

## TESTING THE NEW PRODUCTS FOR FINISHING FOOTWEAR MADE OF NATURAL LEATHER

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### TESTING THE NEW PRODUCTS FOR FINISHING FOOTWEAR MADE OF NATURAL LEATHER

**ABSTRACT.** In order to create a footwear model, it is necessary to take into account the chosen materials, the manufacturing system and, last but not least, fashion trends, because fashion can be a determining factor for the industry. Finishing improves the appearance of the shoe and preserves it. Various wax mixtures combined with natural and synthetic oils are used to finish footwear, such as water-resistant mixtures and leather polishing products, with the purpose of improving the appearance of footwear uppers made of natural leather finished by polishing. The obtained ecologic wax emulsion may be used in surface finishing of natural bovine leather and footwear, in the final dressing composition. This paper presents the technological process of footwear manufacturing and the finishing composition for footwear made of natural leather based on complex metal dyes, ethyl alcohol, nitrocellulose aqueous emulsion, wax emulsion (made from triethanolamine monostearate and paraffin oil), used to obtain glossy finish.

**KEY WORDS:** natural leather, finishing footwear

### TESTAREA NOILOR PRODUSE PENTRU FINISAREA ÎNCĂLȚĂMINTEI FĂCUTE DIN PIELE NATURALĂ

**REZUMAT.** Pentru a crea un model de încălțăminte, este necesar să se țină cont de materialele alese, de sistemul de fabricație și, nu în ultimul rând, de tendințele modei, deoarece moda poate fi un factor determinant pentru industrie. Finisajul îmbunătățește aspectul încălțăminteii și îl păstrează. Pentru finisarea articolelor de încălțăminte, se utilizează diverse amestecuri de ceruri combinate cu uleiuri naturale și sintetice, cum ar fi cele rezistente la apă și pentru lustruit produse din piele, cu scopul îmbunătățirii aspectului fețelor de încălțăminte din piele naturală finisate prin lustruire. Emulsia de ceară ecologică obținută poate fi folosită la finisarea suprafeței pielii naturale de bovine și încălțăminteii realizate din această piele, în compoziția apretului final. Această lucrare prezintă procesul tehnologic de fabricare a încălțăminteii și compoziția de finisare pentru încălțăminte din piele naturală pe bază de coloranți metalici complecși, alcool etilic, emulsie apoasă pe bază de nitroceluloză, emulsie de ceară (fabricată din monostearat de trietanolamină și ulei de parafină), folosită pentru obținerea unui finisaj lucios.

**CUVINTE CHEIE:** piele naturală, finisarea încălțăminteii

### ESSAI DES NOUVEAUX PRODUITS POUR LA FINITION DE CHAUSSURES EN CUIR NATUREL

**RÉSUMÉ.** Pour créer un modèle de chaussures, il est nécessaire de tenir compte des matériaux choisis, du système de fabrication et, enfin, des tendances de la mode, car la mode peut être un facteur déterminant pour le secteur. La finition améliore l'aspect de la chaussure et la préserve. Différents mélanges de cires combinés avec des huiles naturelles et synthétiques sont utilisés pour la finition des chaussures, tels que des mélanges résistants à l'eau et des produits pour le polissage du cuir, dans le but d'améliorer l'apparence des tiges de chaussures en cuir naturel finies par polissage. L'émulsion de cire écologique obtenue peut être utilisée pour la finition de la surface du cuir bovin et des chaussures réalisées en utilisant ce cuir, dans la composition de la couche finale. Cet article présente le processus technologique de fabrication de la chaussure et la composition de finition pour la chaussure en cuir naturel à base de colorants métalliques complexes, alcool éthylique, émulsion aqueuse de nitrocellulose, émulsion de cire (à base de monostéarate de triéthanolamine et d'huile de paraffine), utilisé pour obtenir un fini brillant.

**MOTS CLÉS :** cuir naturel, finition de la chaussure

## INTRODUCTION

In order to create a footwear model, it is necessary to take into account the chosen materials, the manufacturing system and, last but not least, fashion trends, because fashion can be a determining factor for the industry. Obtaining a high quality product is also conditioned by the designing and manufacturing preparation activity, in terms of providing technical and technological parameters and high economic efficiency. The manufacturing process comprises a series of distinct operations, executed in a given order, determined according to:

- the characteristics of the product

to be executed;

- the characteristics of raw materials;
- the characteristics of the equipment used.

The technological manufacturing process must ensure:

- high productivity indices;
- reduced consumption of materials;
- high quality products.

The technological process of footwear manufacturing comprises the following groups of operations [1-3]:

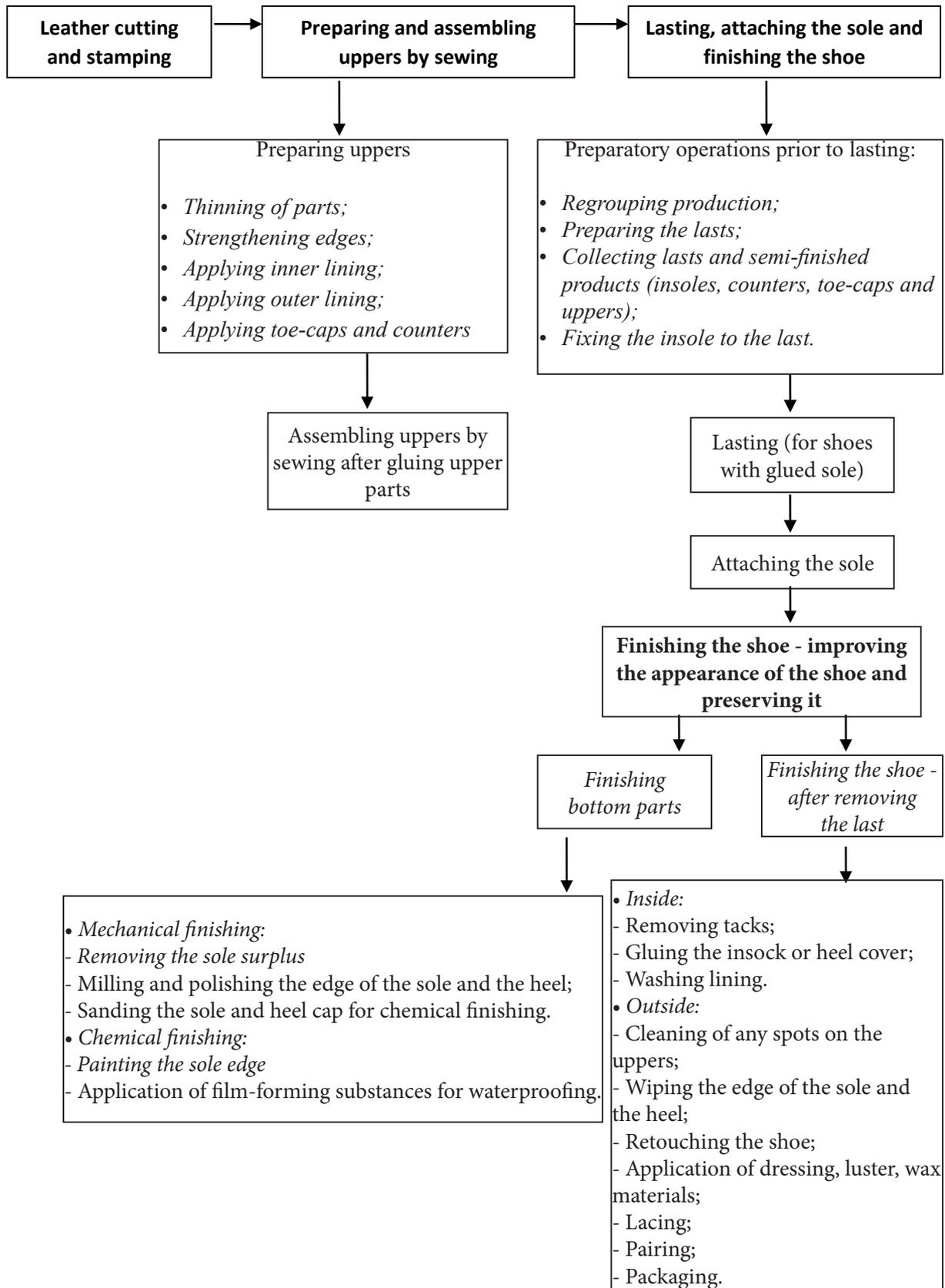


Figure 1. Technological process of footwear manufacturing

## Types of Natural Leather Assortments Used in Making Footwear

The main types of leather used in footwear manufacturing are the following:

- Natural grain box leather is made of bovine hides, it has a smooth, evenly finished grain, fullness, medium softness, at least 10% section dyeing, coating dye colour close to full dyeing colour, well polished velour side. It is a mineral tanned assortment and is most often used. The finest box leathers come from calfskins;
- Natural grain nappa, made from bovine hides (mineral tanned), has a smooth, uniformly finished, full grain, accentuated softness, at least 10% section dyeing, coating dye colour close to full dyeing colour, well polished velour side;
- Bison leather is a mineral tanned leather, with a pressed grain (to form a characteristic design on the leather surface to cover some imperfections), uniformly finished, full and thicker than box leathers. It is used for making men's footwear;
- Buffo is a mineral tanned bovine leather with polished grain, fullness and 100% section dyeing. It is used for making men's footwear;
- Suede is a velvet-like assortment of leather obtained by polishing mineral tanned leather on the flesh side (velour). The smoothness, uniformity and size of the nap define the quality of the suede. The best varieties of suede are obtained from calfskins [4-7].

## The Finishing of Footwear Made of Natural Leather

For the finishing of footwear, various mixtures of waxes combined with natural and synthetic oils, such as water-resistant ones

and for polishing leather products, are used to improve the appearance of polished leather for footwear uppers. Both natural and synthetic waxes are used to finish the natural leathers, to reduce the stickiness of the thermoplastic binders and to obtain a certain handle or color darkening effect (in the waxed leather varieties, which are fashionable) [8, 9]. Also, for the finishing of footwear, various mixtures of waxes combined with natural and synthetic oils, such as water-resistant ones and for polishing leather products, are used to improve the appearance of polished leather for footwear uppers. As the aqueous finishing dispersions used to finish the natural leathers are fluid, they are suitable for rheological measurements. Finishing systems are applied to the surface of leather by spraying or by means of roll-coating and reverse-coating machines. The correct determination of their composition, as well as the control of rheological behavior, leads to obtaining adherent finishing films uniformly set on the surface of leather, with suitable physical-mechanical resistance, and to the prevention of undesirable effects, especially in the case of aqueous systems with deviations from the ideal or Newtonian flow.

Obtaining a uniform finish of the leather, as well as of footwear made of natural leather, is determined by a number of factors such as: evaporation rate of volatile components, quality of volatile components (solvation power, surface tension), viscosity of aqueous dispersion of pigments, viscosity of the binders, surface tension, the heat of vaporization, the coalescence of droplets in the case of emulsions, the evaporation rate of the emulsions [10, 11]. One of the most important factors is the viscosity of the aqueous finishing systems. In order to obtain a uniform finish, each system must have a specific viscosity profile, and the finishing technician must take into account each component of the viscosity to obtain the desired and correct finish of the natural leather, as well as footwear made of natural leather.

## Machines Used for Footwear Finishing

Table 1 presents the main machines used to finish footwear [12].

Table 1: Machines used for footwear finishing

| No. | Footwear finishing chamber  | No. | Equipment with brushes for footwear finishing                                      |
|-----|---|-----|--|
| 1   |  | 2   |  |
| 3   |  | 4   |  |

## EXPERIMENTAL

### Materials

- Stearin (S.C. Stera Chemicals S.R.L., Bucharest) – solid substance, with specific grease odour, white colour, melting point 69-70°C;
- Triethanolamine (SC Stera Chemicals S.R.L., Bucharest) – colourless liquid, melting point – 20-21°C, boiling point – 277-279°C, density – 1.124 g/cm<sup>3</sup>, refractive index – 1.4852;
- Paraffin oil (MOL, company, Hungary) – colourless, odorless, non-fluorescent and free of aromatic compounds;
- Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (SC Elton Corporation SA., Bucharest), density – 0.95 g/cm<sup>3</sup> at 40°C, pH (10% solution) – 7-8;
- Wax emulsion (marked TP) used as handle modifier: dry substance – 14-16%, pH (10% solution) – 6.0-7.0 (INCDTP–Division Leather and Footwear Research Institute Bucharest, Romania) [13, 14];
- Roda lacquer 93 (Triderma, Germany), nitrocellulose emulsion used as a fixing

agent (final dressing) for finishes applied to natural leather: dry substance – 15%, pH (10% solution) – 5.5, Ford cup viscosity  $\Phi 4$  – 125, flash point – 82°C;

- Finishing composition (marked FC-1, black and FC-2, brown) based on nitrocellulose emulsion, wax emulsion (TP), metal complex dyes and ethyl alcohol, for footwear made of natural leather: dry substance – 10-12%, pH (10% solution) – 7.0-8.0 (INCDTP–Division Leather and Footwear Research Institute Bucharest, Romania);
- The footwear made of natural leather (mineral tanned and wet finished by retanning, fatliquoring and dyeing, 1.2-1.4 mm thick, dyed black and brown (INCDTP–Division Leather and Footwear Research Institute Bucharest, Romania).

### Methods

- Chemical characteristics of the finishing composition for footwear, and of the wax emulsion were determined according to the following standards: dry substance (%) – SR EN ISO 4684:2006; pH (10% solution) – SR-EN ISO 4098: 2006.

- Optical microscopy images were captured using a Leica stereomicroscope S8APO model with optic fiber cold light source, L2, with three levels of intensity [13]. Magnifying was 100X for the wax emulsions and 20X for surface of finished leather and footwear made of natural leather.
- Physical-mechanical characteristics of footwear made of natural leather were determined according to the following standards: elongation at a load of 10 N/mm<sup>2</sup> (%) and tensile strength (N/mm<sup>2</sup>) – 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; strength to dry and wet abrasion (1-5 ranking) – SR EN ISO 11640:2002; water vapour permeability, (mg/cm<sup>2</sup>) – SR EN ISO 3377-1: 2012.
- Finishing composition for footwear viscosities were determined with Ubbelohde KPG capillary viscometers, Schott, Jenaer Glaswerk Schott & Gen. Mainz, Germany [10, 11].

#### Obtaining the Wax Emulsion for Finishing the Footwear

The wax emulsion obtained by emulsifying a mixture of triethanolamine monostearate, paraffin oil and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide. The wax emulsion (TP) was added into the nitrocellulose final dressing.

#### Finishing Composition for Footwear Made of Natural Leather (FC)

It is made of the following components:

- 5-10 g/L metal complex dyes (black, brown);
- 10-20 g/L ethyl alcohol;
- 700 g/L nitrocellulose aqueous emulsion;
- 30-50 g/L wax emulsion (TP);
- and water.

The finishing composition FC can be applied to film-coated leather shoes using a hand

spray gun as final operation using an amount of 100% finishing composition on the entire leather surface of the shoe, to get a glossy effect. This operation is repeated two to three times, until the desired effect is achieved, after which the shoes are dried in the hot-air drying machine and polished in the polishing machine.

## RESULTS AND DISCUSSIONS

#### Characterization of Wax Emulsion for Finishing the Footwear

The physico-chemical properties of the wax emulsion TP are: dry substance – 14-16%, pH (10% solution) – 6.0-7.0. The microscopic image obtained for the prepared emulsion is presented in Figure 2.

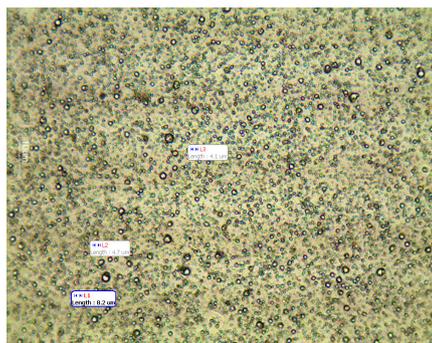


Figure 2. Optical image, 100X, of TP wax emulsion

The wax emulsion obtained by emulsifying a mixture of triethanolamine monostearate, paraffin oil and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide has homogenous appearance and particle sizes ranging mostly between 4 and 8  $\mu\text{m}$  [15].

#### Characterization of Finishing Composition for Footwear Made of Natural Leather

Finishing composition (marked FC-1, black, and FC-2, brown) for footwear made of natural leather based on complex metal dyes, ethyl alcohol, nitrocellulose aqueous emulsion, wax emulsion (made from triethanolamine monostearate and paraffin oil), used to obtain glossy finish: dry substance – 10-12%, pH (10% solution) – 7.0-8.0. Viscosities (at 25  $\pm$ 0.1°C) of footwear finishing compositions (FC-1, FC-2) are

11,0986 cSt and 11,4953 cSt. The constant of viscosimeters used to conduct tests is 0,0522.

### Characterization of Footwear Uppers Made of Natural Leather by Mechanical Methods

Table 2 presents physical-mechanical characteristics of tested footwear uppers made of natural leather (samples 1 and 2).

Table 2: Physical-mechanical characteristics of footwear uppers made of natural leather

| Sample/ Characteristic                             | 1        | 2        | Test method standard  |
|--|----------|----------|-----------------------|
| Elongation at a load of 10 N/mm <sup>2</sup> , %   | 25       | 29       | SR EN ISO 3376: 2012  |
| Elongation at break, %                             | 56       | 67       | SR EN ISO 3376: 2012  |
| Tensile strength, N/mm <sup>2</sup>                | 24.70    | 24.53    | SR EN ISO 3376: 2012  |
| Seam tear strength, N/mm                           | 101.80   | 106.28   | SR 5045:2008          |
| Water vapour permeability, mg/cm <sup>2</sup>      | 147.84   | 238.56   | SR EN ISO 3377-1:2012 |
| Resistance to repeated bending, number of flexions | 250,000  | 250,000  | SR EN ISO 5402-1:2012 |
| Strength to dry and wet abrasion (1-5 ranking)     | 5/5; 4/4 | 5/4; 4/3 | SR EN ISO 11640:2002  |
| Dyeing fastness to raindrop, (1-5 ranking)         | 5        | 5        | STAS 8259/3-82        |

Values of physico-mechanical characteristics (elongation under load and at break, tensile strength, tear strength, seam strength and water vapor permeability) of the tested natural leather footwear uppers correspond to ST 1619:1994 standard [16]. The physical-mechanical resistances of the footwear uppers finished with the film coating compositions, have values of 5/4-5/5 for dry abrasion, values of 4/3-4/4 for wet abrasion, values of 250,000 flexions, for resistance to repeated bending, and conforms to the norms provided for natural leather finished with film coating. The water drop resistance of the footwear uppers (leather with smooth grain, box-type natural grain, black and brown) finished with finishing compositions (FC), has values of 5, on a scale of 0-5.

#### Qualitative Assessment of Finished Footwear

As a result of applying the finishing compositions (FC-1 for the black colour and FC-2 for the brown colour), high quality footwear was obtained, with resistant and aesthetic finishes, in black and brown colors. The values of chemical and physical-mechanical characteristics of

footwear uppers fall within the limits of standards for finished leathers.

#### CONCLUSIONS

- The emulsion obtained by emulsifying a mixture of triethanolamine monostearate and paraffin oil stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide has homogenous appearance and particle sizes ranging mostly between 4 and 8  $\mu\text{m}$ .
- High quality footwear was obtained by applying the finishing compositions, with resistant and aesthetic finishes.
- Footwear finishing compositions for film-coated footwear are evenly spread on the surface of natural leather uppers and have the following physical-chemical characteristics: dry substance 10-12%, pH 7.0-8.0, viscosity 11.0986 - 11.4953 cSt.
- The footwear finishing compositions (FC), consisting of complex metal dyes (black, brown), ethyl alcohol, aqueous nitrocellulose emulsion, wax emulsion (TP) and water, gives the leather uppers with natural grain box-type a glossy appearance, and leads to improved

characteristics of natural leather goods regarding the resistance to wet and dry abrasion and to water drop (raindrop).

- The values of chemical characteristics (chromium VI, free formaldehyde) of the natural leather footwear uppers tested are below the detection limit (3 mg/kg).
  - The values of physical-mechanical characteristics (elongation under load and at break, tensile strength, tear strength, seam strength and water vapor permeability) of the natural leather footwear uppers tested correspond to ST 1619:1994 standard.
  - The physical-mechanical resistances of the footwear uppers finished by film coating, using the finishing compositions, have values of 5/4-5/5 for dry abrasion, values of 4/3-4/4 for wet abrasion, values of 250,000 flexions for resistance to repeated bending, water drop resistance has values of 5, on a scale of 0-5, and comply with the norms provided for natural leather finished with film-coating.
3. Croitoru, D.F., Dragomir, A., Machines for Leather Goods Industry. Laboratory Guidelines (in Romanian), Rotaprint, Iasi, 2003.
  4. Schubert, R., Leather Finishing, Leather Library, vol. VI, Umschau, Frankfurt, 1982.
  5. Chiriță, G., Leather and Fur Technology (in Romanian), vol. II, Technical Press, Bucharest, 1985.
  6. Chiriță, A., Auxiliaries and Dyes for the Leather Industry (in Romanian), Technical Press, Bucharest, 1988.
  7. Chiriță, Gh., Chiriță, M., Treatise of Leather and Fur Chemistry and Technology, vol. I and II, Gh. Asachi Press, Iași, 1999.
  8. \*\*\*, CLARIANT, Germany – Leather finishing auxiliaries, 2013.
  9. \*\*\*, TRIDERMA, Germany – Leather finishing auxiliaries, 2017.
  10. Mandru, I., Leca, M., Chemistry of Colloids and Macromolecules (in Romanian), Didactical and Pedagogical Press, Bucharest, 1977.
  11. Voiutsky, S., Colloid Chemistry, Mir Publishers, Moscow, 1975.
  12. \*\*\*, LENOX PROD, Romania–Machines for Footwear Finishing, 2018.
  13. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions (Integrated Pollution Prevention and Control).
  14. Niculescu, O., Coara, G., Albu, L., Compositions for Finishing Footwear Made of Natural Leather, Romanian Patent Application, OSIM A 00983/2018.
  15. \*\*\*, Optical microscopy handbook, Leica, 2007.

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#### **REFERENCES**

1. Cociu, V., Malureanu, G., Volocariu, R.S., Laboratory Guidebook for the Fundamentals of Leather and Substitute Product Technology (in Romanian), Rotaprint, Iasi, 1993.
2. Malureanu, G., Mihai, A., Fundamentals of Footwear Design (in Romanian), Performantica Press, Iasi, 2003.

16. \*\*\*, Collection of standards, according to SMC Quality Control Testing Laboratory, National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute Bucharest, Romania.

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