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## GETTING LINING LEATHERS WITH IMPROVED ANTIBACTERIAL PROPERTIES

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## ОТРИМАННЯ ШКІРЯНОЇ ПІДКЛАДКИ З УДОСКОНАЛЕНИМИ АНТИБАКТЕРІАЛЬНИМИ ВЛАСТИВОСТЯМИ

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*Solution of materials microbial resistance problems is related to the study of the nature and extent of changes in chemical and physical structure of the material and the preservation of its inherent complex of operational and technological properties. The positive impact of mineral filler of semi-finished leather to its physical, mechanical, and some hygienic characteristics has been noted. However, the issue remains open for providing leather materials, especially insole and linen skins, with long biostable antiseptic properties, and points to the urgency of the problem to be solved. Rationality of the research results will be in the creation of innovative technology for tanneries biostable materials through the creation of low-cost multifunctional biocidal products to ensure a high biological activity, a wide range of action, safety for humans, and at the same time available and cheap.*

***Key words:*** *lining skin, cationic polyelectrolyte, polyhexamethylene guanidine hydrochloride, zeolite, montmorillonite, biocide, antibacterial properties*

*Вирішення проблем мікробної стійкості матеріалів пов'язане з вивченням характеру і ступеня зміни хімічної та фізичної структури матеріалу та збереження комплексу технологічних властивостей. Відзначено позитивний вплив мінерального наповнювача напівфабрикату на його фізичні, механічні та деякі гігієнічні характеристики підкладкової шкіри. Раціональність результатів досліджень полягає у створенні інноваційних технологій для шкіряних матеріалів шляхом створення недорогих багатофункціональних біоцидних продуктів для забезпечення високої біологічної активності, безпеки людей та одночасно*

*доступних і дешевих.*

***Ключові слова:*** *підкладкова шкіра, катіонний поліелектроліт, полігексаметилен гуанідин гідрохлорид, цеоліт, монтмориллоніт, біоцид, антибактеріальні властивості.*

**Introduction**

Problems of improving the quality, reliability and the biological stability of the finished product is inextricably linked to the quality of the materials used to produce it. The widespread use of substandard materials for manufacturing of footwear crucially influences comfort of shoes, contributing to the creation in inner part of the shoe the environment that accelerates development of harmful microorganisms. In addition to direct action associated with damage to the structure of the skin, bacteria reduce hygiene and physiological properties of the footwear. This contributes to premature wear of joints and, consequently, self-development of pathogens inside the shoe [1], which negatively affect the human body.

The relevance of this study is due to demand in developing biocidal agents for leather materials and products that do not pollute the environment, withstand microorganisms of different taxonomic groups (bacteria, fungi, etc.), have a long term protective actions, are available and cheap.

Protection of shoes and, accordingly, the user's feet from the ravages of pathogens is closely associated with increased bio-stability of interior materials of shoes – materials of first category that are in direct contact with the skin of the foot and are standardized by QEKO TEX Standart 100. Finding ways to increase the biological stability of lining and insole materials using biocide drugs that are able to resist micro-organisms of different taxonomic groups (bacteria, fungi, etc.), have a long-term protective action, do not pollute the environment and at the same time are available and cheap, this area of research is urgent and promising.

The task of increasing the biological stability of materials has two solutions:

- application of biocidal disinfectant on the surface of the material or the finished product;
- formation of microbiological resistance of the material together with the other functional and application properties in the production process.

Solution of materials microbial resistance problems is related to the study of the nature and extent of changes in chemical and physical structure of the material and the preservation of its inherent complex of operational and technological

**Problem**

1. Creating multifunctional polymeric biocide formulations using natural minerals zeolite, montmorillonite and polymeric guanidine derivatives for antibacterial and antifungal leather treatment.

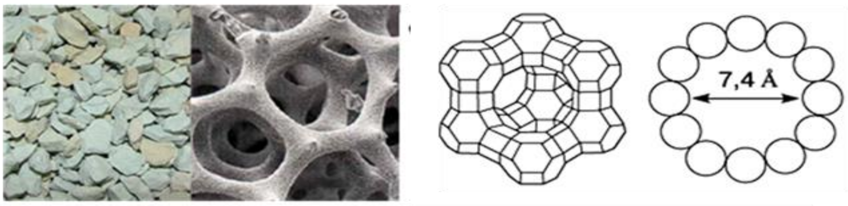
2. Introduction of polymeric biocides into leather texture as a filler at post tanning leather manufacturing processes.

3. Getting bio-resistant leather materials, especially lining and insole leather, using environmentally friendly, non-toxic, cheap and available materials, which significantly improve the physiological and hygienic properties of footwear and other leather products.

**Objects and methods of research**

Minerals of various crystal-chemical structure zeolite and montmorillonite, polymeric guanidine derivatives (PGMG-GC), semi-finished leather for lining and insole, as well as model collagen preparation (gelatine) will be used for the study. To modify the minerals alkaline peptizing agents will be used that are capable of dispersing the mineral particles in suspensions, align their electrical inhomogeneity and create anionic structured and aggregate stability system.

Chrome semi-finished product from cattle raw material (thickness 1,2-1,4 mm), outgrowth (thickness 1,1-1,3 mm) and pig skin lining (thickness 0,6 – 0,8 mm) has been used for testing as objects of research for shoe uppers. At the stage of filling and retanning of semi-finished leather, instead of expensive mineral filler Tanicor FTG of company "Clarian" (Poland) modified dispersion of natural minerals were injected into the structure of the dermis - the most common types of aluminosilicate extracted in Ukraine: zeolite (fraction 0,02-0,08 mm ), which has a solid frame tetrahedral skeleton with a system of cavities and channels (Figure 1) and montmorillonite, which by the nature of the crystal lattice refers to a clay layered hydrated silicate of alumina of lamellar structure. Deprived of water zeolite is a microporous crystalline "sponge", in which the pore volume




а б в

*Fig.1. The appearance of natural zeolite (a), its image of microporous (б) and crystal (в) structure with large and small pores, formed by sodalite units (zeolite Y)*

**Zeolite** - $M_{m/n}[(Al_2)_x(Si_2)_y] \times zH_2O$
(TU 14.5-00292540.001-2001) - Sokyrnytsky field, Transcarpathian region., Ukraine.
The main mineral is **clinoptilolite.**

is up to 50% of the zeolite framework (Figure 1, b).

This "sponge", with a diameter of ports from 0,3 to 1,0 nm is high adsorbent. Features of adsorption on zeolites are due to the fact that tracery of crystal structure creates a large adsorption volume (0.54 $cm^3$ to / g), and its geometry determines molecular sieve properties

To modify the selected minerals alkaline rubber peptizing agent hexametaphosphate of sodium $(NaPO_3)_6 \times 6H_2O$ of 10% of the dry weight of the mineral, which is able to disperse mineral particles in suspension, align electrical inhomogeneity and create anionic structured and stable aggregation systems.

To assess the effectiveness of formation of leather structure and definition of its functional properties resulting from the modification with modified dispersion of montmorillonite (MDM), zeolite (MDZ) and their mixtures (MDZ:MDM) a set of traditional chemical, physical, chemical, physical, mechanical and several modern research methods including spectroscopy, chromatography, differential thermal analysis DTA, TGA thermogravimetric analysis and derivative of thermogravimetry DTG, methods of mathematical analysis and planning of the experiment have been used.

For technological investigation, semi chrome finished item of light steers from butt was used (Fig.2). The raw material treatment was performed according to traditional technology of chrome leather for the upper of shoes production used by Public Joint Stock Company ″Chinbar″.

It is well known that organic compounds containing in their structure the guanidine moiety, possess antibacterial properties and are used as therapeutic drugs and fungicides. They are not inactivated with proteins and at the same time biodegradable and therefore are widely used as a physiologically active substances, drugs, antiseptics, pesticides [1,2].

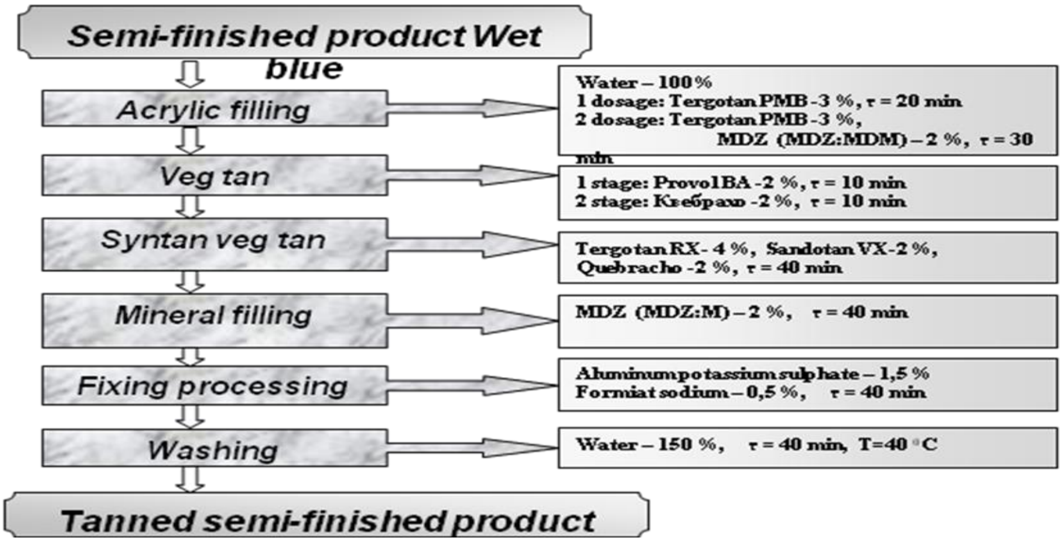



*Fig. 2. Technological scheme of filling-tanning process of leather semi-finished product modified with zeolite dispersion*

Hexamethylenediamine is an antibacterial, antiseptic, sterilizing and preventing coming into existence „ugly" of smells element in polymer. Guanidine groups are giving it cationic character. It is a well known and willingly applied biocide, eliminating both Gramm positive and Gramm negative bacteria, some viruses, yeast, mushrooms, unicellular algae. On the world market it is available in the form of the salt of inorganic acids, most often hydrochloride - CAS 57028-96-3 and phosphate CAS 89697-78-9. Additionally PHMG is high thermal resistant, non-inflammable and stable chemically in very wide range of pH (1-10) [3,4].

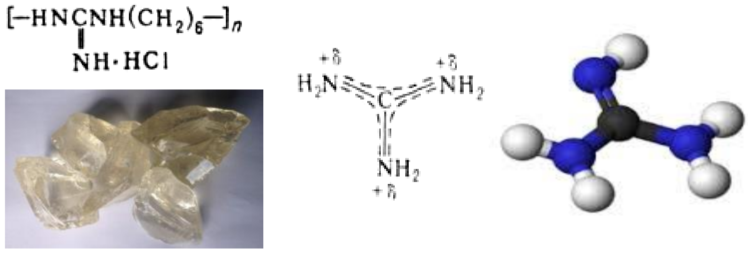


*Fig. 3. Polyhexamethylene guanidine hydrochloride*

Destructive PHMG (Fig.3) action against microorganisms is being explained by the fact, that positively charged polymer is being pulled to contrary charged cell walls of the micro-organism, what is making it impossible to expel ions of potassium from cells by and causes the diffusion of nucleotides. Simultaneously it is non-toxic for people, isn't causing irritation to the skin, eyes and mucous membranes. The index of the toxicity for micro-organisms is 3000 times bigger than for people and terrestrial animals (for the rat orally $LD_{50}$=610 mg/kg, for the skin contact $LD_{50}$>2000mg/kg). Moreover it is compatible with the majority of remaining elements of disinfectants and doesn't influence their form - perhaps to be applied in compositions for forms of liquid, cream, gel, aerosol, emulsion, pastes, etc. It is possible to apply it with other available germicides so as the copper sulphate, zinc sulphate, quaternary ammonium salts, hydrogen peroxide and peracetic acid in the concentration much smaller than in case of other disinfectants. It shouldn't been linked with anionic surface-active agents so as soaps or alkyl- and aryl- sulphonates, because it can cause their throwing solution off [4-6].

Due to the high incidence of guanidine its bactericidal activity has been well studied.

The apparent advantage of guanidine is a low human toxicity and virtually no corrosion activity in respect to most materials [7]. Moreover, guanidine is capable of forming a film on the treated surfaces, allowing suggesting the prolonged activity of the surface treatment of agents without subsequent rinsing.

**Results and discussions**

The research results of chemical and physical changes that occur under the influence of heat between macromolecules of collagen and particles of mineral, changes in the degree of structure crystallinity of the dermis and the internal heat capacity of the system support the hypothesis of a thermal stabilization of the structure of collagen involving acrylic-mineral composition and its partial transition from amorphous to crystalline state. Thermal impact facilitates phase transformation in the structure of the dermis and the transition to a more sustainable modification that determines rate increase of thermal stability of investigated skins [8,9].

Analysis of differential thermal curves (Fig. 4) allows asserting effective regulation of the dermis structure at different levels of its organization by sealing micro and mesostructure.

The results of thermal studies show that the thermooxidative destruction of filled dermis collagen is a multistage process that takes place in at least two stages.

The first stage takes place in the temperature range 25 ... 125 ° C and is characterized by almost the same amount of weight loss of all samples (~ 10%) and low speed 1.61 ... 2.0 mg / min. At this stage of thermal destruction modified mineral fillers help to reduce speed destruction of skin samples compared to the control sample. It also confirms the value of activation energy, which is 18

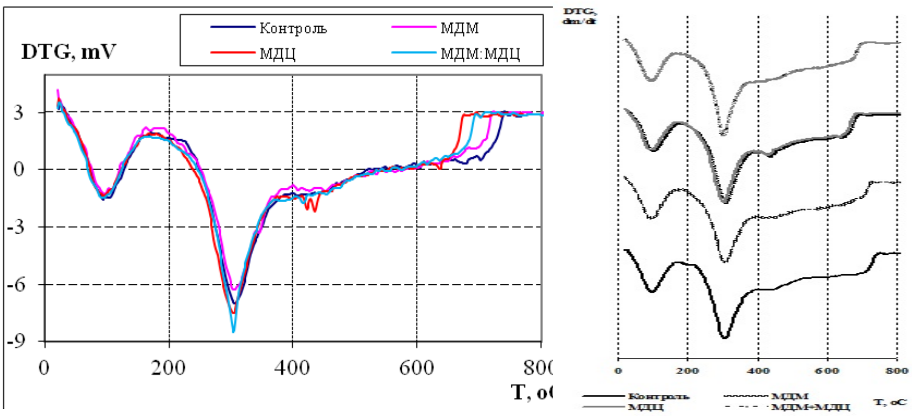



*Fig.4 Differential thermogravimetric curves of the samples of filled skin*

... 24% more (90.3 ... 92.5 kJ / mol to 76.4 kJ / mol) than in the control sample. The growth of activation energy of skins filled with mineral compositions may indicate the formation at the structure of the dermis additional physical and physical-chemical bonds type hydrogen and Van der Waltz, which will strengthen the structure of the treated leather and a certain increase in thermal resistance [10].

This process is likely also associated with dehydration of mechanically bound water in the process of heating of samples as well as the formation of new hydrogen bonds between the structural elements of the skin by removing water and seal of structure.

**Conclusion**

To sum up, there are grounds for the assumption of the possibility of obtaining biostable lining and insole leather through the development of highly active biocide compositions based on natural minerals and polymer derivatives of guanidine and then applying them as a filler to the semi-finished leather at post tanning leather production processes.

Rationality of the results of the project will be the creation of an innovative technology for obtaining bio stable leather materials through the creation of low-cost multifunctional biocidal products to ensure a high biological activity, the widest range of action, safety for humans and the environment, and at the same time available and cheap.

Physiological and useful properties of the shoe will be improved, as the risk of possible negative influence of the material on the skin of the foot will be reduced. The project also includes the development of methods for studying the mechanisms of processes of adhesion, sorption, diffusion and fixation of biocidal products with leather collagen.

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## ДОСЛІДЖЕННЯ ЯКОСТІ БАРВНИКІВ ДЛЯ ХУТРА

Лапа О. А., Мокроусова О. Р.

## RESEARCH OF QUALITY DYES FOR FUR

Lapa Oleksandra, Mokrousova Olena

*В статті наведені результати дослідження впливу різноманітних факторів на процес фарбування хутрових шкурок кролика кислотними барвниками американської компанії «Lowenstein». Визначено властивості волосяного покриву після фарбування цими барвниками.*