ANNOTATION

of the dissertation work of PhD student Baidildayeva Assel Kuanyshevna on the topic «Research of microencapsulation technology of leather for footwear of people with pathological deviations of the feet» submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D07211 – «Leather goods industry»

General characterization of the work. This dissertation work deals with the microencapsulation technology of leather footbeds. In this dissertation work, the antibacterial properties of footwear leather with microparticles from essential laurel oil were researched.

According to the statistics of the Ministry of Health of the Republic of Kazakhstan on the population health and the activities of healthcare organizations in 2024, published in 2025, 1,193,381 people were diagnosed with diseases of the musculoskeletal system and connective tissue, and 328,300 people with diabetes. The high level of development of modern society focuses on the health of the population and the comfort of the environment. In this regard, footwear needs to be improved as a vital element that accompanies a person.

One of the most common products in everyday life is footwear. It is important that footwear have properties that improve the quality of life of people with pathological deviations of the foot. Research in the field of footwear in the Republic of Kazakhstan had shown that there are a number of issues and barriers to development.

Diabetes is a global problem. Currently, the number of patients is growing, and the amount of money spent on treatment is growing. 20% of patients with diabetes suffer from foot ulcer. People with diabetes need special care for their feet. In such patients, any scratch, even the smallest wart, can lead to very serious consequences, leading to amputation. Callus is the accumulation and proliferation of thickened skin tissue, which is visible because of overproduction of epidermal cells. These pathological changes occur due to damage to the skin and subcutaneous tissue. The main factor in the violation of the integrity of the skin is the compression caused by improper distribution of the load on the human leg. Heel hyperkeratosis is a condition that affects the foot. Its shape can reach several centimeters. Dry dermis easily causes scratching, which can lead to discomfort and bleeding. In addition, most importantly, the damage leads to infection.

Mild and moderate skin infections are the most common pathology. Every year, about 10 million people seek emergency care for traumatic soft tissue injuries of varying severity. These and other pathological defects of the foot require the creation of a comfortable environment in the footwear in accordance with the hygienic requirements. Introduction of microcapsulation technology for footwear leather enables the production of products with modern, innovative indicators.

Microencapsulation technology was first introduced in the pharmaceutical industry as an attractive production process due to the widespread use of spray drying. Today, this technology is used in the textile, leather, pharmaceutical, food

and agricultural industries. Microencapsulation technology is the process of converting a liquid or solution from a liquid state into a powder by spraying it in a hot drying medium. Microcapsule methods allow the production of particles of different sizes, up to hundreds of microns.

The relevance of the work. The footwear is used in everyday life, and its quality is important for hygiene and health. It is especially important to create a comfortable footwear environment for people with pathological neuropathic foot deviations such as loss of sensation, dry skin, ulcers, and infections. The use of essential oil (laurel) creates an antibacterial environment in footwear, as it is a natural plant-derived material and contains numerous antibacterial components. With the help of microencapsulation technology, antibacterial properties are introduced into footwear for people with pathological deviations of the foot, such as persistent hyperkeratosis, onychomycosis, and diabetes.

Degree of problem research. This technology is not sufficiently studied in the Commonwealth of Independent States countries, there are only studies in the field of textiles: Odintsova O.I, Levshitskaya O.P, Chernova E.N, and etc. A patent research shows that technology not used in the leather and footwear industry of the Republic of Kazakhstan. However, global research shows that scientists like Karavana H., Bielak E, Marcinkowska E, Lawinska K, Liu G, Vieira Kopp V, etc. have made significant contributions in this field. Academician of the National Academy of Sciences of the Republic of Kazakhstan O.K. Madiev and et al. proposed the use of various antiseptic substances during tanning. Among them are metallic iodine, zinc oxide and chitosan. However, it is not possible to use microencapsulation technology during tanning. This is due to the volumetric dimensions of microparticles. Therefore, in this study, work was carried out with a leather footbeds.

The purpose of the work. Use of specific equipment for microencapsulation technology, improving the antibacterial properties of leather footbeds and footwear linings with chitosan and laurel oil, which contain antibacterial components, and increases the hygienic properties of footwear. The following **tasks** were investigated to achieve this goal:

1. Development of a complex for preparing solutions based on natural components of chitosan and laurel essential oil and conducting microencapsulation technology.
2. Development of a method for finishing coatings using microparticles containing natural components.
3. Analysis of the composition of microparticles.
4. Determination of the physicochemical properties of coatings and substrates coated with microparticles obtained on the basis of natural components.
5. Study of the microbiological parameters and antibacterial properties of coatings and substrates coated with microparticles.

Research object and materials. Wet-blue crust footwear leather without dye, three different footwear lining materials, laurel oil and chitosan.

Research methods. The following methods were used in the work: spray drying method, dip-coating and spraying, and microbiological tests. The MPs and

leathers were assessed for morphology and chemistry via SEM, particle size distribution, FT-IR, UV-Vis spectroscopy, and antibacterial assays.

Experimental research was conducted in the laboratories of Ege University and Dokuz Eylul University (Izmir, Türkiye) and M.Kh. Dulaty Taraz University.

Scientific novelty of the dissertation research:

- Seven different natural solutions based on chitosan and laurel essential oil components for the production of microparticles were prepared and the technology was developed.
- The increase in the physicochemical properties of the footbeds treated with microparticles based on natural components was proven.
- The results of *in vitro* release of laurel oil from the samples showed that it was gradually and slowly released.
- Microbiological analyses of leather footbeds and footwear linings samples coated with microparticles confirmed antimicrobial properties.
- The results revealed the possibility of using them not only for footwear for people with pathological foot deviations, which was the primary goal, but also in general.

The theoretical and practical significance of the work lies in the use of microparticles prepared from natural chitosan and laurel oil to produce leather footbeds and footwear linings with antibacterial properties.

This study suggests that advancements in production methodologies could substantially enhance foot health and hygiene. In addition, employing this optimised method has significant potential to manufacture footbeds with a rapid and enduring antimicrobial effect. Therefore, this work is promising and in demand for the footwear industry.

The main provisions proposed for protection:

- Technology for obtaining microparticles in a Unopex B 15 mini spray dryer.
- Results of the influence of process parameters (component ratio, surfactant concentration, temperature, feed rate) on the yield and characteristics of microparticles.
- Application methods (spray and dip-coating) affecting the distribution of microparticles and the functional properties of the coatings.
- Results of the stability of the antimicrobial effect to no rubbing and mechanical rubbing (flex resistance, dry rubbing and wet rubbing).

The degree of reliability and approbation of the results.

The reliability of scientific findings, conclusions and recommendations is confirmed by the similarity of the research results.

The results of the dissertation work were implemented at the enterprise «Tarazski Kozhevennyi Zavod» LLP (The act of the implementation of the results of scientific research work at enterprises, 11.10.2025) and «TarazKozhObuv» LLP (The act of the implementation of the results of scientific research work at enterprises, 13.04.2026).

The results of the dissertation work were implemented at the educational process. Discipline was «Sanitary and hygienic requirements for leather products», studied in the 5th semester of the 3rd year in 2025-2026 academic year. (The act of

the implementation of the results of scientific research work at educational process, 06.03.2026).

As part of the research conducted in this dissertation work, an application for a patent has been submitted (Incoming № 2026-67676. Barcode 4109542).

Publication of research results. The main provisions of the dissertation work were reported and discussed at the journals and conferences.

The article was published in journal included in the Web of Science and Scopus databases:

1. Assel Baidildayeva, Gizem Ceylan Türkoğlu, Mustafa Ökeer, Bayri Eraç, Huseyin Ata Karavana. «Microencapsulation of Laurel Essential Oil with Chitosan for Enhanced Durability and Antimicrobial Properties of Leather Footbeds». // Iranian polymer journal, 2024.

The article was published at an international conference indexed in Scopus:

1. Assel Baidildayeva, Gizem Ceylan Türkoğlu, Mustafa Ökeer, Bayri Eraç, Huseyin Ata Karavana. «Textile-based footwear linings functionalized with laurel oil microparticles: antimicrobial protection». // 10th International Conference «Advanced materials and systems (ICAMS 2024)», Bucharest, Romania, 2024.

Two articles were published in the publication, which was included in the list of the Science and Higher Education Quality Assurance Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan:

1. Assel Baidildayeva, Gizem Ceylan Türkoğlu, Indira Jiyembetova, Gulzira Jumabekova, Bekzhan Abzakbekuly. «Study of the antimicrobial properties of footwear materials of people with pathological deviations of the feet» (Табандарының патологиялық ауытқулары бар адамдардың аяқ киім материалдарының антимикробтық қасиеттерін зерттеу). // Mechanics and technology, Taraz, 2025, №1.

2. Assel Baidildayeva, Huseyin Ata Karavana, Indira Jiyembetova, Gulzira Jumabekova, Bekzhan Abzakbekuly. «Loading efficiency and *in vitro* release studies of microparticles treated on leather and footwear linings» (Былғары мен аяқ киім астарына өңделген микробөлшектердің жүктеу тиімділігі және *in vitro* босату зерттеулері). // Mechanics and technology, Taraz, 2025, №3.

Two articles were published at international conferences:

1. Assel Baidildayeva. «Analysis of orthopedic insoles available on the Kazakhstan market» (Анализ ортопедических стелек представленных на рынке Казахстана). // International Scientific and Practical Conference, “Soha korxonalari uchun yuqori malakali kadrlar tayyorlashda milliy va xorijiy tajribalar”, Tashkent, Uzbekistan, 2022.
2. Assel Baidildayeva, Indira Jiyembetova. «Pathological deviations of the feet and the importance of corrective footwear» (Адамдардың табандарының потологиялық ауытқулары мен оларға арналған түзетпе аяқ киімдердің маңыздылығы). // XIII International scientific and practical conference of young scientists «Innovative development and the requirement of science in modern Kazakhstan”, Taraz, 2019.

Structure and volume of the dissertation. The dissertation consists of 113 pages, including normative references, definitions, abbreviations, introduction, 3

sections, conclusion, list of references, and annexes. The structure of the dissertation consists of 29 tables, 31 figures and 5 equations.

Main content of the work:

The **first part of the dissertation** presents a comprehensive literature review and an analysis of the current state of research in the field of functional footwear materials and technologies. Particular attention was given to the materials used in footwear production, with an emphasis on their hygienic, physical, and functional properties. The existing technologies for the microencapsulation and application of active compounds to leather were reviewed, including their potential for improving the functional performance of footwear materials. The antibacterial properties of footwear materials and the mechanisms of antimicrobial action were also analyzed. Special consideration was given to chitosan as a natural biopolymer with antimicrobial and film-forming properties, as well as to essential oils, particularly laurel essential oil, as promising natural antibacterial agents. In addition, the literature data concerning pathological deviations of the feet were examined. Existing types and designs of footbeds intended for people with pathological foot deviations were analyzed.

Conclusion on the first part.

1. Based on the studied literature sources and patent data, the main requirements for the main materials for footwear: leather and lining materials were determined. Among them, special attention was paid to antibacterial properties.

2. It is very important to create an antibacterial environment for people with pathological deviations. Especially for people, whose footwear should have antibacterial properties to prevent the spread of infections and ulcers when wearing footwear.

3. One of the most promising methods of antibacterial treatment is the treatment of materials with microencapsulated drugs. Spray drying is the most common method of microencapsulation.

4. Various studies are presented that describe the use of chitosan in the textile and footwear industry to create an antibacterial environment with promising results. Chitosan is used as an encapsulating agent because it is a natural, biodegradable, low toxic and biocompatible substance with antibacterial properties. The laurel oil has antibacterial, anti-infectious, analgesic, antiviral, and antiseptic qualities.

5. It was found that the footbeds on the Kazakhstan market help regulate the external shape of the foot. In addition, the need to create for the footbeds an additional antibacterial environment made from natural solutions was identified.

The **second part of the dissertation** describes the methodology used in the experimental research. The study involved the use of selected reagents, chemicals, footwear materials, laboratory equipment, and analytical techniques. The experimental procedures included preparing chitosan and laurel essential oil solutions and the production of microparticles using a spray-drying method. The production yield of the obtained microparticles was determined, followed by morphological and chemical characterization using scanning electron microscopy and Fourier-transform infrared spectroscopy. Ultraviolet–visible spectrophotometry was used to quantitatively determine the concentration of laurel essential oil, while

encapsulation efficiency and loading capacity were determined using appropriate analytical procedures and solvents, including methanol and n-hexane. In vitro release studies were carried out to investigate the release of laurel essential oil from the microparticles. The prepared microparticles were applied to leather and lining materials using the selected application methods, followed by drying and washing procedures. The treated materials were subjected to dissolution, flexing and rubbing tests, and color measurements. Antimicrobial assays were also conducted to determine the antimicrobial activity of the treated footwear materials against selected test microorganisms.

Conclusion on the second part.

1. Leather and three different lining materials (cotton woven fabric, PET woven and PET weft knitting) were used as the main material. To prepare microparticles were used chitosan, Laurel essential oil, acetic acid (glacial), surface-active agents Tween 40 and Span 20, binder Tanapur One, wetting agent Periwet ELR and thickening agent Sodium carboxymethyl cellulose used. Microparticles were obtained on Unopex B 15 Mini Spray Dryer. Microparticles were collected using a soft brush and transferred into zip-lock bags. Microparticles were applied to leather and linings by two methods: spraying and dip-coating.

2. Morphological and chemical characterisations of microparticles, antimicrobial assays of microparticle-coated materials were determined in accordance with relevant standards.

3. SEM images were used to determine the morphological structure. FT-IR was used to determine the chemical structure. The determination of encapsulation efficiency was conducted through a solvent extraction method. After finishing treatment, the materials were dried and washed.

4. Physical tests such as flex resistance test, to and fro rubbing fastness test and colour measurement were used. The flex resistance test was conducted to determine the ability of the material to withstand repeated bending and deformation without the formation of cracks, delamination, or structural damage. The to-and-fro rubbing fastness test was employed to evaluate the resistance of the material surface to abrasion and color transfer under repeated friction. Instrumental color measurements were performed using a colorimetric system based on the CIE L*a*b* color space, allowing precise quantification of color parameters, including lightness (L*) and chromatic coordinates (a*, b*).

5. Antibacterial and antifungal properties of the leather footbeds and footwear lining materials were systematically evaluated against representative Gram-positive and Gram-negative bacterial strains, namely *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*, as well as the fungal strain *Candida albicans*. These test microorganisms were selected due to their relevance as common pathogens associated with skin infections and their frequent involvement in microbial contamination of footwear materials.

The **third part of the dissertation** discusses the results obtained from the experimental investigations of the developed laurel essential oil microparticles and their application to footwear materials. The evaluation of the microparticles included analysis of their physicochemical characteristics, Fourier-transform infrared

spectroscopy spectra, encapsulation efficiency, and loading capacity. The encapsulation efficiency was investigated using different solvents, including methanol and n-hexane, and the *in vitro* release behavior of the microparticles was evaluated in order to determine the release characteristics of laurel essential oil. Scanning electron microscopy was used to examine the morphology of the treated leather surfaces and the distribution of microparticles. Changes in the color characteristics of the investigated leather and lining materials were evaluated following microparticle application. Particular attention was given to the antimicrobial properties of the treated materials, including leathers and lining materials, against the selected test microorganisms. Finally, the economic and environmental efficiency of the developed technology was assessed to determine its practical applicability and potential for implementation in footwear production.

Conclusion on the third part.

1. Microparticles obtained from chitosan and laurel oil solutions were used for the study. The morphological characteristics of the microparticles in each solution were examined using a scanning electron microscopy. As a result, the most effective L_5 formulation was identified for further study.

2. It was concluded that the optimum microparticle formulation with LEO had wider size distribution than the blank chitosan.

3. The results of colour changes data with L*, a* and b* of footwear Lining 1, 2, 3 and leather footbeds applied with 5 solutions showed that most materials became darker than the original one.

4. The FT-IR spectra of chitosan, LEO, and L_5 were studied. The consistent nature of the peaks in the encapsulated powder indicated that there was no significant chemical interaction between LEO and the wall material. The study confirmed that LEO was incorporated into the polymeric matrix without notable chemical interactions with chitosan.

5. The encapsulation efficiency and *in vitro* release results of n-hexane and methanol showed that n-hexane offered better solubility and concentration results, and was therefore chosen as the solvent for LEO.

6. SEM images of the treated leathers revealed the successful transfer of microparticles onto the leather, with preserved structural integrity post-application. Between the two used methods, it was demonstrated that the spraying method was a more appropriate technique for applying microparticles to the leather footbeds than the dip-coating method.

7. Between all five solutions, the loading efficiency of laurel oil in linings with DC-M was higher than in linings treated with other solutions. After three washes, the essential oil ratio has decreased, but all the linings could retain the essential oil in their structure.

8. The *in vitro* release results of all microparticles treated leathers increased based on time, as the *in vitro* release results of microparticles with PBS: n-hexane. The drug release of S-M leather had a similar concentration to n-hexane microparticles.

9. All types of leather footbeds and footwear lining samples demonstrated pronounced antimicrobial activity against the tested microorganisms, confirming the

effectiveness of the applied functional treatment. The results indicated that the materials exhibited inhibitory effects against both bacterial strains (*Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa*) and the fungal strain *Candida albicans*, suggesting a broad-spectrum antimicrobial performance. Notably, the largest inhibition zones were recorded against *Candida albicans*, indicating a higher susceptibility of the fungal strain compared to the bacterial cultures. Overall, the obtained results demonstrate that the developed leather footbeds and footwear lining materials possess effective and stable antimicrobial properties, with particularly strong activity against fungal microorganisms, thereby enhancing their functional and protective performance in practical applications.

10. The results of the study demonstrated that only 1 g of microparticles is sufficient for the functional finishing of one pair of footbeds, with a cost of 1268 tenge. This finding confirms the economic feasibility of the proposed technology and indicates that it does not lead to a significant increase in production costs.

Conclusion

In carrying out this dissertation work, a method for using LEO and chitosan to achieve prolonged antimicrobial protection on leather footbeds and linings was developed. The combination of the results obtained in the dissertation work allows drawing the following conclusions:

1. Based on the research literature sources and patent data, it is determined that creating an antibacterial environment for people with pathological deviations is very important. It is recommended for people with syndrome of diabetic foot syndrome, infections, foot cellulitis, gangrene and hyperkeratosis to wear footwear with some antibacterial properties to prevent the spread of infections.

2. Chitosan, Laurel essential oil, acetic acid (glacial), surface-active agents Tween 40 and Span 20, binder Tanapur One, wetting agent Periwet ELR and thickening agent Sodium carboxymethyl cellulose were used to prepare microparticles.

3. Different experimental solutions, including the blank sample and formulations labeled L_1, L_2, L_3, L_4, L_5, and L_6, were collected under controlled conditions using specifically designed preparation protocols. The collection process was carried out at a temperature range of 160-170 °C, with a pump flow rate maintained between 4 and 10 mL/min. These carefully controlled parameters ensured reproducible formation of the solutions and maintained the stability and uniformity of the collected samples for subsequent analyses.

4. The microparticles were examined for morphology and chemical composition using scanning electron microscopy, particle size distribution analysis, FT-IR spectroscopy, and UV-visible spectroscopy. SEM imaging revealed that, among the various microparticles, L_5 exhibited excellent product yield, a uniform particle size distribution, and a near-spherical morphology. L_5 microparticles demonstrated high encapsulation efficiency of 90.02% and a surface oil content of 9.98%. The L_5 microparticles with methanol showed lower encapsulation efficiency, it was about 10%.

5. The spraying and dip-coating methods were used to apply microparticles to materials. A study demonstrated that the spray method is more suitable for applying microparticles to leather footbeds, as spraying resulted in a uniform distribution of the microparticle layer under a thin, continuous coating.

6. The FT-IR spectrum of chitosan revealed its characteristic peaks at 3450 cm^{-1} corresponded to stretching vibrations N-H and O-H, at 2912 and 2862 cm^{-1} corresponded to asymmetric and symmetric stretching vibrations of C-H bonds, respectively. The spectrum of LEO represented its characteristics bands in the 3600-3200 cm^{-1} range due to O-H stretching vibrations (alcohol group), and the band 2881 and 2966 cm^{-1} indicated the presence of a C-H stretching. FT-IR spectrum of L_5 MPs did not undergo significant changes and resembled both shell polymer and the essential oil.

7. The results of *in vitro* release of microparticles with n-hexane showed a gradual and slow release from 0.985 mg/mL in 1 hour to 6.86 mg/mL in 6 hours, which increased with time upon contact with phosphate buffer saline. This observation indicated the rapid disintegration of laurel oil within the medium. The *in vitro* release results of MPs with methanol did not show release, it was 0.01 in 60 min mg/mL, and after 360 min still was around 0.01 mg/mL.

8. Scanning electron microscopy analysis of the leather samples treated with microparticles revealed the successful transfer and uniform distribution of the microparticles across the surface. High-resolution images confirmed that the microparticles adhered effectively to the footbeds without agglomeration or uneven deposition. Furthermore, the leather's structural integrity was maintained after application, as evidenced by the absence of cracks, fibre disruption, or surface deformation at the microscopic level. These results indicate that the applied microparticle treatment is compatible with the leather matrix, allowing for the incorporation of functional agents while preserving the intrinsic morphological characteristics of the material.

9. *In vitro* leather release studies showed that DC-O release from microparticles gradually increased over time when exposed to phosphate-buffered saline, indicating rapid degradation of LEO.

10. The results of the colourimetric analysis, expressed in terms of the L (lightness), a (red-green), and b* (yellow-blue) parameters, for Lining 1, 2, 3, and leather samples treated with the five different solutions indicated noticeable changes in colour characteristics. Overall, the majority of the treated materials exhibited a decrease in L* values compared to their original, untreated state, suggesting that the samples became darker after application. Additionally, variations in the a* and b* values were observed, reflecting subtle shifts in the hue and chromaticity of the materials. These findings demonstrate that the applied treatments had a measurable impact on the visual appearance of both the leather and lining materials, which is important for evaluating the aesthetic compatibility of the finishing processes.

11. Microbiological analyses conducted on leather footbeds and footwear lining samples coated with microparticles confirmed that footwear leather and lining possesses pronounced antimicrobial properties. All leather and lining sample variants demonstrated significant antimicrobial efficacy against the tested

microorganisms, with DC-O effectiveness against *Candida albicans* being particularly noteworthy. In flex resistance tests, it demonstrated zones of 12+13 mm, while in both no rubbing and wet rubbing tests, it demonstrated zones of 12+10 mm. These analytical data confirm that the application of laurel oil and chitosan microparticles to leather footbeds and linings is an effective method of hygiene control using natural ingredients.

12. All test and analysis results demonstrate that antibacterial microparticles were produced via spray drying and successfully incorporated into footbeds. When studying the negative impact of unpleasant odours and bacterial growth in the footwear of people with pathological deviations on their quality of life, this study can address an important issue and offers advantages over other antibacterial chemicals due to the solution's non-toxic nature. In conclusion, this research could be useful not only for people with pathological foot deviations, but also for all consumers.