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MANUFACTURE OF SHOE INSOLES BY ENVIRONMENTAL TREATMENT OF CATTLE SKIN

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This research work is aimed at considering the scientific and practical foundations of the use of cattle skins for shoe insoles through environmentally friendly processing methods. Currently, one of the most pressing problems is the negative impact of traditional chrome tanning technology on the environment and human health. The purpose of the research work is to identify effective ways of processing cattle skin by environmentally safe methods and to study the possibilities of using the resulting leather for shoe insoles. In the course of the study, the main directions of bioprocessing, that is, enzymatic processing, tanning using microorganisms, plant-based Kneaders and chromium-free technologies were considered. The environmental, technological and qualitative advantages of each method were compared with traditional methods and a comprehensive analysis was carried out. The scientific novelty of the study is aimed at summarizing environmental methods of skin treatment and demonstrating on a scientific basis the possibilities of their application in the production of insoles. In the methodological context of the research work, methods of comparative analysis, ethical review, structural systematization were used. This study paves the way for the introduction of new approaches to leather production aimed at protecting the environment. Using the presented technologies in domestic production, it is possible to prepare high-quality, safe and durable shoe insoles. The results of the study contribute to the areas of leather processing and light industry.

Keywords: processing, cattle leather, eco-leather, insoles, enzyme, tannin, chromium-free tanning.

ІРІ ҚАРА ТЕРІСІН ЭКОЛОГИЯЛЫҚ ӨҢДЕУ АРҚЫЛЫ АЯҚ КИІМ ҰЛТАРАҒЫН ЖАСАУ

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Бұл ғылыми-зерттеу жұмысы ірі қара мал терісін экологиялық таза өңдеу әдістері арқылы аяқ киім ұлтарағына арнап қолданудың ғылыми және практикалық негіздерін қарастыруға бағытталған. Қазіргі уақытта теріні дәстүрлі хроммен илеу технологиясының қоршаған ортаға, адамның денсаулығына кері әсер етуі өзекті мәселенің бірі. Зерттеу жұмысының мақсаты ірі қара терісін экологиялық қауіпсіз әдістермен өңдеудің тиімді тәсілдерін анықтау және алынған былғарыны аяқ киім ұлтарағына қолдану мүмкіндіктерін зерттеу. Зерттеу барысында биоөңдеудің негізгі бағыттары, яғни ферментативті өңдеу, микроорганизмдерді пайдаланып илеу, өсімдік негізіндегі илегіштер мен хромсыз технологиялар қарастырылды. Әр әдістің экологиялық, технологиялық және сапалық артықшылықтары дәстүрлі тәсілдермен салыстырылды және кешенді талдау жүргізілді. Зерттеудің ғылыми жаңалығы тері өңдеудің экологиялық әдістерін жинақтап, олардың ұлтарақ өндірісіндегі қолдану мүмкіндіктерін ғылыми негізде көрсетіге бағытталған. Зерттеу жұмысы методологиялық тұрғыда салыстырмалы талдау, әдебиеттік шолу, құрылымдық жүйелеу әдістері пайдаланылды. Бұл зерттеу қоршаған ортаны қорғауға бағытталған былғары өндірісінің жаңа тәсілдерін енгізуге жол ашады. Ұсынылған технологияларды отандық өндірісте қолдану арқылы сапалы, қауіпсіз және ұзақ мерзімді аяқ киім ұлтарақтарын дайындауға болады. Зерттеу нәтижелері тері өңдеу және жеңіл өнеркәсіп салаларына үлес қосады.

Негізгі сөздер: өңдеу, ірі қара терісі, экологиялық былғары, ұлтарақ, фермент, таннин, хромсыз илеу.

ИЗГОТОВЛЕНИЕ СТЕЛЬКИ ОБУВИ С ЭКОЛОГИЧЕСКОЙ ОБРАБОТКОЙ КОЖИ КРУПНОГО РОГАТОГО СКОТА

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Данная научно-исследовательская работа направлена на рассмотрение научных и практических основ применения шкур крупного рогатого скота для обувной стельки с помощью экологически чистых методов обработки. В настоящее время одним из актуальных вопросов является негативное влияние традиционной технологии дубления кожи хромом на окружающую среду, здоровье человека. Целью исследовательской работы является выявление эффективных способов обработки кожи крупного рогатого скота экологически безопасными методами и изучение возможностей применения полученной кожи на стельках обуви. В ходе исследования были рассмотрены основные направления биообработки, то есть ферментативная обработка, замешивание с использованием микроорганизмов, дубильные вещества на растительной основе и нехромированные технологии. Экологические, технологические и качественные преимущества каждого метода сравнивались с традиционными подходами и проводился комплексный анализ. Научная новизна исследования направлена на обобщение экологических методов обработки кожи и демонстрацию на научной основе возможностей их применения в межрасовом производстве. В исследовательской работе методологически использованы методы сравнительного анализа, этического обзора, структурной систематизации. Это исследование прокладывает путь к внедрению новых подходов к производству кожи, направленных на защиту окружающей среды. Используя представленные технологии в отечественном производстве, можно изготовить качественные, безопасные и долговечные стельки для обуви. Результаты исследования вносят вклад в области кожевенной и легкой промышленности.

Ключевые слова: обработка, кожа крупного рогатого скота, экокожа, стелька, фермент, танин, дубление без хрома.

Introduction

The use of cattle leather for shoe insoles through environmentally friendly processing methods will focus on the negative impact of traditional chrome tanning technology in leather production on the environment and human health. In the field of leather processing, the requirements for environmental safety have increased in recent years, but there are few widespread research and production solutions for the widespread introduction of leather bio-processing technologies in the Republic of Kazakhstan. Therefore, deep scientific research is becoming more and more important in accordance with the requirements of the present time. The relevance of the research work is directly related to the desire to introduce "green technologies" at the international level, the need to comply with environmental standards and the efficient use of Natural Resources. The theoretical significance of the work is to combine interdisciplinary connections in the fields of Biotechnology, ecology, chemistry, materials science and light industry and to propose scientifically based approaches. With the use of bio-processing technologies in real production, it is possible to obtain high-quality and safe leather products.

The purpose of the work is to scientifically substantiate the possibility of producing high-quality, safe and durable leather shoe insoles by processing cattle leather with environmentally friendly processing methods.

Literature Review

Cattle hides are an important by-product in the meat industry, which can be made useful by processing and making leather. Leather is a high-strength, wear-resistant, breathable valuable material [1]. It is necessary to effectively use large volumes of cattle skins collected after meat production, that is, to make it useful without turning it into waste [2]. But in traditional leather tanning technology, chromium compounds, etc.harmful chemicals are often used. When tanning with chromium, toxic inclusions are released into the environment in large quantities. These substances pollute the soil, water sources and harm the environment [3]. Therefore, at present, the emphasis is placed on environmentally friendly bio-methods of skin treatment. Environmental bioprocessing methods use enzymes, microorganisms, natural reagents to reduce the harmful effects on the environment. The research direction is also important in the production of leather insoles for shoes,

since leather obtained using environmentally friendly methods makes it possible to obtain products that are safe for human health, comfortable for the feet and harmless to natural resources.

Recently, a method of bio-processing alternative to traditional chemical methods has been developing in skin processing. Among them are technologies of enzymatic processing, tanning with the use of microorgnisms and chromium-free tanning. In the enzymatic method, special biological enzymes are used instead of chemical reagents at some stages of skin treatment, especially in the hair removal process. Usually, strong alkalis and toxic sodium sulfide are used to remove hair, and in the enzymatic method, enzymes such as protease break down the keratin protein in the skin, softening the fur. As a result, the fur will detach without difficulty, and the skin will be ready for tanning. Since enzymes are biodegradable, it has been reported that chemical oxygen demand (COD) decreases by about 50%, while biological oxygen demand (BOD) decreases by up to 40%, reducing environmental pollution by toxic substances [4]. At the same time, since sulfuric alkali is not used in this method, no toxic gases (H2S) are released and a safe environment is also created for workers. In this treatment, the structure of the fibers is preserved intact, that is, the surface layer of the skin remains intact and the strength increases. In enzymatic bioprocessing, by-products such as wool and oil are separated intact and turned into useful products as glue, fertilizer or feed for livestock [5]. Currently, companies such as Ultez, Novozymes offer commercial types of enzymes for the leather industry [6].

Tanning of the skin using microorganisms is one of the directions of bio-treatment. In this processing, the vital activity of living microorganisms is used in some stages [7]. The widely used microorganism bacterium *Bacillus subtilis* is known for its ability to produce the enzyme Protease and is used in leather production for skin hair removal [4]. Bacterial fermentation can also be used in other stages of tanning. For pickeling, that is, preparation for tanning, lactic acid can be used instead of mineral acids at the acidification stage, and lactic acid is obtained from sugar in a natural way with the help of lactobacilli. Research is underway to normalize which microorganisms biotransform some tannin and adhere better to the skin fibers. Microbial tanning, although at the stage of scientific research, is distinguished by the transfer of the process to a fully updated biological system, affecting the ecological development of leather production.

Replacing the tanning process with chromium salts with alternative natural or harmless reagents is a major environmental trend in the leather industry. Chromium-free tanning includes ways in which chromium (Cr3+) is not used to stabilize skin collagen.

If bio-processing methods are used in leather processing, the resulting leather will be environmentally safe, high-quality and suitable for shoe insoles. This work contributes to the development of an environmentally friendly production system, the use of domestic scientific potential, which increases the competitiveness of the National Leather Industry.

Chrome-free tanning technologies.

Replacing the tanning process with chromium salts with alternative natural or harmless reagents is a major environmental trend in the leather industry. Chromium-free tanning includes ways in which chromium (Cr3+) is not used to stabilize skin collagen. Types of chromium-free tanning include tanning with plant tannins, that is, a method of tanning with natural extracts from tree bark, plant shrubs and fruits. Plant tannins are obtained from the bark and leaves of plants such as oak, birch, Mulberry, currant, etc. Producers prepare this raw material from wood products grown in a sustainable way or indirectly [8]. The peculiarity of this method lies in the use of a completely renewable natural material and the unique properties of the resulting leather [9]. According to the results of the study, some plants growing in Kazakhstan contain very high amounts of natural tannins. In particular, it was found that the root of the medicinal dandelion *(Sanguisorba officinalis)* contains 21% tannin, and the leaf of the elderberry *(Bergenia crassiofolia)* contains 20% tannin [10]. At the moment, 10-20% of world production is tanned leather by plants.

The most commonly used today in tanning leather with aldehydes is glutaraldehyde. The leather semi-finished product tanned by this method is chrome-free and is often used for car interior, children's and medical products. With this method, the tanned leather has a whitish color and low heat resistance. It also creates wastewater treatment problems due to the fact that additional chemical treatments may be required to fix collagen fibers in the tanning process [8]. But, completely eliminates heavy metal residue and serves as a good alternative in certain situations. The leather tanning with this method becomes soft, stretchy, the disadvantage is that over time, the leather tanning with aldehyde turns yellow.

The chemical analogues of tannins are syntheetic tannins, that is, synthanes. These include tannins based

on phenolic synthanes, phosphate compounds, aluminum, zirconium and titanium salts. Kazakh scientists have studied complex kneaders with partial replacement of chromium. They proposed a heteropolyader complex of zirconium as an environmentally harmless tannin [11]. In addition, methods of tanning aluminum and vegetable tannins by combining are also known. This can affect the properties of the leather of some when using an alternative reagent. For this reason, research is being done to find an effective composition of alternative tannins.

In recent years, an innovative method of tanning based on zeolite has appeared. Zeolite is the structural name for natural aluminosilicate minerals that have the ability to absorb or release water. This method does not use heavy metals, nor does it require aldehydes, but is implemented using an inorganic mesh structure with the ability to stabilize collagen [8]. Because tsiolite tanned leather is able to absorb and reproduce water well and prevent rotting, it is an important property for comfort inside shoes. This technology will also be effective from the point of view of ecology, there will be no heavy metal in the residual water, and the reagent used is a harmless mineral. Zeolite tanning is currently considered a new direction and an innovation that may become widespread in the future.

Comparative advantages of traditional and ecological tanning methods

Bio-processing methods have a number of important advantages when it comes to traditional chrome tanning. The weight on the environment is reduced, that is, the environmental friendliness of waste water and solid waste from production is higher due to the fact that harmful heavy metals and toxic reagents are not used or very little is used. For example, in the enzymatic method, organic wastewater pollution has been reduced, safe for workers health, and hydrogen gas released in the traditional chromium treatment technology is eliminated [4].

In environmental methods, bio-products with renewable raw materials are used, and tibial resources are used effectively. Plant tannins are obtained from renewable plant sources. Therefore, dependence on synthesized substances in the chemical industry is reduced [8]. Processing with the help of enzymes and microorganisms saves energy, since many bioprocesses occur at normal temperature and pressure. Enzymes work effectively at around 37°C, and in some stages of traditional methods, heating or cooling is required to carry out the reaction. One of the advantages of ecological bioprocessing approaches is the ability to use leather waste. Chrome-tanned leather residues are dangerous to soil and water due to their heavy metal content, so they must be buried in the ground or burned. And by recycling the waste of chromium-free biobes, it is possible to obtain products such as fertilizer, glue, collagen hydrolyzate [5]. Wool, fat residues obtained by the enzymatic method are suitable for conversion into animal feed or industrial raw materials, since they do not contain a harmful substance. This corresponds to the principles of closed-cycle industrial ecology [12]. Bioethics have a positive effect on the quality of leather. The traditional whitewashing-sulfidation process damages the skin fibers in a certain amount, breaking down some of the collagen. And enzymatic softening and hair removal gently cleanses the skin structure, and the glossy surface and elasticity of the resulting leather are well preserved. The thermal stability of chrome tanned leather is very high at 100°C, and the stability of vegetable tanned leather is 80°C. Plant-tanned leather has antiseptic properties, because tannins have the effect of inhibiting the growth of bacteria, and the insoles of leather shoes have a less unpleasant odor [13]. Table 1 presents some comparative indicators of traditional and modern methods in leather processing.

Table 1 - Comparative indicators of traditional and modern methods in leather processing

Comparison indicator	Traditional chrome tanning	Environmental bio-processing
Main reagents used	Chromium salts (Cr^{3+}), sodium sulfide, strong acids, formaldehyde, etc.	Enzymes, plant tannins, organic acids, natural polymers, etc.
Impact on the environment	There will be heavy metal and toxic residues, contaminated tap water, require special treatment.	There will be no or little toxic substances, most of the waste can be biodegradable, and cleaning will be easy.
Safety of the working environment	Chemical vapors and gases (Cr, H_2S) are dangerous, workers need special protection.	Bioreagents are relatively safe, there will be less odor and toxic gas in production, and the working conditions will be safe.
Energy and water consumption	Fast process (tanning with Chrome for 1 day), but significant loss in water (requires more rinsing).	Some methods take longer, but the possibility of reusing water is higher, and enzyme processes require less energy.
Leather quality	Very high heat has stability, softness and durability; due to the presence of chromium, which can be an allergen, it is possible to smell in shoes over time.	In terms of quality, some properties are superfluous, natural tannins have antibacterial and odor-repellent properties. High air permeability, does not contain harmful substances.
Waste use	Chrome leather residue is toxic, wool and oil residues are absorbed by the chemical, difficult to use.	Chromium-free waste can be converted into products such as fertilizer, animal feed, glue, collagen. Wool can be dosed and used in the textile industry.

The table provides a comparison of the general leather tanning process. Depending on production technologies, indicators may change. For example, research is currently being done in Chromium tanning methods to save water and reduce the residual chromium content as well [8]. Bio-processing methods are effective in terms of Ecology and Occupational Safety, and in terms of product quality are not inferior to the traditional method.

The quality of the insole material must be very high, as the insole of the shoe is the part that is in direct contact with the sole. Leather has been used for many centuries to make insoles due to its property to provide a comfortable microclimate inside shoes. Eco-friendly leather insoles produced by pure method have such important characteristics as ductility, durability, air permeability, moisture absorption, resistance to abrasion, antibacterial properties. Leather tanned with plant tannins, although dense at first, becomes softer and more comfortable on the feet as it is used. Since such leather insoles are durable to wear for a long time, are able to absorb and evaporate moisture to the outside, the foot does not sweat, a soft dry environment is maintained and the appearance of an unpleasant odor is reduced [13]. It has been scientifically proven that plant-based tannins are polyphenolic compounds and inhibit the development of microbial cells [14]. For example, tannins from oak and spruce bark reduced the reproduction of bacterial strains such as *Escherichia coli* [15]. The use of natural chitosan biopolymer in leather finishing is widespread because chitosan is a natural substance capable of killing bacteria. It has been established that harmful bacteria such as *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa* do not grow on chitosan-coated leather [16].

Results and discussion

Currently, a lot of scientific research and industrial initiatives have been carried out in Kazakhstan on the treatment of skin with environmentally friendly methods. One of them, scientists from Taraz regional university named after M.H. Dulaty, studied the environmental problems of mineral tanning of leather and proposed ways to solve the problem. In 2023, the results of practical testing by members of the group contribute to the development of environmentally friendly leather production [3].

Researchers of the Al-Farabi Kazakh National University found that plants growing in East Kazakhstan

contain tannins necessary for tanning in large quantities and offered opportunities for their use in leather production [10]. This can serve as the basis for the development of plant tanning methods in our country.

The leather industry of light industry in Kazakhstan has passed a difficult period, when many large tanneries have ceased to exist. But now there are attempts to revive the leather industry. In 2021, the Semey leather plant was launched in East Kazakhstan. With the support of investors, the enterprise for the processing of animal skins of the company "KazBeef" produces semi-finished products and exports them to foreign countries such as China, India, Italy [2]. This project in Semey is an example of how to make the agricultural sector of Kazakhstan financially and environmentally efficient, using agricultural products.

In Kazakhstan, a startup called URPAQ to create alternative ecological types of leather produces eco-leather from coffee waste. This material obtained by processing coffee powder is suitable for the production of shoes and accessories, and its use does not harm both animals and ecology and saves water resources [17]. This product is a completely organic composition, that is, it does not contain such a petrochemical derivative as polyurethane.

In general, researchers confirm that Kazakhstan has the potential to transfer the leather industry to a sustainable development channel. Experts point out that it is more effective to treat leather with responsible and clean methods instead of completely disposing of it [5]. This is because animal husbandry produces thousands of tons of skin every year, and if they are not processed, they will rot, damage the environment and cause losses. The transformation of the same raw material into leather will make it possible to create shoes, leather products for the population, as well as a solution to eliminate large amounts of waste. Therefore, the introduction of environmental biotechnologies in the development of domestic leather production will be doubly useful. Firstly, it is environmentally friendly, and secondly, it offers high-quality competitive clean products. With constant research and innovation in this direction, support from the state and business, Kazakhstan has every chance to form not only eco-leather insoles, but also the brand "green leather" as a whole.

Conclusions

In general, summing up, the creation of shoe insoles by environmentally friendly processing of cattle skin is an important scientific and technological direction in accordance with the requirements of our time. These methods reduce the disadvantages of traditional leather production and allow you to obtain environmentally friendly, high-quality leather products. Enzymatic and microbiological processing, plant-based and other chromium-free tanning technologies together form the concept of "green leather". Insoles made of such leather are distinguished by the properties of pliable, resistant, breathable, odorless and bacteria-free. Kazakhstan's science and industry are taking their first steps in this direction and have the potential for further development. The production of eco-friendly leather is not only a concern for nature, but also an investment in human health and a purely technological legacy that we will leave to future generations.

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