IMPROVING OF LEATHER LIQUID FINISHING THROUGH USAGE OF POLYMERIC COMPOUNDS

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Nowadays, leather industry is suffering from low quality of raw materials, usage of efficient and environment unfriendly materials. This situation may be corrected by upgrading the existing or developing new technologies using efficient chemical materials, such as polymeric compounds. The aim of the study was to improve the leather dyeing processes through usage of water-soluble polymers derivatives of acrylic and maleic acids in the direction of simplification and reduction of processing materials consumption, ensuring high product quality, establishing the mechanism of interaction between these materials and collagen. The reactions in the "collagen-polymeric compounds-dye" system were studied using IR-spectroscopy. The fiber preparation from the untanned leather industry waste was used for the collagen prototype. The data obtained show correlation between interaction type in the system under study as well as leather properties and processing conditions. We have established a positive effect of investigated polymers on the physical, mechanical, and hygienic leather properties. It can be explained through their ability to be absorbed on the surface of the derma structural elements; to interact with them and other applied reagents (tannins, dyes etc.), there by promoting structure formation and improving product quality.

Keywords: liquid finishing of leather, polymeric compounds, IR-spectroscopy.

INTRODUCTION

While conducting finishing processes, leather is given some elastic-plastic, hygienic, aesthetic qualities as well as colour. A wide range of chemicals is used for this purpose. Thus, in practice, from 50 to 100 dyes of different types are needed in order to dye leather, mostly they are acid, basic, metal complex, active and sulphur-containing ones. The choice of dyes depends on products assortment and fashion trends.

Majority of synthetic dyes, intended for dyeing natural leather, are practically non-biodegradable due to their complex structure and xenobiotic features (Tamil Selvi *et al*., 2013). As a result, there is a need for leather dyeing technology modernization. This new technology must ensure better dyes absorption from work solutions, which means decrease of their quantity in factories sewages. This can be achieved either by creating new types of dyes of biological origin, which are capable of quick biodegradation, or by improvement of existing technologies, using effective chemical materials. For example, the paper by Tamil Selvi *et al*. (2013) is dedicated to research on the possibility of applying the dye, extracted from the seeds of *Bixa orellana*, to the leather dyeing process. In the paper by Sudha *et al*. (2016) the dye of microbiological origin with *Penicillium minioluteum* has been studied. This dye has been used for dyeing a wet-blue semi-finished product made of goatskin. The authors have discovered that at the high level of abrasion resistance and sweat finished leather has low resistance to light. We should mention that synthesis and industrial implementation of new types of dyes mean considerable money, time and material investment. For this reason researches (Haroun and Mansour, 2008; Danylkovych *et al*., 2016) are being done, dealing with the use of chemicals which can influence the colour and aesthetic qualities of finished leather positively without damaging its consumer properties in liquid finishing processes. To understand the interaction between collagen of derma, materials used and dyes better various analytical methods are used, such as the method of Fourier infrared spectroscopy (Sudha *et al*., 2016; Pellegrini *et al*., 2015; Campos Vidal and Mello, 2011; Sukhodub *et al*., 2004; Kanagaraj *et al*., 2015).

In this paper we have studied the influence of water-soluble polymeric compounds (derivatives of maleic and acrylic acids) on the liquid finishing and finished leather qualities.

EXPERIMENT

Materials Used

In this research we have used chemical materials common for leather industry: *savenol NWP* (6-00-00205601-37-92, Ukraine) – gel-like colourless liquid, surface-active neoionogenic substance, which includes, mass content, %: polyethyleneglycol – 5, water- 45, nylon AF 9-10 – 50, *anionic acid violet C dye* (*D*); *OLEAL 145* – anionic fat material manufactured by CODYECO S.p.A (Italy), which is an orange-brown transparent liquid with 66.0±3% active material content; *quebracho extract* – vegetative tanning extract, which is a red-brown hygroscopic cold water-soluble powder with 85% tannin content. Polymeric compounds based on maleic and acrylic acids, a collagen-containing preparation and a leather semi-finished product were also used. Their properties are described below.

Polymeric Compounds

In the research we have used polymeric compounds based on maleic (Kro) and acrylic (TP, CP) acids (Lukianets and Andreyeva, 2009). These are liquids, whose main properties are stated in table 1.

Table 1. Characteristics and main properties of polymeric compounds (Lukianets and Andreyeva, 2009)

Index	Polymeric compounds		
	*Kro**	*TP*	*CP*
Dry residue, %	21,5	13,5	32,5
Density, g/cm^3	1,078	1,060	1,158
Superficial tension of 10% solution, dyn/cm	54,1	76,6	76,9
Relative viscosity	2,00	13,33	78,00

Note: * good stability to light

Collagen-containing Preparation

A Ukrainian protein preparation has been used as a collagen model for Fourier infrared spectroscopy tests. This preparation is extracted from untanned collagen-containing waste products of leather industry from cattle raw materials. In terms of its properties and amino acid composition it is identical to derma collagen (Tehza and Andreeva, 2011; Andreyeva and Maistrenko, 2016). The following are properties of the collagen preparation, mass content % (in terms of completely dry substance): hide substance – 90.1±0.4; mineral substances – 3.9±0.2; substances, extracted with organic solvents – 1.0±0.3.

Leather Semi-Finished Item (Wet-Blue)

During the experiment we have used a leather semi-finished product of chrome tanning method, obtained from cattle skin (medium cowhide). The properties of this semi-finished product are given in table 2.

Table 2. Original wet-blue properties

Index	Value
Shrinkage temperature, °C	123±1,0
Thickness, mm	2.2±0,1
Mass content, %:	
– humidity	33.90±0.13
– chromium oxide*	5.75±0.12
– hide substance*	91.58±0.30
– mineral substances*	6.54±0.34
– substances, extracted with organic solvents *	0.71±0.12

Note: * the data are given for completely dry substance.

Research Techniques

In the research we have used both traditional for leather industry techniques and more modern and accomplished analytical ones: microscopy, infrared spectroscopy, statistical processing of experimental data.

To get statistically significant results, all measurements were carried out no less than 3-5 times. Control studies were performed simultaneously with the data correction process.

Chemical Analysis and Physico-Mechanical Tests

Chemical and physico-mechanical indices have been identified with the help of basic techniques: moisture content ISO 4684:2005, mineral substances content ISO 5397:1984, hide substance content ISO 5397:1984, chromium oxide content ISO 5398-1:2007, content of substances extracted with organic solvents ISO 4048:2008, shrinkage temperature ISO 3380:2015, determination of tensile strength and percentage extension ISO 3376:2011, strength of surface ISO 3379:2015, vapour permeability ISO 14268:2012, determination of bending force ISO 14087:2011, determination of abrasion resistance ISO 17076-1:2012, test for adhesion of finish ISO 11644:2009, determination of surface coating thickness ISO 17186:2011, determination of water absorption by capillary action (wicking) ISO 19074:2015.

Infrared Spectroscopy Analysis Technique

Infrared spectroscopy analysis technique has been used to identify optical density of seepage zones and chromed collagen preparation active groups before and after processing with polymeric compounds and dye (spectrophotometer TENSOR 37 (Brucer, Germany) (Stuart, 1997; Jie *et al.*, 2014; Sarver and Krueger, 1991; Maistrenko and Andreyeva, 2011). Samples of the collagen preparation (after processing with chrome tanning agent in the quantity of 10%) have been processed with polymeric compounds and dye in glass vessels, using the installation for agitation, under the following conditions: water consumption was 500%, temperature was 20°C, continuation was one hour and a half, polymeric compounds and dye consumption –

10% of the samples mass. Later the original and processed samples of the preparation were fined, pressed into a pill containing potassium bromide and sent to infrared spectroscopy test.

Microscopical Analysis Technique

To identify the depth of derma staining by dye we have used an optical microscope with 40-1000 times magnification Bresser Researcher Bino (Bresser, Germany).

RESULTS AND DISCUSSION

Infrared Spectroscopy Tests of the System "Chromed Collagen-containing Preparation – Polymeric Compounds – Dye"

On the infrared spectrogram of the chromed collagen preparation we can see the bands at the following frequencies the most distinctively: 3394, 1650, 1537, 1236 and 526 cm^{-1}, which correspond to oscillation of amides A, I, II, III, VI with various proportions of constituents; 1448, 1200, 1082, 1033 cm^{-1} of hydroxyl groups; 602 cm^{-1} of chromium compounds. Presence of different active groups (carboxyl, hydroxyl) in the structure of polymeric compounds shows ability of these materials to interact with active groups of collagen (Maistrenko and Andreyeva, 2011) (Figure 1).

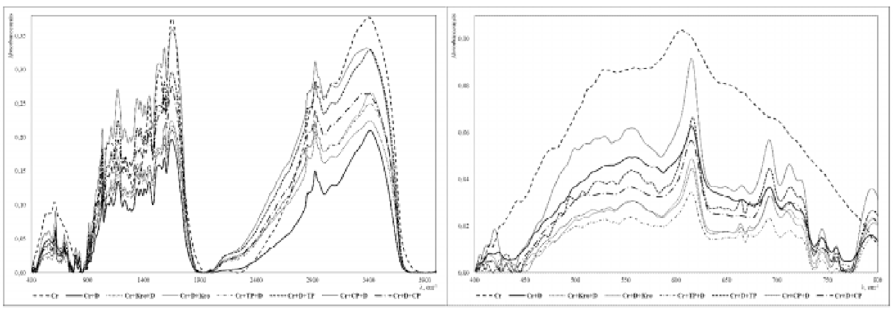

Figure 1. IR-spectrums of collagen-containing preparation after treatment by polymeric compounds and dye

Peaks intensity at the spectrograms of chromed collagen preparation (*Cr*), chromed preparation after processing with dye (*Cr+D*), polymeric compound and dye (*Cr+Kro+D, Cr+TP+D, Cr+CP+D)* or dye and polymeric compound (*Cr+D+Kro, Cr+D+TP, Cr+D+CP*) is caused by interaction between polymeric compounds and nitrogen-containing and hydroxyl collagen groups, as well as chromium complexes. Peaks intensity decrease and change of their pattern in the chromed collagen preparation at low frequencies can probably be explained by interaction between the dye and the polymeric compounds with creation of bonds of different types (hydrogenic, ionic etc.)

Wet-Blue Semi-Finished Product Processing

In order to simplify technological scheme and decrease materials consumption of the liquid finishing processes the use of polymeric compounds at the dyeing stage has been researched. Semi-finished product processing scheme has been chosen with the help of typical chromed leather production of upper of shoes made of cattle raw material: washing – neutralization – washing – dyeing – fatting – retanning with quebracho tannins. Tannins consumption in the control group was 4%, while in groups under study it was half as much as that (2%) due to polymeric compounds use. Polymeric compounds, which constituted 2% of shaved wet-bleu mass (in terms of dry residue), were added at both at the beginning (*b.d.*) and at the end of dyeing process (*a.d.*).

There were no complications during the processing of the groups under test. The leathers obtained were soft to the touch, filled (thickness output at 85-100%), heatproof. Even visually both facing and flesh surface looked bright and saturated.

Polymeric compounds influence on finished leather properties has been tested after coating with acryl. As compared to control group, tensile and surface strength of investigated leathers has increased by 1.1-1.5 times, percentage extension at the 10 MPa has gone up by 1.2-1.8 times, porosity – by 1.4-1.5 times, water absorption by capillary action – by 1.1-1.3 times, adhesion of finish to dry leather – by 1.4-2.2 times (table 3). Indices of bending force and abrasion resistance of dry friction of the coating, as well as those adhesions of finish to the wet leather are mostly the same as corresponding indices of the control group.

Table 3. Chemical and physico-mechanical properties of finished leather products

Index	Group						
	1	2	3	4	5	6	7
Polymer type	Kro b.d.	Kro a.d.	TP b.d.	TP a.d.	CP b.d.	CP a.d.	control
Mass content, %							
- humidity	14.1	14.2	13.4	14.6	16.2	13.3	14.1
- chromium oxide*	71.4	71.6	77.2	79.1	77.4	73.0	71.0
- hide substance*	4.3	4.9	4.1	4.8	4.8	4.1	4.9
- mineral substances*	6.3	5.6	5.8	5.2	5.9	5.9	5.2
- substances, extracted with organic solvents *	6.1	10.7	9.0	9.5	7.5	5.4	9.8
Tensile strength, MPa	19.8	12.7	13.1	18.7	11.1	14.1	11.8
Strength of surface, MPa	17.5	12.0	12.2	14.1	10.9	12.9	11.8
Percentage extension at 10 MPa, %	42.5	52.5	64.5	43.0	80.5	53.5	35.0
Porosity, %	54.3	53.1	54.4	56.0	53.2	56.8	38.5
Water absorption by capillary action (wicking), min	333	290	303	342	253	316	256
Water vapour permeability, $mg/cm^2 \cdot h$	3.3	2.9	3.1	3.3	2.8	4.1	4.0
Bending force, points	4	4	4	4	4	4	4
Abrasion resistance, terns							
- dry friction	>500	>500	>500	>500	365	>500	>500
- wet friction	98	136	82	57	61	100	80
Adhesion of finish, N/m							
- dry leather	574	545	349	360	493	488	257
- wet leather	129	133	130	110	225	127	126
Depth of derma staining by dye, %	50	40	40	40	80	25	40
Colouring uniformity, ΔE	0.0	3.2	7.9	1.3	2.5	2.3	9.2
Surface coating thickness, g/dm^2	0.25	0.25	0.33	0.25	0.20	0.25	0.31
Yield of area, %	95.0	100.0	90.0	110.0	100.0	80.8	85.5

Thus, according to the results of this series of tests, we can note that application of polymeric compounds based on maleic acid before dyeing of chrome leathers is the most advisable. The reason for this is that such processing technique provides the whole range of necessary consumer properties of chrome leather (strength, softness, filling, shaping, bright and even colouring and quality coating, good hygienic properties).

CONCLUSION

In order to simplify the technological scheme of processing and to decrease materials consumption of the liquid finishing processes the use of chrome leather, processed with polymeric compounds, based on maleic and acrylic acids, before and after dyeing process has been researched. We have also identified efficient conditions of liquid finishing, which require a semi-finished product processing with polymeric compound *Kro* in the amount of 2% before dyeing at the temperature of 50 ^{o}C during 1.0-1.5 hours (water consumption 200%). Previous and further processing using typical procedure are also required. It has been proved by experiment that the usage of investigated polymers during liquid finishing improves both usability and cutting properties of chrome leather, such as quality of colouring and coating. At the same time, they allow us to use deficient and expensive material resources, such as leather raw materials and vegetable tanning agents, more effectively.

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