Characterization of Coating Aqueous Disperse Systems Used in Natural Leather Finishing

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In the composition of aqueous disperse systems for natural leather finishing, the following auxiliary materials are used: pigments, binders, dyes, waxes, preservatives, plasticizers, thickeners, fillers, penetrators, etc. Binders used in the composition of aqueous systems for natural leather finishing are of acrylic, polyurethane, protein and butadiene type and are applied in various finish layers (ground coat, starch) to obtain the desired finish. This paper presents the chemical and physico-mechanical characterization of disperse aqueous coating systems used in natural leather finishing, made by foreign and Romanian companies in order to establish optimal finishing technologies. New materials were tested for natural leather finishing, with the aim of replacing final nitrocellulose dressings with dressings based on acrylic aqueous dispersions, without toxic solvents and to replace protein binders from pigment pastes, which require crosslinking with formaldehyde (toxic), with acrylic binders. To assess the physico-chemical characteristics of coating aqueous dispersions and physico-mechanical characteristics of films obtained from different types of binders used as such or in mixtures in certain proportions, analytical methods were used.

Keywords: leather finishing, pigments, acrylic binders, polyurethane binders, protein binders, nitrocellulose emulsions, epoxy resins

Leather finishing has the purpose of enhancing, colouring, obtaining lustre and pleasant feel, covering surface defects and the formation of a surface layer that protects the leather during wear and responds to fashion trends.

In the composition of disperse finishing systems the following auxiliary materials are used: pigments, binders, dyes, waxes, preservatives, plasticizers, thickeners, fillers, penetrating agents.

Binders are film-forming macromolecular compounds, giving finished leather a film-like coating, flexibility, adhesion and resistance to wear and to external factors. Binders used in the composition of natural leather finishing systems are of acrylic, polyurethane, protein and butadiene type, with different particle sizes and degrees of hardness. Depending on particle sizes and degrees of hardness, these binders are used in various layers of finish (ground coat, starch) to obtain the desired finish (glossy, matte, with touch) and corresponding physical and mechanical characteristics (tensile strength and tear strength, resistance to elongation, cracking, wet and dry friction, bending, light, etc.).

Natural skins (cattle, sheep, goats) are finished by coating with coating aqueous dispersions consisting of 2-3 acrylic, polyurethane, casein or butadiene polymers in which pigments, waxes, metal complex dyes, fillers, penetrating agents, etc. are embedded for ground layers, and then applying the final nitrocellulose or acrylic starch emulsions (fixing).

These dispersions and emulsions are applied to the leather surface by spraying in several layers, forming thin, adherent and compact films, which are resistant in terms of physico-mechanical characteristics (elongation, tensile strength, tear strength, repeated bending, wet and dry friction, etc.).

Spraying is carried out manually, using special guns fitted with nozzles of 0.8-1.0 mm at a pressure of 2-3 atmospheres, from a distance of 30-50 cm and an angle of 35-45°, or using an installation with continuous supply equipped with batteries of 12 guns with photocells allowing nozzle opening when leathers pass by the latter.

Experimental part

Within experiments conducted, new materials were tested for natural leather finishing, with the aim of replacing final nitrocellulose dressings with dressings based on acrylic aqueous dispersions, without toxic solvents and to replace protein binders from pigment pastes, which require crosslinking with formaldehyde, with acrylic binders.

- Acrylic, polyurethane, protein and nitrocellulose type binders (made by foreign companies) were subjected to physico-chemical characterization, used in the composition of coating disperse systems for finishing and in the composition of pigment pastes as follows:

- binder based on acrylic copolymer used in natural leather finishing solution, in combination with acrylic and/or polyurethane binders, protein binders, pigment pastes, metal complex dyes, waxes, penetration agents, etc. (Vecosol Binder AC 310, VECO, Italy), marked **AC-310**;

- binder based on acrylic copolymer used in natural leather finishing solution, in combination with acrylic and/or polyurethane binders, protein binders, pigment pastes, metal complex dyes, waxes, penetration agents, etc. (Vecosol Binder AC 408, VECO, Italy), marked **AC-408**;

- polyurethane binder used in natural leather finishing solution, in combination with acrylic and/or protein binders, pigment pastes, metal complex dyes, waxes, penetration agents, etc. (Vecosol Binder PU 410, VECO, Italy), marked **PU-410**;

- nitrocellulose binder used as fixing agent (final starch) for finishes applied to natural leathers (Vecoemul AL, VECO, Italy), marked **EM-AL**;

- binder based on acrylic copolymer used in natural leather finishing solution, in combination with acrylic and/

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or polyurethane binders, protein binders, pigment pastes, metal complex dyes, waxes, penetration agents, etc. (Corial grund IF, BASF, Germany), marked **AC–IF**;

- polyurethane binder used in natural leather finishing solution, in combination with acrylic and/or protein binders, pigment pastes, metal complex dyes, waxes, penetration agents, etc. (Astacin finish PUM, BASF, Germany), marked **PU-PUM**;

- ethoxylated casein-based binder used in natural leather finishing solution, in combination with acrylic and/or polyurethane binders, pigment pastes, metal complex dyes, waxes, penetration agents, etc. (Luron glanz E, BASF, Germany), marked **CA-E**;

- binder based on acrylic copolymer used in dispersing and preparing pigment pastes from inorganic and/or organic pigments and emulsifying agents (sulphated castor oil) etc.; the acrylic copolymer replaces protein binders in the composition of pigment pastes, thus eliminating crosslinking with formaldehyde, which is toxic (Acrylic Bindex, PEBEO, France), marked **AC-30**;

- binder based on acrylic copolymer used in dispersing and preparing pigment pastes from inorganic and/or organic pigments and emulsifying agents (sulphated castor oil) etc.; the acrylic copolymer replaces protein binders in the composition of pigment pastes, thus eliminating crosslinking with formaldehyde, which is toxic (Acrylic Bindex, PEBEO, France), marked **AC-50**.

New Romanian products based on acrylic copolymers in aqueous dispersion (developed at ICPAO, Medias) were subject to physico-chemical analysis:

- binder based on acrylic copolymer used in natural leather finishing solution, in combination with pigment pastes, metal complex dyes, waxes, penetration agents, etc. It is an aqueous dispersion for finishing based on acrylic copolymers which are self-crosslinkable with a monomer composition containing butyl acrylate, methyl methylacrylate, acrylic acid, N-methylolacrylamide, in various proportions. Copolymerization was done in emulsion with potassium persulphate as initiating agent and aryl alkyl ether sulphate ionic emulsifiers, which would ensure emulsion stability and finally, the product was conditioned by a *p*H correction with trisodium phosphate solution. The polymerization technology is semi-continuous on batches, by prepolymerization of a quota of monomer emulsion, followed by continuous batching for 2.5-3 h. The acrylic binder ensures film formation for leather finishing and gives aesthetic and functional properties to finished leather semi-products (Medacril EFP33, marked **AC-33)**;

- Binder based on acrylic copolymer with epoxy resin addition used as fixing agent (final starch) for finishing natural leathers, replacing fixation with nitrocellulose aqueous emulsions and ensuring highly resistant finishes to wet and dry friction. It is a water soluble acrylic copolymer self-crosslinkable with epoxy resin addition, used as fixing agent. The monomer composition made of butyl acrylate, acrylonitrile, N-methylolacrylamide and epoxy resin is copolymerized in the presence of potassium persulphate and aryl alkyl ether sulphate ionic emulsifier at temperatures ranging between 85 and 92°C. The polymerization technology is semi-continuous on batches, by prepolymerization of a quota of monomer emulsion, followed by continuous batching (Medacril EFP34, marked **AC-34)**.

Aqueous dispersions of acrylic copolymers were prepared using the technique of semi-continuous copolymerization with prepolymerization and batching in monomer emulsion.

The coatings obtained from acrylic and polyurethane binders presented above, as well as coatings obtained from acrylic, polyurethane and protein binder blends (from BASF) were subject to physico-mechanical analysis, used in various proportions in the composition of film-forming finishing disperse systems, namely:

- AC-IF 45% +PU-PUM 45%+CA-E 10 % ;
- AC-IF 40% +PU-PUM 40%+CA-E 20 % ;
- AC-IF 35% +PU-PUM 35%+CA-E 30 % .

Pilot experiments were conducted to establish optimal leather finishing technologies in various assortments.

Results and discussions

In order to assess characteristics of film-forming aqueous dispersions and obtained coatings analytical investigation methods were used.

Physico-chemical characteristics of film-forming aqueous dispersions tested and obtained coatings are given in table 1.

Graphical representations (figs. 1-10) of physical-mechanical characteristics (elongation at break, %, and tensile strength, N/mm^2) of binder coatings analyzed are given:

- Acrylic binders, Vecosol Binder AC 310, marked **AC-310** and Vecosol Binder AC 408, marked **AC-408,** form films with high resistance to water absorption and water solubility, for 24 h, after crosslinking at a temperature of 140–150^{0}C. It is recommended that these binders be used in ground layers, in combination with polyurethane binders (which provide finishing coatings with high resistance to low temperatures) and/or casein binders (which provide finishing coatings with high lustre).

- Polyurethane binders, Vecosol Binder PU 410, marked **PU-410** and Astacin finish PUM, marked **PU-PUM** form films with high resistance to water absorption and water solubility, for 24 h, after crosslinking at a temperature of 140–150^{0}C. It is recommended that these binders be used in ground layers, in combination with acrylic and/or casein binders.

- Acrylic binders, Medacril EFP33, marked **AC-33** and Medacril EFP34, marked **AC-34,** form films with high resistance to water absorption and water solubility, for 24 h, after crosslinking at a temperature of 140–150^{0}C.

- Binder **AC-33** is recommended to be used in ground layers in finishing natural leathers.

- Binder **AC-34,** based on acrylic copolymer with epoxy resin addition is recommended to be used as fixing agent (final starch) of finishes applied to natural leathers, replacing fixation with nitrocellulose aqueous emulsions and which ensure finishes with high resistance to dry and wet friction.

- Acrylic binders, Acrylic Bindex, marked **AC-30** and Acrylic Bindex, marked **AC-50** (PEBEO, France), due to determined physical-chemical characteristics, are recommended for dispersion and preparation of pigment pastes from inorganic and/or organic pigments and emulsifying agents (sulphated castor oil), etc.; these acrylic copolymers can replace protein binders in the composition of pigment pastes, thus eliminating crosslinking with formaldehyde, which is toxic.

- Physico-mechanical characteristics of coatings obtained from tested film-forming dispersions have values of 140.000- 250.000 flexions for resistance to repeated bending, values of 1.51-6.67 N/mm^2 for tensile strength and values of 768-1586 % for elongation at break. Acrylic binders AC-34, AC-408 and polyurethane binders PU- PUM, PU-410 have the highest values of physico-mechanical characteristics.

Characteristics of film-forming dispersions											
Characteristics	AC-310	AC-408	PU-410	NI –AL	AC-IF	PU-PUM	CA-E	AC-30	AC-50	AC-33	AC-34
Appearance	Homogen ous white emulsion	Homogen ous white emulsion	Homogen ous white emulsion	Homogen ous white emulsion	Homogen ous white emulsion	Homoge nous white emulsion	Homoge nous white emulsio n	Homoge nous white emulsio n	Homoge nous white paste	Homoge nous white emulsio n	Homoge nous white emulsio n
Dry substance (%)	34.40	39.92	34.24	16.08	39.42	41.66	15.58	30.24	48.80	40	39
Density (g/ml)	1.026	1.035	1.017	1.076	1.039	1.063	1.028	1.965	2.524	1.042	1.033
pH	6.0	6.0	5.5	5.5	6.0	7.0	7.5	6.5	6.5	4.5	5.5
Ford Viscosity Φ4 (sec)	12	14	16	125	13.5	15	16,5	18	20	13	12
Hoppler Viscosity, cP	8.26	9.02	13.4	189.24	24.73	26.75	25.94	6.89	8.32	7.32	7.05
Residual Monomers (%)	0.81	0.78	0.68	0.78	0.82	0.73	0.62	0.68	0.79	0.78	0.72
Characteristics of binder coatings heat untreated											
Characteristics	AC-310	AC-408	PU-410	EM–AL	AC-IF	PU-PUM	CA-E	AC-30	AC-50	AC-33	AC-34
Appearance	Continuou s film, yellowish, soft	Continuous film, yellowish, soft	Continuous film, white, soft	Discontin uous film, yellowish	Continu ous film, yellowis h, soft	Continu ous film, yellowis h, soft	White film, brittle	Continu ous film, white, soft	Continu ous film, white, hard	Continu ous film, yellowis h, soft	Continu ous film, yellowis h, soft
Water absorption, 2h (%)	8.25	13.13	6.04	-	6.6	4.9	-	-	-	10.8	8.4
Water absorption, 24h (%)	40.21	51.76	13.87	-	38.2	35.3	-	-	-	25.26	41.30
Water solubility, 24h (%)	3.42	5.43	3.10	-	2.73	2.52	-	-	-	1.81	2.48
Characteristics of binder coatings crosslinked at 140 – 150°C											
Characteristics	AC-310	AC-408	PU-410	EM–AL	AC-IF	PU-PUM	CA-E	AC-30	AC-50	AC-33	AC-34
Water absorption, 2h (%)	4.35	5.94	3.20	-	3.49	2.16	-	-	-	4.09	1.99
Water absorption, 24h(%)	25.05	27.34	21.78	-	20.8	7.68	-	-	-	17.10	9.20
Water solubility, 24h (%)	0.04	0.08	0.06	-	0.04	0	-	-	-	0.03	0

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF FILM-FORMING AQUEOUS DISPERSIONS AND OBTAINED COATINGS, HEAT TREATED OR UNTREATED

Table 2
PHYSICO-MECHANICAL CHARACTERISTICS OF COATINGS OBTAINED FROM TESTED FILM-FORMING DISPERSIONS

Physical-mechanical characteristics of binder coatings											
Characteristics	AC-310	AC-408	PU-410	AC-IF	PU-PUM	AC-33	AC-34	AC-IF 45% + PU-PUM 45%+ CA-E 10 %	AC-IF 40% + PU-PUM 40%+ CA-E 20 %	AC-IF 35% + PU-PUM 35%+ CA-E 30 %	Standard method No.
Elongation (%) At break	1402	1586	990	894	772	1134	1384	866	828	768	SR EN ISO 3376: 2003
Tensile strength (N/mm^2)	1.58	4.62	6.67	2.13	5.82	1.51	4.34	4.54	4.45	3.27	SR EN ISO 3376: 2003
Resistance to repeated bending, (no. of flexions)	250.000	250.000	150.000	250.000	250.000	250.000	200.000	200.000	180.000	140.000	SR EN ISO 5402: 2003
Resistance to pressing, 120°C	Resistant at 100°C	Resistant at 110°C	Resistant at 120°C	Resistant at 120°C	Resistant at 120°C	Resistan t at 120°C	Resista nt at 120°C	Resista nt at 120°C	Resista nt at 120°C	Resista nt at 120°C	
Contractility index (%)	0	0	0	0	0	0	0	0	0	0	SR 5053: 1998

- Physico-mechanical characteristics (elongation at break, tensile strength, re resistance to repeated bending) of coatings obtained from acrylic, polyurethane and protein binder blends (from BASF), used in various proportions in the composition of finishing film-forming disperse systems, have higher values for variant AC-IF 45% + PU-PUM 45% + CA-E 10 %, in which the casein binder proportion is 10% in the binder blend, values which decrease in the variant

BINDER COATING AC-310
Sample a –elongation % break 1176; N break 1,49
Sample b –elongation % break 1628; N break 1,67

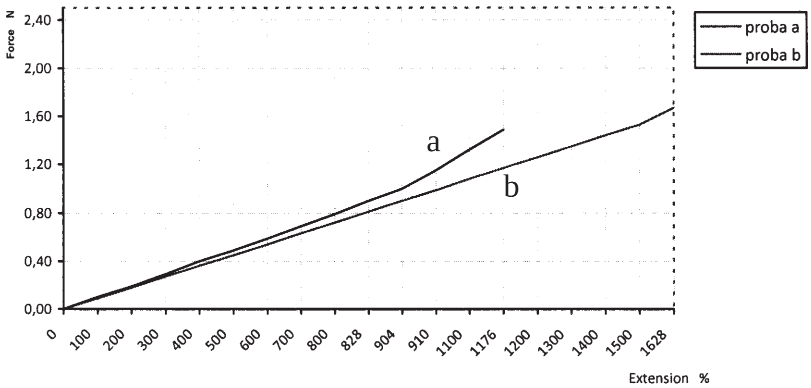

Fig. 1. Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder AC-310

BINDER COATING AC-408
Sample a – elongation % break 1804; N break 4,93
Sample b – elongation % break 1368; N break 4,32

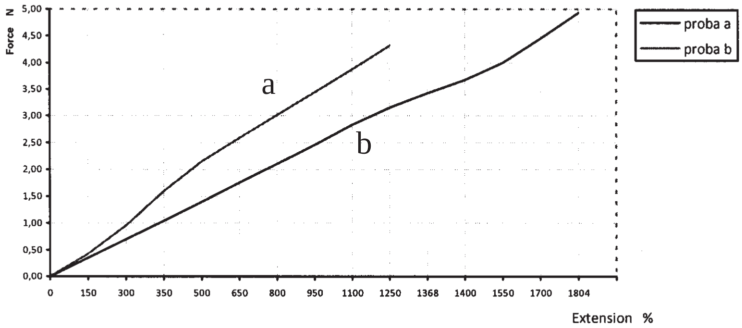

Fig. 2. Elongation at break (%) and strength (N/mm^2) of the coating obtained from binder AC-408

BINDER COATING PU-410
Sample a –elongation % break 1056; N break 7,08
Sample b –elongation % break 924; N break 6,25

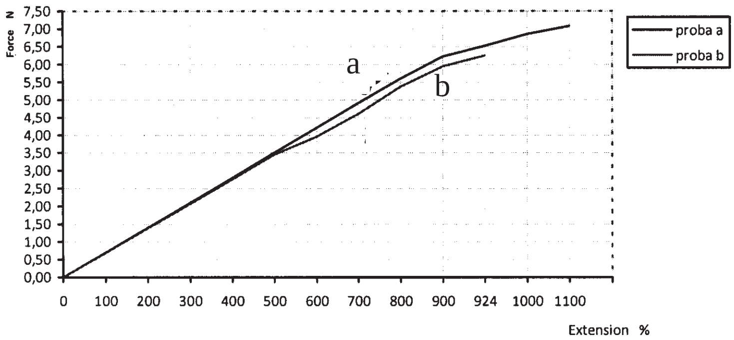

Fig. 3. Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder PU-410

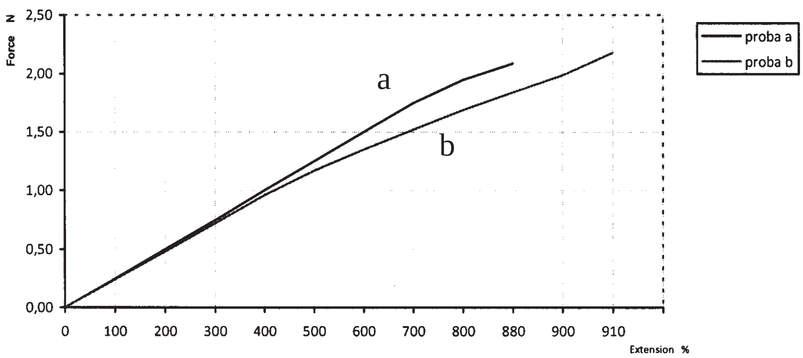

Fig.4. Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder AC –IF

BINDER COATING PU-PUM
Sample a – elongation % break 790; N break 5,90
Sample b – elongation % break 754; N break 5,74

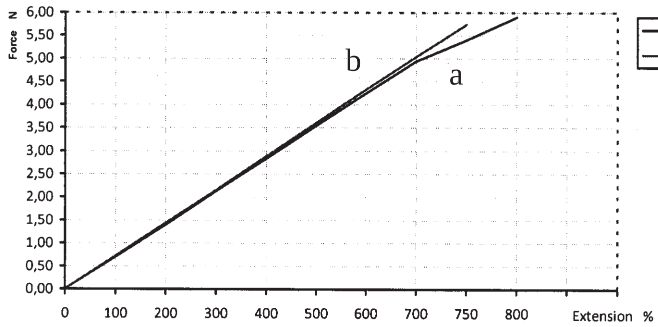

Fig. 5 Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder PU-PUM

BINDER COATING AC-33
Sample a – elongation % break 1104; N break 1,57
Sample b – elongation % break 1165; N break 1,45

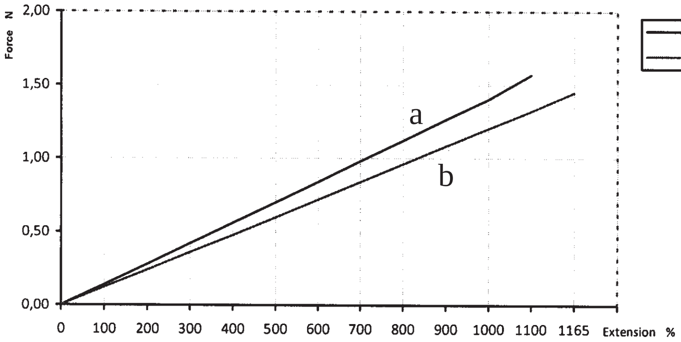

Fig. 6 Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder AC-33

BINDER COATING AC-34
Sample a – elongation % break 1392; N break 4,57
Sample b – elongation % break 1376; N break 4,11

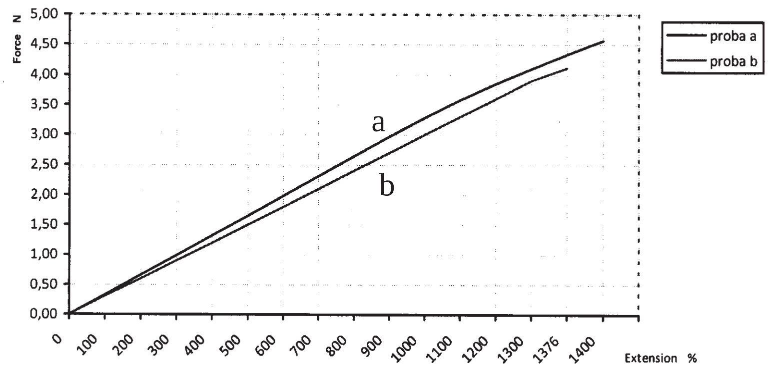

Fig. 7 Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder AC-34

BINDER COATING AC-IF 45% + PU-PUM 45% + CA-E 10 %
Sample a – elongation % break 904; N break 4,60
Sample b – elongation % break 828; N break 4,49

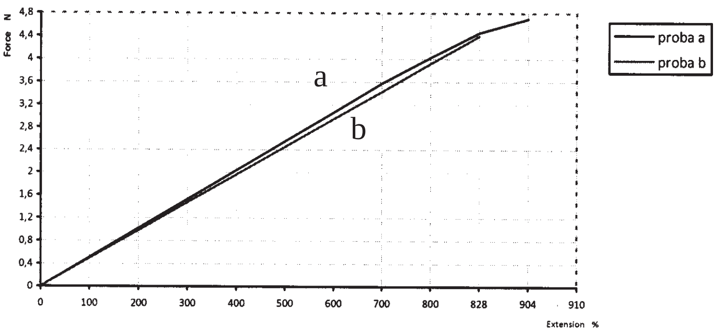

Fig. 8 Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder AC-IF 45% + PU-PUM 45% + CA-E 10 %

BINDER COATING AC-IF 40% + PU-PUM 40% + CA-E 20 %
Sample a – elongation % break 836; N break 4,43
Sample b – elongation % break 820; N break 4,48

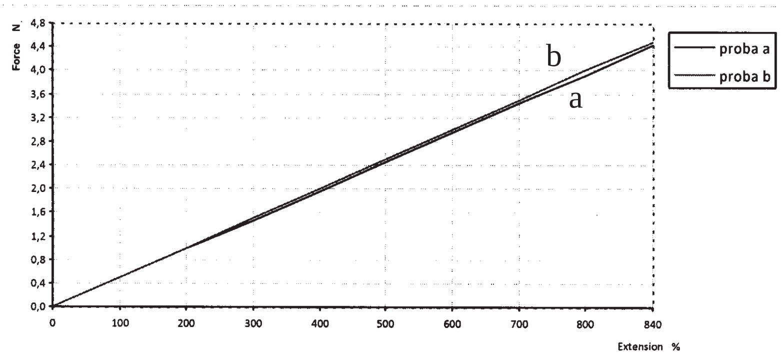

Fig. 9. Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder blend AC-IF 40% + PU-PUM 40% + CA-E 20 %

BINDER COATING AC-IF 35% + PU-PUM 35% + CA-E 30 %
Sample a – elongation % break 755; N break 3,25
Sample b – elongation % break 781; N break 3,29

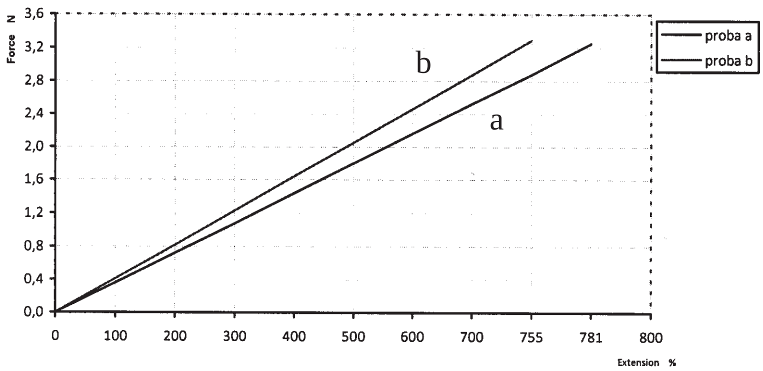

Fig.. 10. Elongation at break (%) and tensile strength (N/mm^2) of the coating obtained from binder blend AC-IF 35% + PU-PUM 35% + CA-E 30

AC-IF 40% + PU-PUM 40% + CA-E 20 % , in which the casein binder proportion is 20% in the binder blend and in the variant AC-IF 35% + PU-PUM 35% + CA-E 30 %, in which the casein binder proportion is higher, 30% .

Casein binders can be used in the finishing system, in higher amounts for high lustre and crack finish look, which are fashionable.

Conclusions

This paper presents the chemical and physical-mechanical characterization of disperse aqueous coating systems used in natural leather finishing, made by foreign and Romanian companies in order to establish optimal finishing technologies.

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