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MODIFIED POLYSACCHARIDES APPLICATION FOR ANTISEPTIC LEATHER PROCESSING

Urgency of the research. *The leather is very sensitive to microbial degradation during processing, storage, transportation and use. Therefore, it is important to search for preparations and methods of leather treatment, providing specific fungicidal properties, depending on the purpose.*

Target setting. *To establish the possibility of using a composition based on modified polysaccharides with the addition of PVA and Quaternary ammonium salts for leather treatment to give fungicidal properties.*

Actual scientific researches and issues analysis. *Recent open access publications have been reviewed regarding polymeric materials, antiseptic and fungicidal preparations used to obtain of insole leather with special properties.*

Uninvestigated parts of general matters defining. *The principle of action of many fungicidal or bactericidal products when used together has not been established. In particular, in the case of the simultaneous use of modified polysaccharides and quaternary ammonium salts for antiseptic treatment of the leather.*

The research objective. *The purpose of the work is to research antiseptic properties of the coating based on modified polysaccharides with the addition of quaternary ammonium salts (QASc) for insole leather.*

The statement of basic materials. *It is established that the polymer composition based on modified starch and polyvinyl alcohol with the addition of a quarter of ammonium salts gives the leather antiseptic properties, this is proved by the delay of growth of microorganisms by 3-4 mm from the edge of the sample. The relative air permeability of the leather is reduced by almost half (from* $1.18 \cdot 10^3$ *to* $0.54 \cdot 10^3$ $cm^3 / cm^2 \bullet h$*), the leather porosity is also reduced by 5-10 % and the stiffness is increased by 40 %.*

Conclusions. *As a result of the conducted researches it is established that although treatment of leather surface by a solution CMS: PVA and QASc reduction of the tensile strength of leather but in its physical and mechanical properties the treated leather meets the requirements for the lining, has antiseptic properties and can be used for the manufacture of insoles.*

Keywords: *modified polysaccharides; antiseptic treatment; leather; quaternary ammonium salt.*
Table: 2. References: 18.

Introduction. During the operation of leather shoes, its internal parts (insole and lining) are subject to a complex of mechanical loads with simultaneous action of sweat, heat, moisture and microorganisms [1]. One of the effective methods of increasing the resistance of the leather to microbiological damage is the treatment of fungicidal and bactericidal preparations. There is a method of obtaining leather for shoes [2], which involves the processing of semi-finished wet-blue such a composition containing bactericidal and fungicidal agent. Triclosan, biguanidine, isothiazolinone, Quaternary ammonium compounds can be used as the bactericidal preparation. As a fungicide, propiconazole, thiabendazole, tebuconazole, zinc compounds can be used. Due to this treatment, the antimicrobial properties of the leather are preserved after at least 5 washing cycles. The use of 2- (thiocyanomethyl-thio) benzothiazole (TCMTB) as a fungicidal drug is proposed for the treatment of leather intended for the manufacture of army shoes [3].

The essential oils of thyme can be used as a preservative in a mixture with a synthetic biocide. In this case the amount of the necessary synthetic biocide can be reduced from 0.2 % to 0.05% of the wet-blue mass. The use of such mixture could solve two problems at once: firstly, by decreasing the amount of synthetic preservative needed for leather treatment and thus reducing the irritant effect on consumers, and secondly, by decreasing the amount of essential oil, which is fairly expensive [4].

Target setting. Microbiological destruction of the leather is accompanied by the occurrence of cracks, folds, grooves, shrinkage of the leather area and increase it thickness, reducing the strength of whole leather and its surface, increasing the stiffness and brittleness, darkening the color and may cause mycoses for some people. In order to prevent the appearance and development of various types of microorganisms, to improve leather resistance to biological attack and to prevent thedeteriorationof the physical-mechanical and chemical properties of leather, it is treated with certain biocides. Antimicrobial agents (biocides), currently used in the leather industry, are generally harmful to human health and the environment, and their use has been or shall be restricted or even banned [5].Therefore, it is relevant to search for preparations and methods of leather treatment to give it specific fungicidal properties, depending on the purpose.

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Actual scientific researches and issues analysis. Polymers with antimicrobial properties are a valuable alternative to conventional antibiotics and are actively used for coatings, food packaging, personal care products and biomedical applications.A natural polymer – casein and ZnO nanoparticles are known to be used for the production of antimicrobial films that improve mechanical properties, water resistance and antibacterial activity against *S. Aureus and E. Coli* [6].

Antibacterial [7], antifungal [8] and antiviral properties [9] of chitin and its derivatives make them attractive for wide application, from nutrition and cosmetics to biomedicine and environmental protection. Chitin and its derivative - chitosan belong to the class of polysaccharides, the typical representative of which is cellulose. Chitin ranks second after cellulose in nature. Although its use is limited due to the specificity of obtaining chitin. The antibacterial properties of chitosan can be useful in the production of durable paper intended for the restoration of historical and cultural heritage [10]. There is a method of treatment with chitosan to impart antibacterial properties to cotton fabrics [11]. However, it should be noted that the antimicrobial properties of chitosan appear only in high enough concentrations, which when applied to the surface of the tissues may impair their breathability.

The interest in starch as an antimicrobial agent carrier is accrued from its film-forming properties and high molecular weight. Although, the poor solubility of starch in cold water limits its potential applications. Thus, starch modification is desirable not only to mitigate these challenges but also to bring about other functional properties [12; 13].

Durable antimicrobial wool fabrics were prepared by using a simple chemical finishing process. Carboxylate groups in wool protein were employed to form ionic interactions with cationic antimicrobial agents, such as cetylpyridinium chloride (CPC) and other quaternary ammonium salts, under the isoelectric point of wool protein, and such interactions were proven effective. The uptakes of the agents were dependent on their chemical structures, pH values of treatment solutions, concentration of the agents, and treatment temperature. The ionic interactions between the agents and the protein could survive repeated washing, with CPC showing the best durability among three tested quaternary ammonium salts [14; 15].

Quaternary ammonium compounds (QACs) are widely used in disinfection of water, surfaces and instruments as well as in textile, leather and food industries because of their relatively low toxicity, broad antimicrobial spectrum, non-volatility and chemical stability [16; 17].

Uninvestigated parts of general issues defining. The mechanism of the simultaneous action of sweat and microorganisms on the leather is not clear. So is the principle of action of many fungicidal or bactericidal preparations when used jointly. In particular, in the case of the simultaneous use of modified polysaccharides and quaternary ammonium salts for antiseptic treatment of the leather.

In particular, according to the authors [18], the antifungal and antimicrobial properties of chitosan are due to its polycationic nature, whereby it can bind to negatively charged macromolecule residues on the surface of bacterial cells and thus slow their growth. Moreover, the antimicrobial properties of chitosan depend on many factors, in particular the type of chitosan, its molecular weight, pH and solution concentration.

The research objective. The purpose of the work is to research antiseptic properties of the coating based on modified polysaccharides with the addition of quaternary ammonium salts (QASc) for insole leather. The influence of coating composition content based on polyvinyl alcohol (PVA), modified starch (CMS) and QASc as antimicrobial additives on antiseptic properties of insole leather was investigated. To optimize parameters for obtaining of antiseptic coating composition and its application, its rheological properties, permeability, density and porosity of the treated leather were determined and mechanical tests were performed.

The statement of basic materials. The study was conducted on samples of semi-finished leather, obtained from pig leathers. The thickness of the test samples was 1.5-1.6 mm. Beamhouse and tanning processes and operations were performed by conventional methodic for production of chromium leathers at JSC "Chinbar" (Kyiv).

Carboxymethylated starch (CMS) (TU U 6- 04872 671.061-96) was used as a polymeric matrix for biocide finished leather:

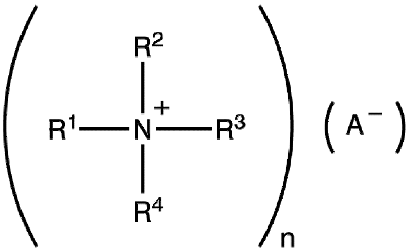
$[C_6H_7O_2(OH)_3]_n + xNaOH \rightarrow [C_6H_7O_2(OH)_3 \cdot xNaOH]_n \rightarrow$

$\rightarrow [C_6H_7O_2(OH)_3 \cdot xNaOH]_n + nxClCH_2COONa \rightarrow$

$\rightarrow [C_6H_7O_2(OH)_{3-x}(OCH_2COONa)_x]_n + nxNaCl + nxH_2O$

PVA – Polyvinyl alcohol (grade 16/1, Mass portion of acetate groups not more than 0.9-1.7 %).

Quaternary ammonium salt(QASc) –biocide $[R(CH_3)_2NCH_2C_6H_5]^+Cl^-$ (CAS №: 21954-74-5). A quaternary ammonium salt is an ionic compound that has the following general structural formula.



n = positive whole number R^1, R^2, R^3, and R^4 could be hydrogen atoms, alkyl groups, aryl groups, or any combination thereof. A^-could be any anion present in salt.

The coating composition was a 3 % solution of CMS:PVA in a ratio of 1:1 with the addition of 2-10 % of QASc. The density of the resulting solution is 1.04 - 1.12 g/cm^3. The composition was applied to the surface of the insole leather made from pig raw material by a method of sawing in two passes with a consumption of coating material of 125 g/m^2. After that, the treated leather was dried at a temperature of 30-35 °C for 40 minutes.

Strength indexes of leather (tensile strength, relative elongation) were determined using conventional methods (A2. Standard ISO 3376:2011. Leather – Physical and mechanical tests – Determination of tensile strength and percentage extension).

For evaluation of the obtained materials activity, were used reference strains of microorganisms regulated by the WHO for determination of the preparations antimicrobial activity: Staphylococcus aureus ATCC 25923, Escherichia coli ATCC 25922, Bacillus subtilis ATTC 6633. Results were processed in 2-6 days for bacteria and in 5-7 days for fungal (Table 1).

Table 1

Results antimicrobial treatment of leather samples by CMS:PVA and QASc

Sample	Preparation	Concertation, g\l	*Esheriehia coli*		*Bacillus subtilis*		*Staphilococus aureus*		*Fuserium oxusporum*
			BC[4]	BS	BC	BS	BC	BS	BC
1[1]	-	-	0	0	0	0	0	0	0
1[2]	CMSc:PVA	30	0	1	0	0	1	0	1
1[3]	QASc	2	0	1	1	0	1	0	1
2	CMS:PVA / QASc	30 / 2	0	4	0	0	0	0	0
3	CMS:PVA / QASc	30 / 5	0	4	0	0	3	0	1
4	CMS:PVA / QASc	30 / 7	0	4	2	0	1	0	1
5	CMS:PVA/ QASc	30 /10	0	4	3	0	1	0	1

1 Antimicrobial leather surface treatment was not performed.

2 Leather surface treatment was performed without the addition of a bactericidal agent.

3 Leather surface treatment was performed with an aqueous solution of the bactericidal preparation without PVA and starch.

BC is a bactericidal activity; BS is a bakteriostatic activity; "0" – the activity is absent.

Qualitative indexes of leather (tensile strength, relative elongation) were established using conventional methods (Table 2). Samples of leather are almost indistinguishable for the content of QASc.

Table 2

Physical-mechanical properties of leather

Sample	QASc, %	Tensile strength, N/mm^2	Strain when grain layer breaks, N/mm^2	Relative elongation, %	Air permeability, cm^3/cm^2·hrs	Stiffness, N	Porosity, %
1[1]	0	13,8[2]	9,7	74,0	1180	2,2	61,2
2	2	12,4	9,6	114,0	790	2,9	56,8
3	5	12,6	9,3	102,0	688	3,0	58,2
4	7	12,7	9,6	100,0	680	3,0	57,4
5	10	12,5	9,6	94,0	540	3,1	55,3

[1] Antimicrobial leather surface treatment was not performed.

[2] According to GOST 940-81. Leather for shoe lining. TU, the tensile strength of the tensile specimens shall be not less than 12 MPa.

As can be seen from the above data, treating the surface of the leather with a solution of CMS: PVA and QAS causes a decrease in the tensile strength of the leather, although within the requirements of the regulatory technical documentation for the lining. The leather's breathability is also diminished due to a decrease in its porosity, which increases the trend in QAS consumption by increasing this trend.

The bactericidal and bacteriostatic action of the substances that have treated the leather surface has been considered.

A small number of small colonies of white and yellow bacteria of homogeneous structure of regular and irregular shape were observed on and around the untreated samples. When using QASc, a small amount of bacteria was observed at a distance of 3-4 mm from the edges of the specimens. Samples of leather treated with QASc 7 g/l already have antimicrobial activity. No specimen had a sterile (bactericidal action) zone for Esheriehia coli. In this type of bacteria, QASc treatment acted bacteriostatically, ie, delayed the growth of the culture.

Conclusions. It is found that leather treatment with a composition based on modified polysaccharides with the addition of quaternary ammonium salt has antiseptic properties, indicating that the growth of microorganisms is delayed 3-4 mm from the edge of the sample; the relative permeability decreases from $1.18 \cdot 10^3$ to $0.54 \cdot 10^3$ cm^3 / cm^2 · h, the porosity decreases from 61.2 % to 55.3 %, the stiffness increases from 2.2 N to 3.1 N.

As a result of the conducted researches it is established that although the treatment of the surface of the leather with CMS: PVA and QASc solution and causes a decrease in the tensile strength of the leather, however, in terms of its physical and mechanical properties, the treated leather meets the requirements of the normative-technical documentation for the lining and can be used for the manufacture of soles.

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ЗАСТОСУВАННЯ МОДИФІКОВАНИХ ПОЛІСАХАРИДІВ ДЛЯ АНТИСЕПТИЧНОЇ ОБРОБКИ ШКІРИ

Актуальність теми дослідження. *Шкіра дуже чутлива до деградації мікроорганізмами під час обробки, зберігання, транспортування та використання. Тому актуальним залишається пошук препаратів та методів обробки шкіри, надання специфічних фунгіцидних властивостей залежно від призначення.*

Постановка проблеми. *Встановити можливості використання композиції на основі модифікованих полісахаридів із додаванням ПВС та четвертинно амонієвих солей для обробки шкіри з метою надання фунгіцидних властивостей.*

Аналіз останніх досліджень і публікацій. *Були розглянуті останні публікації у відкритому доступі стосовно полімерних матеріалів, антисептичних та фунгіцидних препаратів, які використовують для одержання спеціальних властивостей.*

Виділення недосліджених частин загальної проблеми. *Принцип дії багатьох фунгіцидних чи бактерицидних препаратів у разі їх спільного застосування не з’ясований. Зокрема, у разі одночасного використання модифікованих полісахаридів і четвертинних амонієвих солей для антисептичної обробки шкіри.*

Постановка завдання. *Дослідити вплив обробки шкіри композицією на основі модифікованого полісахариду на фізико-механічні та фунгіцидні властивості матеріалу.*

Виклад основного матеріалу. *Встановлено, що полімерна композиція на основі модифікованого крохмалю та полівінілового спирту з додаванням четвертино амонієвих солей надає шкірі антисептичних властивостей, це доведено затримкою росту мікроорганізмів на 3-4 мм від краю зразка. Відносна повітропроникність шкіри зменшується майже вдвічі (з 1,18 · 10^3 до 0,54 · 10^3 см^3/см^2 · год), також зменшується пористість шкіри на 5-10 % та збільшується жорсткість на 40 %.*

Висновки відповідно до статті. *В результаті проведених досліджень встановлено, що застосування модифікованих полісахаридів надає шкірі спеціальних властивостей хоча викликає зниження межі міцності шкіри при розтягуванні, однак за своїми фізико-механічними властивостями оброблена шкіра відповідає вимогам нормативно-технічної документації до підкладкових шкір і може використовуватись для виготовлення устілок.*

Ключові слова: *модифіковані полісахариди; шкіра; антисептичні властивості; четвертинно амонієві солі.*
Табл.: 2. Бібл.: 18.

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