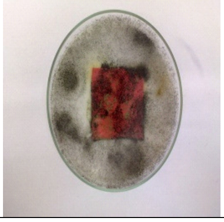
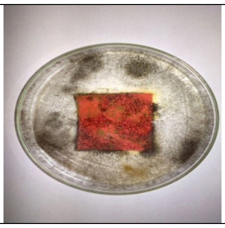
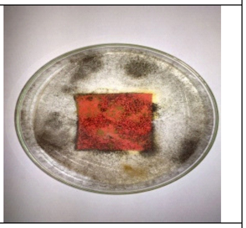
The samples treated with antifungal products AF-C-1 and AF-C-2 used in varied proportions in the final dressing, as well as the untreated ones were inoculated with *Aspergillus niger* spores. The goal was to monitor the influence of the treatment applied to the sample on mold growth through the mold resistance under simulated contamination, according to STAS 12697/A 9:2008 „Finished leathers. Mold resistance testing".

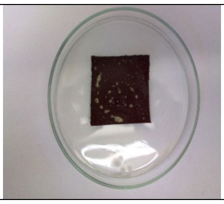
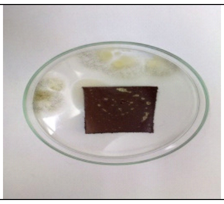
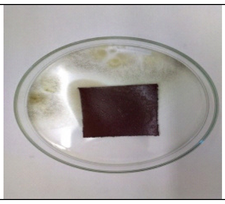
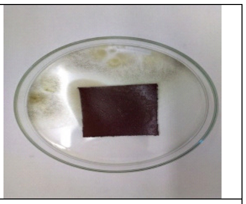
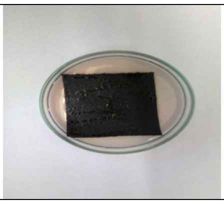
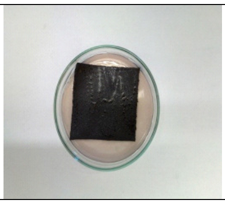
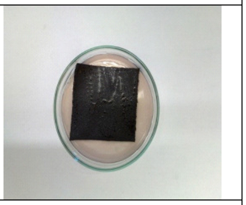
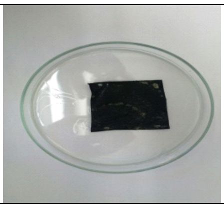
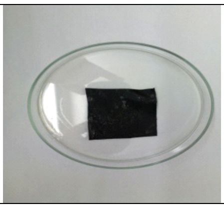
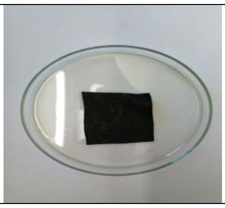
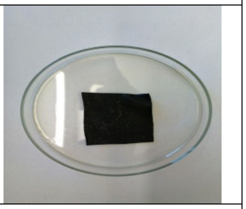
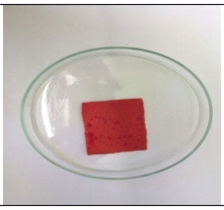
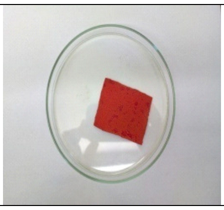
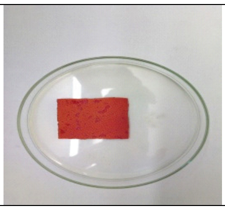
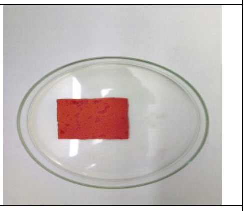
Aspergillus niger spores were inoculated in three areas: right side, center and left side of the sample, according to the procedure specified in ASTM D 4576-86 „Standard test method for mold growth resistance of blue stock (leather)". Incubation was 28 days, but observations were also performed at 7, 14 and 21 days.

Aspergillus niger strain development was assessed by ranking: 0 – absence of stems and a strong fungitoxic effect, 5 – an almost non-existent effect (the mold covers the entire surface of the specimen).

Mold development on leather specimens, and macroscopic images of samples from table 7.8 treated with AF-C-1 and AF-C-2 after 7, 14, 21 and 28 days from treatment, are presented in table 8.20. The numbers under the images are the marks given according to the standard.

Table 8.20. Macroscopic images of samples treated with AF-C-1 and AF-C-2 products after 7, 14, 21 and 28 days

Sample/day	7	14	21	28
AF 1				
	0	0	0	0
AF 7				
	0	0	0	0
AF 8				
	0	2	2	3
AF 14				
	3	3	4	4

AF 17				
	0	1	1	2
AF 18				
	0	0	0	0
AF 19				
	1	1	1	2
AF 20				
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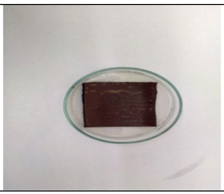
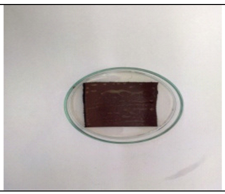
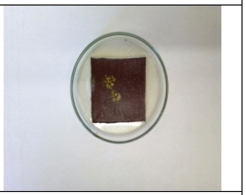
AF 21				
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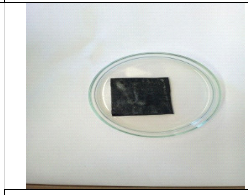
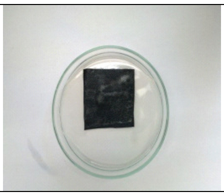
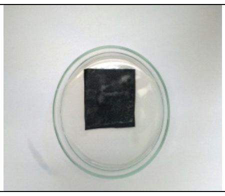
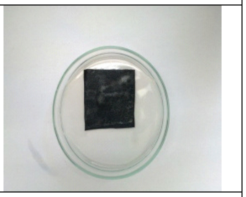
AF 22				
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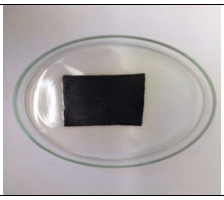
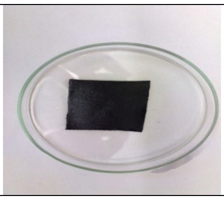
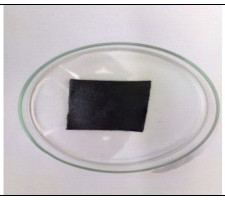
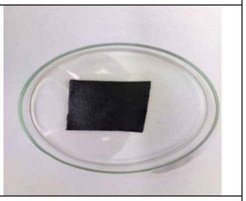
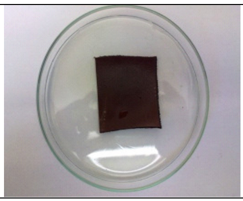
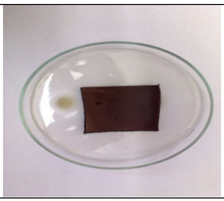
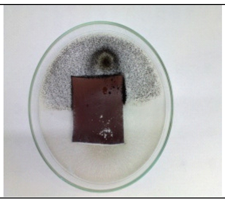
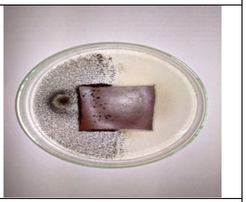
AF 23				
	0	0	0	0
AF 26				
	0	0	2	2

The AF 1-AF 7 assortments treated on the grain or velvet side with AF-C-1 as such (film-coated and uncoated brown and black Box leathers), AF 18 (film-coated black Box leather) and AF 20 (uncoated brown Nappa) treated with Roda pur 5011 containing 40% of each antifungal product, as well as AF 22 (film-coated black Box leather) and AF 23 (uncoated grain treated black Box leather) treated with Roda pur 5011 containing 75% AF-C-1 do not develop mold in the time specified in standard, therefore have maximum resistance.

Leather assortments AF 17 (film-coated brown Box leather) and AF 19 (uncoated velvet side treated black Box) treated with Roda pur containing 40% of each antifungal product, AF 21 (film-coated brown Box leather) treated with Roda pur 5011 containing 75% AF-C-1 and AF 26 (uncoated brown Box) grain treated with Roda pur 5011 containing 65% AF-C-1also have good mold resistance – mark 2 after 28 days. Therefore, for maximum efficiency, the concentration of the antifungal product must not decrease below 65%.

The above show that the most effective antifungal product is the one based on coriander oil, AF-C-1. The prepared antifungal and antibacterial products made of natural components (beeswax, lanolin and coriander or cedar essential oil) improve resistance of finished leather to biological factors (fungi) and can complement the treatment with biocides used for natural leather (based on benzothiazole and sulfone derivatives, beta-naphtol, chloro-methylphenol, organic compounds of sulfur, which are toxic for humans and the environment), within the wet processing operations.

Treatment with AF-C-1 product can be repeated from time to time, by spraying or dabbing. Using the products as such, for maximum antifungal effect, mattifies the film and reduces resistance to abrasion.

Conclusions

- The most resistant to mold are leather samples AF 1- AF 7 treated with AF-C-1 as such, with Roda pur 5011 containing 75% or 65% AF-C-1, as well as those treated with 80% mixture of the two antifungal products in equal proportions; the samples do not develop fungi for 28 days (mark 0).
- Product AF-C-2 is less efficient, and leather samples treated with the product AF-C-2 as such received marks ranging between 3 and 5 after 28 days (AF 8-AF 14).
- Products, compatible with the materials used in the final dressing, can be used in surface treatment of finished leather and leather products in the final dressing composition.
- Product AF-C-1 can be used as such in surface finishing of buffed bovine hides such as suede, buffo or nubuck to obtain a fatty/waxy feel and a better resistance to fungi of the dermal substrate.

8.6. Characterization of fragrant leather assortments

To monitor the fragrance effect and concentration of volatile perfume in the treated leathers, samples PP1-PP15 in table 7.9 were tested using the sensory test.

The most fragrant leathers are samples PP 5, PP 10 and PP 15, treated with products as such. Of these, PP 5, treated with product P-LP-1, has the most intense fragrance, and its effect is preserved for 15-20 days.

The fragrance effect of product P-LP-1, with 30% lavender essential oil and 30% orange essential oil, is stronger than that of products with lower amounts of oils, namely P-LP-2 (containing 20% lavender essential oil and 20% orange essential oil) and P-LP-3 (with 10% lavender essential oil and 10% orange essential oil).

Samples PP 1 – PP 4 treated with product P-LP-1 are more fragrant than PP 6 – PP 9 or PP 11 – PP 14, for which the proportions of fragrance product applied on the surface of finished leather were similar.

Conclusions

- Samples PP 5, PP 10 and PP 15, treated with fragrance products as such, are the most fragrant, and of these, sample PP 5, treated with P-LP-1, the effect lasting for 15-20 days.
- The fragrance effect and persistence decrease when reducing the percentage of natural oils in the final dressing composition.
- Products can be used as such in surface finishing of sheepskins with buffed grain to obtain a waxy feel and a fragrant effect of the dermal substrate.
- Treatment using these products can be repeated from time to time by spraying or dabbing. The products can be used to treat film-coated leathers in proportion of 50-80% in the composition of the polyurethane final dressing.
- Using fragrance products based on vegetable extracts with insecticidal action (lavender, citrus) in the leather and fur finishing process can lead to obtaining garments with durable fragrance and to the biological protection of garments during storage.

8.7. Colorimetric characterization of leather assortments

In the CIE L*a*b* space used in colorimetric analysis by reflection, the tint (represented by fundamental colours – red, green, yellow and blue), brightness or clarity (represented by the chromatic stimulus varying from black to white) and saturation (purity of colour) are expressed according to three coordinates: L*, a* and b*. On the X axis, a* parameter has values between red ($a^* > 0$) and green ($a^* < 0$) stimuli, on the Y axis, b* parameter varies between yellow ($b^* > 0$) and blue ($b^* < 0$) stimuli, and L* parameter, on polar Z axis, represents brightness (grey axis), varying between white and black. [336-340] The colour difference parameters of the analyzed (P) and reference (R) samples are expressed by the following equations:

$$\Delta a^* = a^*_P - a^*_R \qquad (8.1)$$

$$\Delta b^* = b^*_P - b^*_R \qquad (8.2)$$

$$\Delta L^* = L^*_P - L^*_R \qquad (8.3)$$

Based on these equations, the following parameters can be calculated:

- chromatic shifting, through the relation: $\Delta E^* = [\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}]^{1/2}$ (8.4)
- saturation or purity difference, using the relation: $\Delta C^* = [a^{*}_P{}^2 + b^{*}_P{}^2]^{1/2} - [b^{*}_R{}^2 + L^{*}_R{}^2]^{1/2}$ (8.5)
- and tint difference, through the relation: $\Delta H^* = [\Delta E^{*2} - \Delta L^{*2} - \Delta C^{*2}]^{1/2}$ (8.6)

Colorimetric measurements were performed using a MINOLTA spectrophotometer (CM 2002), with light impulses from a xenon lamp with 0.8 cm aperture. Light reflection is focused on a silicon photo diode with wavelengths between 400 and 700 nm (10 nm steps) and L*a*b* values (chromatic coordinates: brightness, red/green and yellow/blue).

Finished leathers were artificially aged and tested according to the CIE LAB system.

Chromatic characteristics of natural grain Box assortments (variants F1, F3, F5, F11, F13, F15, F21, F23 and F25 for finishing and variants FN, FA and FP for final dressing) non-aged and aged using the methods specified in section 8.2.2, plus those aged in artificial light (UV) for 7 days – IUV obtained using the prepared pigment pastes are given in tables 8.21-8.25.

Table 8.21. Values of colorimetric parameters for finished unaged reddish brown, ochre yellow and black natural grain box leather samples

Sample	Technological variant	CIE L*	CIE *	CIE b*	CIE C*	CIE H*
CL 1	F1, FN	42.35	22.51	23.69	32.68	46.46
CL 2	F3, FN	42.64	22.58	23.96	32.92	46.70
CL 3	F5, FN	42.39	21.80	22.70	31.47	46.16
CL 4	F1, FA	42.58	23.09	24.46	33.63	46.65
CL 5	F3, FA	43.09	23.33	24.99	34.19	46.96
CL 6	F5, FA	42.76	22.81	23.87	33.02	46.3
CL 7	F1, FP	41.86	21.31	23.44	31.68	47.72
CL 8	F3, FP	42.17	21.43	23.57	31.85	47.72
CL 9	F5, FP	42.7	21.43	23.33	31.68	47.42
CL 10	F11, FN	35.23	21.40	13.79	25.46	32.80
CL 11	F13, FN	35.33	22.01	14.31	26.25	33.04
CL 12	F15, FN	35.64	21.45	13.71	25.45	32.59
CL 13	F11, FA	34.71	21.93	14.01	26.03	32.56
CL 14	F13, FA	34.59	22.84	14.72	27.17	32.80
CL 15	F15, FA	35.26	21.53	13.65	25.49	32.38
CL 16	F11, FP	34.36	21.23	13.56	25.19	32.56
CL 17	F13, FP	34.42	21.79	14.00	25.90	32.73
CL 18	F15, FP	34.74	20.86	13.34	24.76	32.59
CL 19	F21, FN	25.05	0.23	-0.60	0.65	290.55
CL 20	F23, FN	24.65	0.20	-0.69	0.71	286.47
CL 21	F25, FN	25.47	0.23	-0.51	0.55	294.24
CL 22	F21, FA	25.14	0.16	-0.65	0.67	283.97
CL 23	F23, FA	24.48	0.17	-0.69	0.71	284.08
CL 24	F25, FA	25.16	0.17	-0.64	0.66	285.2
CL 25	F21, FP	24.94	0.21	-0.57	0.61	290.67
CL 26	F23, FP	24.70	0.21	-0.70	0.73	286.32
CL 27	F25, FP	25.25	0.13	-0.54	0.56	284.01

Variation of colorimetric parameters for finished natural grain box leather samples CL 1-CL 9 aged using IT1, IT2, IL and IUV methods is shown in table 8.26.

Table 8.26. Variation of colorimetric parameters for finished aged reddish brown, ochre yellow and black natural grain box leather samples using IT1, IT2, IL and IUV methods

Sample	MI	ΔL*	Δa*	Δb*	ΔE*
CL 1	IT1	0.30	0.52	0.39	0.72
	IT2	0.32	0.35	0.46	0.66
	IL	0.31	-0.45	-0.73	0.91
	IUV	0.86	-0.09	0.15	0.88
CL 2	IT1	0.13	0.25	0.29	0.40
	IT2	0.26	-0.05	0.07	0.27
	IL	0.61	-0.41	-0.06	0.74
	IUV	0.29	-0.20	-0.02	0.31
CL 3	IT1	-0.29	-0.01	-0.06	0.30
	IT2	-0.29	-0.35	-0.45	0.64
	IL	-0.36	-0.83	-0.89	1.27
	IUV	-0.05	-0.20	0.02	0.21
CL 4	IT1	0.24	0.11	0.38	0.46
	IT2	0.36	-0.18	0.21	0.45
	IL	-0.15	-0.29	-0.39	0.51
	IUV	1.08	0.37	1.03	1.54
CL 5	IT1	-0.20	0.08	-0.10	0.24
	IT2	-0.12	0.20	0.07	0.24
	IL	-0.09	0.13	0.07	0.17
	IUV	0.02	-0.09	-0.2	0.22
CL 6	IT1	-0.10	0.23	0.88	0.92
	IT2	0.44	-0.19	0.76	0.90
	IL	-0.14	-0.43	-0.17	0.48
	IUV	0.18	0.05	-0.49	0.54
CL 7	IT1	0.65	0.53	0.75	1.13
	IT2	0.74	0.37	0.94	1.25
	IL	0.26	-0.25	-0.36	0.51
	IUV	0.38	-0.07	0.24	1.18
CL 8	IT1	-0.01	0.14	0.08	0.16
	IT2	0.08	0.17	0.26	0.32
	IL	0.41	0.28	0.53	0.73
	IUV	1.15	0.24	0.40	0.45
CL 9	IT1	-0.21	0.06	-0.20	0.30
	IT2	-0.19	-0.09	0.08	0.22
	IL	0.29	0.39	0.62	0.79
	IUV	0.10	-0.02	0.25	0.27

Parameters of colour difference between aged samples using IT1, IT2, IL and IUV methods (T) and unaged ones (R) were calculated using the following equations:

$$\Delta a^* = a^*_T - a^*_R;\ \Delta b^* = b^*_T - b^*_R;\ \Delta L^* = L^*_T - L^*_R \quad (8.7)$$

Chromatic deviation or shift ΔE* was calculated from Δa*, Δb* and ΔL* parameters, with equation:

$$\Delta E^* = [\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}]^{1/2} \quad (8.8)$$

The first group of samples was finished using reddish brown pastes (CL 1-CL 9) containing castor oil (CL 1, CL 4 and CL 7), flax oil (CL 2, CL 5 and CL 8) or poppy seed oil (CL 3, CL 6 and CL 9) as plasticizers and nitrocellulose (CL 1-CL 3), acrylic (CL 4-CL 6) or polyurethane (CL 7-CL 9) dressing.

After irradiation and thermal treatment, samples CL 7 and CL 8 have positive values for brightness ($\Delta L^*>0$), i.e. they have lighter (brighter) colours than sample CL 9 that has a negative value for brightness ($\Delta L^*<0$), indicating the positive influence of poppy seed oil on the colour. Samples CL 4-CL 9 aged by IL and IUV methods have ΔL* parameters lower than CL 1-CL 3, indicating the positive influence of acrylic and polyurethane dressing on fastness to light of leathers compared to the nitrocellulose dressing. ΔE* colour difference is higher for leather sample CL 1 than for samples CL 2 and CL 3 aged using IT1 and IUV methods.

Sample CL 4 has a higher colour difference than CL 5 and CL 6 aged using IUV method; likewise, CL 7 has a ΔE* value higher than CL 8 and CL 9 similarly aged.

The second group of samples was finished using ochre yellow pigment pastes (CL 10-CL 18) containing the same plasticizers: castor oil (samples CL 10, CL 13 and CL 16), flax oil (samples CL 11, CL 14 and CL 17) or poppy seed oil (samples CL 12, CL 15 and CL 18) and nitrocellulose (samples CL 10-CL 12), acrylic (samples CL 13-CL 15) or polyurethane (samples CL 16-CL 18) dressing. Samples CL 16-CL 18 aged using IT1 and IT2 methods have negative values for brightness (ΔL*<0), therefore are darker than CL 13-CL 15, with positive values, except for sample CL 14, with ΔL*<0, aged using IT2 method. Samples CL 10-CL 13 have positive values for brightness, i.e. become brighter than the thermally aged ones in series II. Therefore, leathers finished with acrylic and polyurethane dressing are more resistant to ageing than those finished with nitrocellulose dressing. Samples CL 13-CL 18 aged using IL and IUV methods have lower values of ΔL* parameter compared to C 10-C 12 and are darker, which indicates a positive influence of the acrylic and polyurethane dressing on fastness to light of leathers finished compared to nitrocellulose dressing. The lower values of ΔL* also indicate the positive influence of plasticizer poppy seed oil used on resistance to yellowing.

The third group of samples was finished using black pigment pastes (CL 19-CL 27) containing the same plasticizers: castor oil (CL 19, CL 22 and CL 25), flax oil (CL 20, CL 23 and CL 26) or poppy seed oil (CL 21, CL 24 and CL 27) and nitrocellulose (CL 19-CL 21), acrylic (CL 22-CL 24) or polyurethane (CL 25-CL 27) dressing. Samples CL 22-CL 27 aged using IL and IUV methods have ΔL* lower than C 19-C 21, and therefore are darker. Samples CL 26 and CL 27 aged using IL and IUV methods have negative values for brightness, i.e. are darker compared to sample CL 25.

Leather samples finished with acrylic and polyurethane dressing and aged using the specified methods have lower ΔL* values and change their colour less compared to those finished with nitrocellulose dressing.

Conclusions

- Thermal and artificial light ageing change colorimetric characteristics (CIE L*a*b*) compared to those of unaged samples, depending on the ageing method, leather assortment and type of final dressing.
- The highest values for fastness to light after artificial light ageing were those of leathers finished with polyurethane or acrylic dressing and the lowest, those finished with nitrocellulose dressing.
- Flax and poppy seed oils, used as plasticizers, improve resistance to yellowing of coating films.

9. FINAL CONCLUSIONS

The aim of the thesis is to obtain and characterize ecologic film-forming disperse systems to be used as auxiliaries in various stages of leather finishing: pigment pastes, wax emulsions, bactericidal, fungicidal and fragrance products, to establish leather finishing technologies (cattle, sheep, goats) for Box and Nappa assortments using the developed auxiliary materials in the disperse finishing systems and to characterize film-coated leather assortments.

To **prepare the pigment pastes**, red, yellow or black iron oxide pigments were used – admitted by the legislation in force, Bindex BRILLANT acrylic binder as carrier resin – also having protective colloid properties, lauryl alcohol ethoxylated with 7 moles of ethylene oxide – fully biodegradable – as a dispersing agent and stabilizer and natural oils as plasticizers: castor oil, flax oil or poppy seed oil. Finely ground powder particles have diameters of 0.6-1.1μm and the obtained pastes have the appearance of homogeneous fluids with pigment particles dispersed uniformly.

Wax emulsions were **obtained** using a mixture of beeswax, lanolin and triethanolamine monostearate as dispersed phase in the ratio 1/3/7 and the same tensioactive compound as for pigment pastes as emulsifier. All emulsions are white fluids, with homogeneous appearance.

Products with antifungal and antibacterial properties contain coriander or cedar essential oil, emulsion of beeswax and lanolin mixture in a 1/3 ratio, stabilized with ethoxylated lauryl alcohol and ethyl alcohol, homogeneous yellowish white fluids, as fungicidal and bactericidal compounds. The composition of oils was determined by gas chromatography combined with mass spectroscopy.

Products with fragrance properties are aqueous emulsions of lavender and orange essential oils mixtures in various ratios, ethyl alcohol and polyethylene glycol stabilized with ethoxylated lauryl alcohol, with homogeneous yellowish-white appearance. The oils were analyzed by GC-MS.

Characterization of the prepared products was performed by methods specific to each class.

Film-forming aqueous binder dispersions were **characterized** by dry substance, density, viscosity and residual monomer content, and films obtained thereof by physico-chemical properties, mechanical – resistance to elongation, tensile strength and repeated bending, resistance to pressing, shrinkage index, scanning electron microscopy and FT-IR.

The characterization of oils used as plasticisers for coating films involved determining the fat content, pH, relative viscosity, and iodine, acidity, and saponification indices.

Prepared **pigment pastes were characterized** by dry substance, pH, relative viscosity, coating power, stationary and dynamic rheological behavior, optical microscopy and FT-IR. They are concentrated pastes with pH of 1/10solution of 6.5-8.0, as the imported ones, 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. Optical analysis shows that those based on red and yellow iron oxide have similar colors to those of imported ones used as control. FT-IR spectra of the films obtained from pastes show characteristic bands of the acrylic binder used. The film made from the paste containing yellow iron oxide shows that it binds to the acrylic binder. Spectra of films made from control pastes Casicolor Brown R and Casicolor Ochre demonstrate that the binder in the pastes is also acrylic. In contrast, the spectrum of the film obtained from Casicolor Black paste is completely different from those of other pastes, therefore the binder is different.

Wax emulsions were characterized by dry substance, pH, density, relative and capillary viscosity, and optical microscopy, and films obtained thereof by FT-IR. Emulsions are of O/W type, with relatively evenly distributed drops within the entire mass and sizes of 4.1 to 5.6 μm for AGE 7 and 5.6 μm for control. FT-IR spectrum of the film from AGE 7 emulsion includes bands of components and a broad band at about 3385 cm^{-1} due to hydrogen bonds formed by water remaining in the film.

The composition of the essential oils used in the preparation of antifungal, antibacterial and fragrance products was determined by GC-MS.

Antifungal, antibacterial products and **fragrance products** were characterized by dry substance, pH and density, and the film obtained after evaporation of the dispersing medium by FT-IR. Spectra contain bands of components with different intensities, determined by the proportions in which they were used.

Coating films resulting from the evaporation of dispersion medium were characterized by resistance to temperature by DTA. The characteristic parameters for thermal degradation show that the films resulting from prepared pigment pastes are more resistant thermally than those containing the control pigment pastes. All films have sufficient thermal resistance to protect the finished leather.

Finishing technologies by coating were established for natural grain Box bovine leather and Nappa sheep and goat skin assortments in reddish brown, ochre yellow and black for shoes, clothing, leather goods, upholstery, book covers and decorative articles.

The framework dry finishing technology was developed **for natural grain black** and **coloured Box bovine leather assortments** for the basecoat using pigment pastes and for the final dressing using wax emulsions.

The framework dry finishing technology was developed for black and coloured Nappa sheep and goat skins using the same components in the basecoat and final dressing.

Antifungal products based on coriander and cedar oil were tested. Samples additionally treated with polyurethane final dressing in the composition of which antifungal products were used in different proportions were inoculated with *Aspergillus niger* spores, according to STAS 12697/A 91:2008, and mold growth under simulated contamination conditions was measured.

Fragrance products based on essential oils of lavender and orange were tested by sensory test, studying the effect of fragrance and concentration of perfume volatilized from the treated leathers. The samples further treated with a final polyurethane dressing contain fragrance products in different proportions.

Finished leather assortments were characterized by chemical analysis, mechanical methods, optical microscopy, SEM, FT-IR, mold resistance, fragrance effect and by CIE L*a*b* colorimetric method.

Chemical characteristics of the uncoated leathers used to obtain natural grain Box bovine and Nappa sheep and goat assortments (brown, yellow and black), determined in accordance with standards ST 1619:1994 and EN ISO 14931:2005 are appropriate.

The **mechanical characteristics** were determined for both finished leathers and for those aged by exposure to heat (50 and 70°C) and by artificial light according to ISO 17228/2006 and they are appropriate.

Leather samples finished using prepared pigment pastes and waxes – natural grain Box and Nappa – are within the limits specified in standards.

After **thermal ageing**, mechanical characteristics have lower values than those of unaged leather samples, depending on the temperature of the heat treatment, leather assortment and the type of final dressing. The highest light fastness after **ageing by artificial light** is that of leathers finished with polyurethane or acrylic dressing, and the smallest ones, for those finished with nitrocellulose dressing.

Optical images obtained for natural grain Box bovine leather finished with red, yellow and black pigment pastes and waxes show films uniformly spread on the dermis.

Scanning electron microscopy images obtained for similarly finished natural grain Box bovine leather show smooth and uniform films.

FT-IR spectra of the leather samples finished with acrylic, polyurethane and nitrocellulose dressing do not have characteristic bands for unfinished leather, therefore the surfaces were fully covered by dressing films. The broad band in the region of 3200-3500 cm^{-1}, attributed to hydroxyl and amide groups is diminished in the spectra of samples finished with acrylic dressing compared to untreated samples, demonstrating that it binds chemically to the basecoat. The same is shown by the disappearance of the band at about 1640 cm^{-1} characteristic of the groups C=O and –OC-N in the polyurethane film spectrum for finished leather samples.

The product based on coriander oil as such, the one containing 75 or 65% of the product, as well as the one containing 80% mixture of coriander and cedar oil in the ratio 1/1have maximum **fungitoxic effect** – do not develop fungi during 28 days. The one based on cedar oil is less effective, and treatment using the product as such develops spores even on the 7th day. The product made from coriander oil can be used as such for surface finishing of bovine suede, buffo or nubuck leather when a better resistance to fungi and oily/waxy handle is desired.

The most powerful and persistent fragrance effect, determined by sensory test, is that of product containing a mixture of 60% lavender and orange essential oils 1/1. It can be used as such for the surface finishing of suede sheep skin, for a waxy handle and fragrance effect for the dermis. Using fragrance products based on plant extracts with insecticidal action (lavender, citrus) in the leather and fur finishing process leads to garments with long-lasting perfume and biological protection during storage.

After **thermal and artificial light aging**, the colorimetric characteristics (CIE L*a*b*) change, depending on the temperature of the heat treatment and UV light, leather assortment, and type of final dressing. The highest resistance to light after **aging under the influence of artificial light** has the leathers finished with polyurethane or acrylic dressing in comparison with those finished with nitrocellulose dressing.

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