This paper has considered the possibility of using new finishing formulations to finish the Crust leather, manufactured from cattle raw materials aimed to finish shoes and leather garments.

The quality indicators of finishing formulations and their elementary chemical composition have been investigated. It was found that the finishing formulations possess a high covering capacity due to the presence of mineral pigments in their composition. X-ray fluorescent analysis has proven that the presence of chromium pigments and copper compounds renders the green color to the composition; the compounds of cobalt, copper, iron, chromium – blue color; cobalt compounds – reddish-brown color.

It has been established that the finishing formulations are resistant to the effect of electrolytes of different nature over a wide pH interval, from 2 to 11.

When determining the uniformity of the composition by using a chromatography method involving fan-shaped paper, it was found that the composition of blue has a pronounced purple hue, of reddish-brown – red.

The effectiveness of the use of finishing formulations to finish the Crust leather has been proven by determining the indicators of its quality. The finishing formulations give the Crust high resistance to dry (exceeding 500 rotations) and wet friction (exceeding 150 rotations), multiple bending (exceeding 50,000 rotations), the effect of water (2 to 5 points), and organic solvents (2 to 4 points). At the same time, the finishing formulations are characterized by rapid diffusion into the structure of the leather with a natural front surface with the simultaneous provision of specific properties to it. Specifically: water-repelling properties (hydrophobicity), shine, wax grain, matte, saturated homogeneous color. The leather with the introduced finishing formulations does not require fixing the resulting coating with water-based varnish.

It is recommended to use the finishing formulations in the production of Crust leather shoe top by applying them onto the surface by spraying or using a brush to create the desired effect

Keywords: Crust leather, composition of finishing formulations, finishing, covering capacity, quality of coating

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DETERMINING PATTERNS IN THE USE OF FINISHING FORMULATIONS FOR TRIMMING THE CRUST LEATHER

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1. Introduction

Today, in the production of genuine leather for the top of shoes, finishing processes and operations occupy perhaps the most important place. It is this cycle of production that accounts for the largest energy and material costs. Despite this, a small-capacity leather company produces at least 4 assortments of finished products. Conventional finishing technologies at the enterprises making natural leather for shoe top imply the application of a multilayered coating of finishing materials onto its surface [1–4]. Taking into consideration the condition of the front surface of the leather and the presence of defects of natural or industrial origin on it, it is possible to produce leather with a natural and ennobled surface [5]. The ennobling cycle can include operations of polishing, embossing, smoothing, slicing, engraving, perforation, etc. The nature of the surface of genuine leather, produced at an enterprise, also predetermines fashion trends for every season. At the same time, to achieve the desired effect, the plant can use a variety of units for the application of finishing formulations, dryers of different types, ironing machines, and hydraulic presses, laser installations, and engravers [6]. Despite the set of production equipment, a leather-making enterprise cannot fulfill small individual or special orders in a short time due to the long duration of the manufacturing cycle of leather production and its resource intensity.

In today's world of high technology and fashion, the issue of purchasing primary necessity goods, such as shoes, to meet the utilitarian needs of the consumer is not relevant. Each person that buys goods of this segment group aims to emphasize his/her individuality, so it is a relevant task to fabricate exclusive goods that are modern, creative, comfortable, as well as easy to manufacture [7]. The exclusivity of an article can be achieved through the creation of a unique design, the use of original materials and finishing formulations to render the required properties and color, trimming in the form of a drawing, embossing, perforation, etc. In order to render uniqueness to an article, it is proposed to use the Crust leather to provide for a personalized approach to the manufacture of shoes and leather goods.

Until recently, Crust was not seen by leather businesses as finished leather but was listed as semi-finished products. The properties of the product were not regulated by the requirements of the state normative documentation [9]. The new international ISO standards (ISO 15115:2019 Leather – Vocabulary) define it (ISO/DIS 20940(en) Leather – Crust – full chrome upper leather – Specifications and test methods) as the leather that was exposed to tannin, greasing, and drying processes. Crust must have a natural front surface without finishing. There are also the types of Crust of chrome and organic tannage, colored or not. The Crust leather in most cases is tanned with a limited amount of chrome tanner; the use of synthetic and vegetable tanners in the manufacturing technology gives it a pastel yellow-brown range of colors. It is important today that Crust belongs to the ecological range, and this, in turn, increases the safety of Crust as a commodity. For shoe manufacturers, particularly interesting is non-colored Crust, which makes it possible to create a unique artistic effect by applying finishing formulations by spraying them or applying with a brush onto finished goods.

The use of Crust makes it possible to preserve the natural pattern of the front layer, characteristic of genuine leather, and, through the use of special finishing formulations, give the article the required shade, vintage effect, as well as exclusivity, which is relevant for ensuring a personalized approach in the manufacture of shoes.

2. Literature review and problem statement

Work [3] that addresses the technology of natural leather production describes conventional compositions of finishing formulations, which include polymeric film-forming agents, mineral pigments, organic solvents, auxiliary substances. In this case, the standard of a finishing's manufacturing implies a different ratio of components in covering compositions to render specific properties to the decorated surface of genuine leather [4]. Study [10] proved that the basis of any finishing formulation is a polymeric film-forming agent, which by its nature can be polyacrylate, polymethacrylate, polyurethane, etc. The range of finishing materials is constantly updated, and the materials are modified. To provide a covering film on leather with high water resistance, the authors of work [11] suggest the use of styrene homo- and copolymers, as well as butyl methacrylate, synthesized by emulsion polymerization. The modification of acrylic and polyurethane film-forming agents by introducing exopolyacrylamide and the structuring agent was investigated in [12]. It is shown that the introduction of exopolysaccharide into a film-forming agent in a combination with the basic chromium sulfate increases the elasticity module and strength of films. In order to determine the rational composition of cover formulations based on modified acrylic and polyurethane film-formers, the authors of [13] employed mathematical planning of the experiment to prove the effectiveness of the modification by achieving high indicators of the physical and mechanical properties, as well as water resistance, of the coating. However, there remain unresolved issues related to preserving the hygienic and physical properties of genuine leather after its finishing. The authors of [14] suggest the use, for finishing, thermosensitive polyurethane, in order to ensure controlled vapor permeability of leather. Work [15] reports a study of changes in the hygienic properties of leather after finishing according to conventional methods of aniline and lacquer coating. The authors of [16] noted a sharp decrease in the vapor permeability of leather after finishing, which could negatively affect the comfort of wearing a shoe. To ensure the comfort of shoes, in addition to changes in the hygienic properties, the physical and thermal protective properties of leather with aniline, pigmented and lacquer coating were investigated in [17]. The cited studies refer to the conventional technologies of leather production for shoes. However, the introduction of new finishing technologies could quickly change the range of finished goods in accordance with the requirements of fashion, while preserving the hygienic properties of genuine leather. This very approach is used in work [18], in which the high vapor permeability, light fastness, and bio-resistance are ensured by the use, for finishing, the nanocomposite organic and mineral materials. And when replacing conventional finishing using modern finishing formulations, one can achieve a high quality of coating while maintaining other properties of genuine leather. All this allows us to argue that it is advisable to conduct a study addressing the use of the modern range of finishing formulations in order to finish the Crust leather.

3. The aim and objectives of the study

The aim of this work is to determine patterns in using finishing formulations when finishing the Crust leather. Our study could make it possible to assess the advantages and disadvantages of finishing the leather with ready-made finishing formulations.

To achieve the set aim, the following tasks have been solved:

– to explore the properties of finishing formulations made by different manufacturers;

– to explore the quality of the Crust leather following the application of finishing formulations;

– to evaluate the effectiveness of the use of finishing formulations to finish the Crust leather.

4. Materials and methods to study the properties of finishing formulations and the quality indicators of the Crust leather following their application

In our study, we used finishing formulations by manufacturers from Italy.

The single-component formulation "Toledo super" of green color was made by Kenda Farben Spa (Italy) [19]. The manufacturer specifications indicate that the formulation is a single-component varnish with a high covering capacity to create an aniline coating on the leather. The formulation is intended for the leathers of vegetable and chromium tanning.

The formulation made by the company IEXI s.r.l. (Italy) of blue color for leather with a natural front surface [20]. The features of the formulation are deep penetration into the structure of the leather, thereby rendering it the effect of a "wax touch".

The formulation made by the company Biar (Italy) of reddish-brown color, with deep penetration into the structure of tanned leather with a natural front surface [21].

A set of studies [22] was used to investigate the quality indicators of finishing formulations. It includes determining a dry residue, the specific weight, and pH level of the formulation; the thickening of formulations under the action of ammonium hydroxide; the resistance of formulations to the action of electrolytes; the uniformity of formulations by using a paper chromatography method.

We identified the mineral component of the finishing formulations using the X-ray fluorescent multichannel energy dispersion analyzer X-Supreme 8000 (Oxford Instruments Analytical Ltd, UK). The analyzer makes it possible to evaluate the qualitative composition of the substance in the range of concentrations from 1 ppm to 100 % [23].

To investigate the effectiveness of the use of finishing formulations in finishing processes, we used the Crust leather with a natural front surface, which was made according to the standard methods, used at the leather producing enterprise PrAT "Chinbar" (Kyiv, Ukraine), from cattle-derived raw materials [24].

The manufacturing technology of the Crust leather implies combined chromium-plant tanning and emulsion greasing. The indicators of the leather before our study were determined in accordance with DSTU 2726-94 "Leather for shoe top. Technical Conditions" [18, 22].

The thickness of the Crust samples is 1.55–1.60 mm. The content, %, in the leather: moisture – 15.0; chromium oxide and substances extracted by organic solvents, in terms of absolutely dry leather, – 3.8 and 7.2 respectively.

For the experimental research, the samples were prepared by applying the finishing formulations, using a brush, on the Crust leather to achieve full coverage. Each layer of the finishing formulation was dried at a temperature of 60–65 °C; and, after every 2 layers, we pressed it at a temperature of 70–75 °C for 5 seconds. We did not fix the coating obtained on the leather with varnish.

We determined the physical and mechanical quality indicators of the coating obtained on the Crust leather after conditioning the samples [25]. The study involved determining the resistance of the coating to dry and wet friction, multiple bending, an adhesion indicator, the suction capacity of the leather surface, as well as the resistance of its coloration to mechanical influence, and the action of organic solvents [22].

5. Results of studying the effectiveness of the use of finishing formulations for finishing the Crust leather

5. 1. Studying the properties of finishing formulations

The finishing formulations used for our study are liquid and have bright, saturated colors. The formulation of green color has a pronounced smell of organic solvent, in the other two formulations, the smell of organic solvent is barely noticeable. When trying to obtain a free film [22] in order to investigate its deformation characteristics, it was found that the film is formed only by the formulation of green color. In this case, the film is rigid, fragile, with a complete lack of stickiness.

The results of determining the basic properties of the examined finishing formulations are given in Table 1.

Table 1

The basic indicators of finishing formulations

Indicator	Finishing formulation made by		
	Kenda Farben Spa	IEXI s.r.l	Biar
Color	green	dark blue	red-brown
Dry residue, %	6.0	12.2	2.5
Specific weight, g/cm^3	0.80	0.82	0.99
Formulation pH	5.9	6.7	6.8
Thickening under the action of ammonium hydroxide, of concentration, %: – 6.25	absent		
– 12.50	absent		
– 18.75	absent		
Resistance to electrolytes	resistant, coagulation threshold is absent		

It should be noted that when drying the finishing formulations at a temperature of 105±5 °C to determine their dry residue, even if the mass was brought to a constant, the formulation of blue color did not dry out completely. This may be due to the presence of heat-resistant wax in the formulation over the specified temperature interval [26]. The presence of wax is confirmed by the manufacturer of the formulation in the accompanying documents for the material.

We determined pH by a potentiometric method for the starting formulations without thinning.

The thickening of a formulation under the action of ammonium hydroxide is determined in order to predict the behavior of the material when raising the pH level above 7. Changes in the system with a gradual increase in pH levels are judged by a change in relative viscosity.

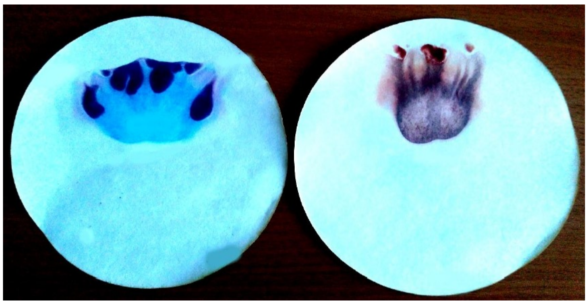
We determined the thickening of the finishing formulation under the action of ammonium hydroxide by measuring its viscosity. Viscosity makes it possible to evaluate the interaction in the system. The absence of thickening of the finishing formulations is evidenced by the stable amount of viscosity when adding ammonium hydroxide solutions of different concentrations.

Resistance to electrolytes of different nature is estimated by changes in formulations, to 10 ml of which one gradually (0.5 ml) adds electrolyte until the system reaches a ratio of the formulation to the electrolyte of 1:1.

The resistance in a wide pH interval from 2 to 11 is confirmed by the absence of the coagulation threshold in the finishing formulations when they are exposed to 1H electrolyte solutions. Specifically: sodium and calcium chloride, hydroxide and ammonium sulfate, aluminum sulfate, acetic and chloride acids.

The ratio of the finishing formulations to water significantly differed in the study. The formulations of blue and reddish-brown colors are quite easily thinned with water. The formulation of green color has no solubility in water at all. The process of the polymerization of a formulation takes place instantly if it enters the water.

Since the formulations of blue and red-brown colors are easily thinned with water, we determined the uniformity of the formulations using a chromatography method involving fan-like paper [22]. When distilled water washes the color formulations on the filter, one can evaluate the homogeneity of the pigment and define its shade (Fig. 1). The observations reveal that the formulation of blue has a pronounced purple hue, and the formulation of reddish-brown color is brown, the shade is red.



a *b*

Fig. 1. A fan-shaped paper chromatography for formulations: *a* – blue; *b* – reddish-brown colors

To render the required color, when finishing the leather, the polymer film-formers are supplemented with pigments of organic or inorganic nature. The examined finishing formulations possess rich and bright colors, which are most likely based on the mineral component. The results of determining the presence of metal compounds in the formulations by using the X-ray fluorescent non-reference analysis applying a method of fundamental parameters are given in Table 2 and in Fig. 2.

Table 2

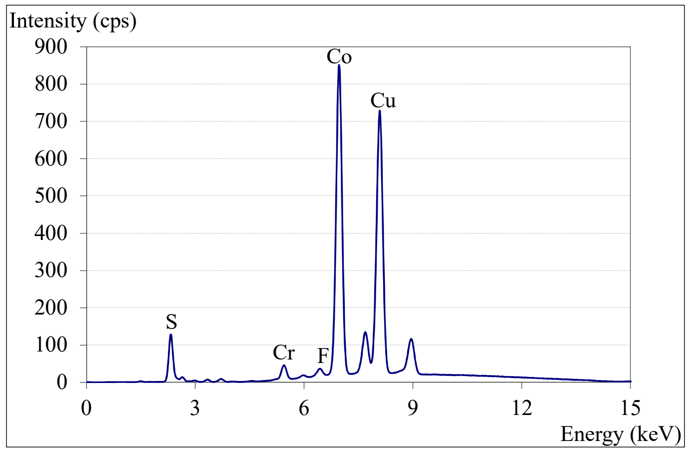
The mineral composition of finishing formulations

Element	The content of an element, % by weight, in the finishing formulation:		
	green color (Kenda Farben Spa)	dark blue color (IEXI s.r.l)	red-brown color (Biar)
Na_2O	2.425	2.615	7.118
Al_2O_3	0.667	4.294	3.303
SiO_2	18.378	3.221	10.627
P_2O_5	2.381	0.917	2.257
SO_3^{2-}	40.639	69.183	12.574
Cl^-	2.335	2.367	1.591
K_2O	0.114	0.432	0.064
CaO	0.829	0.564	0.441
Cr_2O_3	21.422	0.665	<0.01
Fe_2O_3	0.353	0.299	0.239
CoO	<0.01	8.060	61.486
CuO	10.122	7.023	<0.01
ZnO	0.087	0.055	0.134

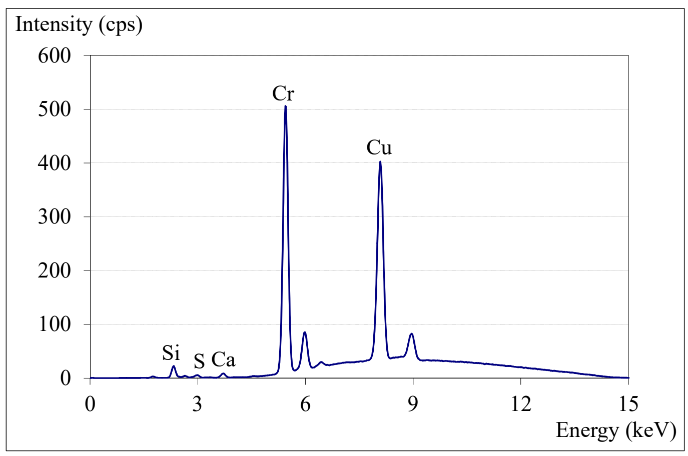
Table 2 and Fig. 2 demonstrate that the color of the finishing formulations is based on the use of mineral pigments, which is advisable due to their high cover capacity and the resistance to external factors [27]. All formulations are characterized by the content of silicates, sulfur compounds.

Compounds of three-valent chromium as part of the first finishing formulation render it a bright green color (Fig. 2, *a*). Copper compounds in the same formulation are a conventional accompanying element in chromium oxide pigments [27].

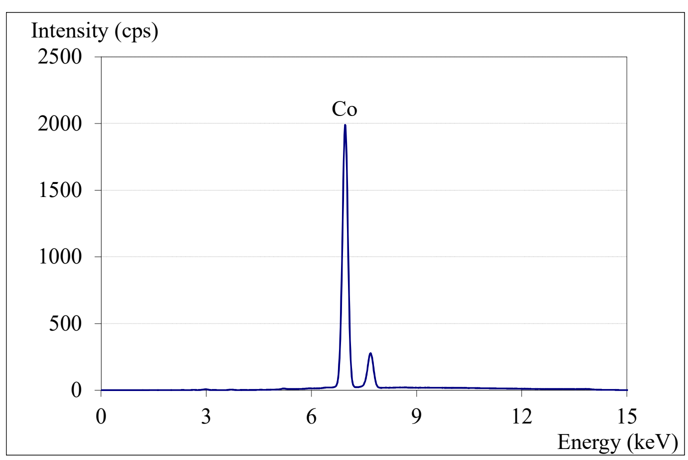
Cobalt compounds that are available in blue samples (Fig. 2, *b*) and reddish-brown (Fig. 2, *c*) samples are also conventional pigments for a variety of paints and varnishes. The different color of pigments is due to the use of waterless cobalt salts (blue) or its crystal hydrates (red) [27]. Indirectly, the presence of blue cobalt pigments in the formulation is evidenced by the fact that the deep blue color on the leather under low artificial light acquires a purple hue. The depth of blue is also provided by the compounds of copper, iron, and chromium.



a



b



c

Fig. 2. X-ray fluorescent analysis of the chemical composition of the finishing formulations: *a* – blue; *b* – green; *c* – reddish-brown colors

5. 2. Determining the quality of the Crust leather trimmed with finishing formulations

The coatings on the leather were formed by layering the finishing formulations with a brush on the Crust surface. In each of the experimental variants, the complete cover was reached in 6 runs.

One should note a fairly rapid diffusion of the finishing formulations into the Crust structure. The suction capacity of the formulation of green color was 14 s, blue – 39 s, reddish-brown – 27 s. Obviously, rapid diffusion is affected by the presence of organic solvents in the formulations, which contribute to the wetting of leather elements.

This confirms that the Crust suction capacity in the case of distilled water is 25 minutes. The suction capacity of the leather after applying the finishing formulations changed dramatically. In the case of using the formulation of green, the suction capacity exceeded 120 minutes, blue – 3 min., reddish-brown – 1.5 minutes. This difference in the results is explained by the properties of the formulation of green color, namely its rapid polymerization in water. The polymerization of the formulation in the leather structure rendered its hydrophobic properties. The basic indicators of quality of the leather following the application of finishing formulations are given in Table 3.

Table 3

The basic indicators of the Crust leather trimmed with finishing formulations

Indicator	Finishing formulation:		
	green color (Kenda Farben Spa)	dark blue color (IEXI s.r.l)	red-brown color (Biar)
Coating resistance to multiple bending, bends	>50.000	>50.000	>50.000
Coating resistance to friction, rotations: – dry	>500	>500	>500
– wet	>500	200	150
Coloration resistance to friction, points: – dry	5	5	4
– wet	5	4	2–3
Coloration resistance to the effect of organic solvent, points	4	4	2

It should be noted that the coating formed on the leather is of high quality.

The resistance of the leather coating to dry and wet friction was determined at the device IPC-1, which involves the abrasion of the front surface of a sample until the appearance of coating defects.

Finishing is considered resistant to dry friction if the leather sample can withstand 200 rotations without damage to the coating, to wet – 100 rotations. The finishing formulations rendered the Crust leather greater stability than that set by the normative documentation on the leather for shoe top. Our observations also revealed that the leather samples of green and blue became glossy after dry friction. The finishing formulation of blue gave the front surface of the Crust leather a wax grain.

In determining the resistance of the coating to multiple bending using the device IPC-2, one calculates the number of bends (cycles) before the appearance of defects such as changing the color tone, cracking, changing the color of the coating on the fold area, chipping the coating. If the leather of chrome tanning for the top of shoes made from cattle leathers can withstand at least 50,000 bends, their stability is considered excellent; not less than 40,000 – good; not less than 30,000 – satisfactory. All samples of the trimmed Crust leather withstood more than 50,000 bends without losing the integrity of the coating, its cracking, and chipping.

5. 3. Determining the effectiveness of the use of finishing formulations in order to finish the Crust leather

Since the film was not formed on the leather surface by the finishing formulations, it was impossible to determine the adhesion, characterized by the strength of sticking a coating to the surface of the leather. Given the absence of the formed film on the surface of the Crust leather, it is also impossible to determine the thickness of the coating by a weight method, which involves removing the film from the front surface with organic solvents. The finishing formulations quickly diffuse into the structure of the leather without forming a visible coating on its surface. However, one should note the high adhesion properties of the formulation of green color to any material used in our study (glass, porcelain, aluminum, etc.).

Taking into consideration the peculiarities of shoe care and leather goods care, we also determined the resistance of the coloration of the surface of the trimmed leather to friction and the action of organic solvents. The resistance, rated in points over a gray benchmark scale, is maximum (5 points) for dry friction in all samples. The high resistance of leather coloration to wet friction in the case of using green and blue formulations is provided by the presence of a polymeric component in the first one and wax in the second.

The resistance of coloration to the action of organic solvents in the leather for shoe tops rarely reaches high rates. Most organic solvents dissolve the finishing materials, rinsing them from the surface of the leather. That is why this indicator is not standardized for shoe leather. Our study has found sufficiently high resistance (4 points) to the action of four-colored carbon in the samples of green and blue colors, which can also be explained by the specific composition of these formulations – the formulation of green color is, as characterized by the manufacturer, varnish, and the formulation of blue contains wax.

6. Discussion of results of studying patterns in the use of finishing formulations when trimming the Crust leather

The low content of dry residue, from 2.5 in reddish-brown to 12.2 % in the blue formulation (Table 1), in the examined materials increases the suction capacity of the examined formulations by the Crust leather. The presence of mineral pigments predetermines a high cover capacity of the formulations, the resistance to electrolytes of different nature over a wide pH interval, from 2 to 11 [28]. And, given that the cover formulations include mineral pigments based on the compounds of cobalt, chromium, copper, iron (Table 2, Fig. 2), the coating on the leather has a rich color.

Taking the above into consideration, it is recommended. before using the finishing formulations, to determine their uniformity and solubility in water. Determining the uniformity would give an idea of the shade that could appear after the finishing formulations are applied on goods made of the Crust leather. Determining the solubility of the finishing formulations in water would give an idea of their possible thinning with water and could define patterns in equipment operations during the application of finishing on the Crust leather.

The seepage of the formulations into the structure of the dermis and the absence of a film formed on the front surface ensure the resistance of the coating to various mechanical influences, including wet friction (Table 3). The latter could greatly facilitate the care of consumers for shoes and leather garments made of the Crust leather, trimmed with the examined formulations.

It was found that the finishing formulations quickly diffuse into the structure of the leather, without forming a visible coating on its surface. Therefore, to achieve the required coverage, the Crust leather surface must be trimmed with several layers of finishing formulations. Given the fact that the fewer the layers the more aesthetically and appealing the coating looks, it has the effect of aniline (translucent) finishing.

Thus, the application of finishing formulations simplifies the technology of leather finishing for shoes, as well as leather goods, and makes it possible for craftsmen to obtain the desired effect on the finished product. And, to achieve a shine on the leather, it would suffice to polish the trimmed Crust leather with a dry cloth and eliminate the use of a water-emulsion varnish, usual in the technology to finish leather.

Today, the market for the ready-made finishing formulations for Crust leather is developing very rapidly; this explains the lack of thorough research into the materials represented in the market. A rapid change in the range is associated with the fashion for special and exclusive goods, so the market of finishing formulations for the Crust leather sees their fast rotation. This requires constant monitoring of the properties and features of the use of the proposed finishing formulations to trim the Crust leather. Therefore, investigating the finishing formulations is currently of applied scientific significance.

7. Conclusions

1. We have determined the properties of the finishing formulations made by Italian manufacturers for finishing the Crust leather. It is established that their coloration is based on the pigments of mineral nature. It was found that green color is rendered to the formulation by pigments based on chromium compounds; blue – compounds of cobalt and copper; reddish-brown – cobalt. At the same time, the finishing formulations have been found to demonstrate high resistance to electrolytes of different nature with changes in pH from 2 to 11. It was also established that organic solvents are present in the formulations.

2. The quality of the Crust leather, trimmed with finishing formulations, has been evaluated. It is established that their use makes it possible to obtain a high-quality coating. The effectiveness of the use of formulations for finishing leather for shoe top has been confirmed by the high resistance to mechanical influence: the resistance to dry (exceeding 500 rotations) and wet friction (exceeding 150 rotations), multiple bending (exceeding 50,000 rotations), the effect of water (from 2 to 5 points) and organic solvents (from 2 to 4 points). It has been proven that no solid film is formed on the leather surface by the formulations. Before use, it is recommended to evaluate the solubility of the finishing formulation in water, which would determine the shade of the finishing formulation and the peculiarities of equipment operation during the application of finishing on the Crust leather.

3. The effectiveness of the application of finishing formulations has been evaluated. It is determined that they change the suction capacity of the Crust leather, providing a coating's resistance to mechanical influence. This makes it easier for the consumer to care for goods made from the Crust leather. It was found that full coverage can be achieved in 6 runs, provided that the brush method of applying the formulations onto the front surface of the leather is applied. To create a thin, translucent coating on the surface of the Crust leather, it is recommended to replace the brush method of applying the finishing formulations with spraying.

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