UDC 675.024 : 675.088

***Olena Mokrousova***
Kyiv National University of Trade and Economics (Doctor of Technical Science, Professor, Ukraine)
olenamokrousova@gmail.com, http://orcid.org/0000-0001-5061-3292
***Olena Okhmat***
Kyiv National University of Technologies and Design (PhD, Associate Professor, Ukraine)
oxmat.oa@knutd.edu.ua, https://orcid.org/0000-0003-0927-8706
***Maryna Zhaldak***
Kyiv National University of Trade and Economics (PhD, Assistant, Ukraine)
m.zhaldak@knute.edu.ua, https://orcid.org/0000-0002-4490-8673

# STUDY OF ECOLOGICAL TECHNOLOGY OF LEATHER TANNING WITH THE USE OF MODIFIED MONTMORILONITE

*The article is devoted to the analysis of the level of environmental friendliness of the chromium tanning process carried out with the use of modified montmorillonite.*

*Leather technology has a complex technological sequence of processes and operations for the processing biogenic material. The leather technology is based on a set of various, consistently performed processing of leather raw materials and semi-finished products. The technology uses chemical materials that are not always environmentally friendly. The principles of greening provide for complete or partial exclusion of environmentally unfriendly materials from technological processes. The eco-destructive impact on the environment of chromium tanning was established. Therefor an innovative direction of eco-friendly leather production is the partial replacement of tanning compounds of chromium with other structuring compounds that have a structuring effect.*

*The aim of the work was to determine the ecological efficiency of the technology of manufacturing leather obtained using modified montmorillonite. The object of research is the process of formation of leather properties in the process of tanning with the use of modified montmorillonite.*

*Environmental friendliness of chromium tanning technology with the use of modified montmorillonite is substantiated by: efficiency of formation of dermis structure; increasing the level of leather quality indicators; partial replacement of chromium compounds during tanning.*

*The technology provides: reduction of the negative impact on the environment of leather production; reducing the amount of chromium compounds in the tanning process; reduction of production costs for purification of waste liquids; increasing indicators of biological and chemical oxygen consumption; obtaining after tanning potentially biodegradable wastewater.*

*Key words: ecological compatibility, natural leather, chrome tanning, modified montmorillonite, environment, quality.*

**Introduction.**

Natural leather is a versatile material. The range of leathers includes leather for shoes, garment leather, leather for haberdashery, etc. The leather must have high vapor permeability, strength, ability of a material to endure alternate wet and dry conditions for a long period without considerable deformation and loss of mechanical strength.

The production of natural leather is a multi-stage technology of the biogenic origin material treatment. The technology involves the sequential conduct of chemical processes and mechanical operations. The chemical materials used in the technology contribute to the production of high leather quality. In this case, the materials can have a negative impact on the environment. In the leather production, the environment is affected by: by-products; waste; emissions into the atmosphere, soil, water, etc. Production is accompanied by the formation of industrial wastewater, noise, vibration, various types of radiation and more.

Leather production in the amount of waste is one of the first places among industrial enterprises. Leather by-products and wastes account for up to 50% by weight of raw materials [9]. In addition, the tannery uses 10-30 $m^3$ of water to process 1 ton of raw materials. Thus, there are a number of problems: increasing the burden of production on the environment; the need to build powerful treatment plants; inefficiency of traditional methods of wastewater treatment, etc. Leather production can deplete natural resources, pollute water bodies and soil, and change the ecological characteristics of the territory. That is why environmental aspects are crucial for improving the technological processes of leather production.

**Theoretical foundations of the study.**

In the leather production, the dermis is the main object of chemical, physic-chemical and mechanical transformations. The main protein of the dermis is collagen. During the execution of technological processes, the structure of collagen changes. As a result of processing, the bonds in the protein itself are broken or formed; a new spatial structure appears, and so on.

Leather technology is used 70 % liquid. The processes are carried out in working solutions using water and a complex of chemical materials. As a result of processing a large amount of waste liquids is formed. Liquids contain a significant amount of unused chemical materials that can pollute the environment.

The technological cycle of natural leather production includes preparatory, tanning, semi-finishing and finishing processes and operations. The main indicators of the quality of natural leather are formed during tanning processes. Traditionally, chromium compounds are used for tanning leather [12]. About 90 % of natural leather in the world is made using chromium compounds. Chromium compounds are the most available, relatively cheap, universal and effective tanning material. But there are a number of environmental problems associated with the ingress of chromium into the company's wastewater. The problems are due to the fact that a third of the chromium compounds used in production are in waste solutions [7]. The release of chromium salts into nature causes pollution and irreversible changes in the ecosystem. Chromium is a necessary element involved in metabolism and metabolism in humans. But high concentrations of chromium are toxic. Chromium (VI) compounds are today among the most dangerous pollutants in the aquatic environment [1].

Leather tanneries s discharge wastewater into reservoirs only if sanitary requirements are met. The main indicator of the amount of pollutants in wastewater is the value of biological oxygen demand (BOD). The indicator characterizes the pollution of wastewater with organic matter and ammonium compounds. But it is impossible to be limited to one indicator of BOD. A clearer idea of the total pollution of industrial wastewater is given by the indicator of chemical oxygen demand (COD). The indicator characterizes wastewater pollution by organic and inorganic compounds. Determining the indicators of BOD and COD makes it possible to assess the ability of wastewater to biodegrade. Indicators indicate the chemical and biological impact of technology on the environment.

The reducing the environmental impact of wastewater from leather tanneries on the environment can be solved by completely abandoning the use of chromium tanning in the technological cycle or partial replacement of chromium tanning with alternative eco-friendly compounds.

One of the innovative areas of greening of leather production is the partial replacement of chromium compounds with other structuring compounds [2, 3, 8]. In practice, often use aluminum, zirconium or titanium tanning agents, synthetic tanning agents, water-soluble polymer compounds, materials of natural origin. The use of natural highly dispersed minerals, such as montmorillonite, for tanning is promising.

The purpose of the work – to determine the environmental efficiency of the technology of production of leather obtained using modified montmorillonite.

**Experiment.**

The object of research - the process of forming the properties of leather in the tanning process using modified montmorillonite.

The subject of research - studying the environmental friendliness of tanning technology using modified montmorillonite.

The main tasks of the work:

– testing of tanning technologies in the laboratory,
– evaluation of the effectiveness of the formation of the structure of the dermis of natural leather,
– evaluation of the ecological condition of waste tanning solutions.

Grain split was used to obtain leathers in the study. Pelt was obtained from raw materials of cattle after the pickling process. The technological scheme of obtaining pelt provided for the processing of raw materials according to the traditional technology of leather production for upper shoe [4].

The basic chromium sulfate with basicity 33 % was used as a chromium tanning agent.

Bentonite clays of Dashukovsky deposit (Ukraine) was used for investigation. Montmorillonite dispersion was modified in stages by sodium carbonate and basic chromium sulfate.

Physic-chemical and physic-mechanical methods were used to evaluate the effectiveness of montmorillonite during tanning [5]. The effectiveness of the use of modified montmorillonite to improve the environmental friendliness of the tanning process was evaluated by the level of BOD and COD. In the work determined the degree of development of tanning solutions [5].

To obtain leathers the traditional method of tanning with chromium compounds was used to obtain leathers. The total amount of chromium tanning agent for tanning was 1.8% of chromium oxide by weight of the pelt.

Modified montmorillonite dispersion was used for the alternative tanning method. To obtain dispersion, montmorillonite was dispersed with sodium carbonate. The consumption of sodium carbonate for dispersion was 6% of the dry weight of the mineral. The resulting montmorillonite dispersion was treated with chromium sulfate. The treatment was performed to cation the surface of the montmorillonite particles. The consumption of chromium oxide for cationization was 10% by weight of the mineral. The resulting dispersion was used for tanning in the amount of 1.25% of dry mineral by weight of the pelt.

Pelts for tanning were formed into two treatment options. The tanning of was carried out according to the standard technology leather for shoes [4]. The technology involved the implementation of the tanning process, increasing the basicity of tanning compounds, laying of the semi-finished product after tanning.

Studies of quality indicators were performed on samples of tanned leather after fat-liquoring and drying. Preparation of samples for research was performed in accordance with the requirements of regulations. Preparation for chemical analysis was carried out according to State Standard of Ukraine ISO 4044: 2020, for physical and mechanical tests – according to State Standard of Ukraine EN ISO 2419: 2020.

The quality of the experimental leathers was determined according to the indicators of State Standard of Ukraine 2726-94 "Upper Leather. Specifications".

**Results and discussion.**

The presented results of the comparative characteristics of the leather quality allow us to assess the effectiveness of tanning using modified montmorillonite (Table 1).

Table 1 **- Indicators of quality of natural leather and characteristics of the tanning process**

| № | Index | Technology: | | Relative changes in indicators *, % |
|---|---|---|---|---|
| | | unified | alternative | |
| 1 | Consumption tannin agent, %, by weight of the pelt | 1,8 | 1,25 | -30,6 |
| 2 | Exhaustion of tanning solution, % | 57,4 | 69,5 | -17,4 |
| 3 | Shrinkage temperature, ºC | 112 | 106 | -5,4 |
| 4 | Moisture content in the leather, % | 11,3 | 12,1 | +6,6 |
| 5 | Chromium oxide content in the leather, % | 4,3 | 4,7 | +8,5 |
| 6 | Protein substance in the leather, % | 72,5 | 60,1 | -17,1 |
| 7 | Yield of area, % | 100,0 | 104,9 | +4,9 |
| 8 | Rigidity of the leather, cH | 2,3 | 1,9 | -17,4 |
| 9 | Air permeability of the leather, $cm^3/cm^2$ per hour | 648,0 | 985,0 | +34,2 |
| 10 | Indicator of BOD, mg $O_2$/l | 1478,3 | 1357,6 | -8,2 |
| 11 | Indicator of COD, mg $O_2$/l | 6365,5 | 4242,6 | -33,4 |
| 12 | Correlation of BOD / COD | 0,23 | 0,32 | +28,1 |

**– a "minus" sign indicates a decrease in the indicator, a "plus" sign indicates an increase in the indicator*

Analysis of the data in table 1 shows the high quality of the leathers of the alternative method of tanning. The results are achieved even by reducing the amount of tanning. Reduction of tanning agent compared to standard technology is significant and is 30.6%. Reducing the amount of tanning did not affect the formation of heat resistance of the leather. The welding temperature of the experimental leathers is 106 ºC. Requirements for the formation of a certain level of shrinkage temperature (more than 100 ºC) of chrome shoe leather are met.

Analysis of the indicators indicates an increase in the degree of development of chromium compounds during tanning in the case of montmorillonite by 17.4%. In our opinion, the increase in the efficiency of derma absorption of chromium compounds is due to the presence of a highly dispersed mineral. Montmorillonite has a highly developed sorption surface and creates additional active centers in the dermis structure for binding to chromium compounds. Additional bonding helps to efficiently test the working solutions and reduce the load on the environment. The result of additional sorption of chromium in the presence of montmorillonite is also an increase in the content of chromium oxide in the leather by 8.5% compared to unified technology.

The effective formation of the dermis structure in the technology of tanning with the use of modified montmorillonite has been revealed. The analysis of the indicators shows an increase in leather yield by area of 4.9%, an increase in leather softness by 17.4%, air permeability by 34.2%. The growth is due to the properties of modified montmorillonite. During the modification of the mineral with alkaline reagents, structural sizes of montmorillonite of different sizes are formed. Particles of modified montmorillonite contribute to the formation of the structure at the level of ultra-, micro- and macropores [10]. The adhesion of the collagen structure of the dermis is reduced. This helps to increase the formation of the structure of the dermis as a whole.

In order to assess the environmental friendliness of the technologies used in the study, the ability of waste liquids to biodegrade was determined. The analysis of the level of BOD and COD indicators of waste liquids shows a decrease in the indicators for tanning technology with modified montmorillonite. In comparison with the typical tanning technology, the BOD indicator decreases by 8.2%, and the COD indicator – by 33.4%. The decrease in indicators indicates an improvement in the biodegradability of wastewater.

An important indicator of reducing the eco-destructive impact of leather production on the environment is the level of the ratio of BOD / COD. According to this indicator, the ability of wastewater to biodegrade is estimated in the range from 0 to 1 [6, 11, 13, 14]: BOD / COD less than 0.3 – wastewater is very difficult to biodegrade, the company needs to involve excipients (coagulants or flocculants, etc.); BOD / COD is 0.3-0.6 – wastewater is considered potentially biodegradable within a certain period of time; BOD / COD is greater than 0.6 – wastewater is capable of self-biodegradation and does not have an negative effect on the environment.

According to the typical tanning technology, the ratio of BOD / COD is 0.23, according to the alternative - 0.32. The wastewater of typical chromium tanning technology should be classified as liquids that are difficult to biodegrade. Wastewater from tanning technology using modified montmorillonite is considered potentially biodegradable within a certain period of time. Reduction of eco-destructive impact on the environment of the alternative technology is significant. The ability of wastewater to biodegrade increases by 28.1% compared to standard technology. The data indicate the expected savings of the leather company for wastewater treatment using alternative tanning technology, which will be the focus of further research.

**Conclusions.**

The efficiency and environmental friendliness of the introduction of chromium tanning with the use of modified montmorillonite were evaluated.

The use of alternative tanning technology ensures high quality leather. Compared with the typical technology, there is a decrease in leather rigidity by 17.4%, an increase in air permeability of the leather by 34.2%. The increase in the yield of leathers of the alternative tanning by area by 4.9% predicts an increase in the company's profit.

The reduction of ecological impact on the environment as a result of partial replacement of chromium compounds has been established. The statement is proved by a decrease of 30.6% in the consumption of chromium compounds for tanning, an increase of 17.4% in the degree of their development. An increase in the ability of wastewater to biodegrade due to a reduction in the level of biological oxygen consumption by 8.2% and chemical oxygen consumption by 33.4%. Reduction of ecological load on the environment as a result of application of tanning with use of the modified montmorillonite makes 28,1%. Wastewater are considered to be potentially biodegradable.

The environmental friendliness of the technology of tanning leather with the use of modified montmorillonite is justified by: partial replacement of chromium compounds during tanning; increasing the degree of absorption of chromium compounds; reducing the negative impact of leather production on the environment; the expected reduction of the company's costs for wastewater treatment; reduction of biological and chemical oxygen consumption.

**Prospects for research.**

Further studies of the implementation of chromium tanning using modified montmorillonite will be aimed at evaluating the cost-effectiveness of the proposed method of tanning using modified montmorillonite at the stage of tanning.

It is also advisable to continue research in the direction of:

- replacement of chromium sulfate in the modification of montmorillonite with compounds of other metals (for example, aluminum);

- study of the targeted effect of montmorillonite dispersions on the transformation of the collagen structure of the dermis during tanning;
- achieving a greater degree of testing of working tanning solutions.

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