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EVALUATION OF ENVIRONMENTAL EFFECT OF PUMP SHOES IN TERMS OF MANUFACTURING PROCESS

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EVALUATION OF ENVIRONMENTAL EFFECT OF PUMP SHOES IN TERMS OF MANUFACTURING PROCESS

ABSTRACT. China is the largest footwear producing country, as well as the largest country producing the footwear manufacturing waste. In order to achieve sustainable development in the footwear industry, we should pay attention to their environmental effect seriously. Therefore, by applying life-cycle assessment (LCA) protocol, we aimed to explore the effect of the manufacturing process on the environment of a classical style of pump shoes. Following guidelines of ISO 14010, we first determined the objective and the scope of this study; then, we collected input and output data from the shoe producing line of a shoe-making enterprise in Wenzhou, China; afterwards, we applied eFootprint software for LCA modeling; finally, we chose three LCA indicators for further analysis: Global Warming Potential (GWP, kg CO_2 eq), Primary Energy Demand (PED, MJ) and Abiotic Depletion Potential (ADP, kg Sb eq). Our results show that by producing one pair of pump shoes, the manufacturing process will emit 11.427 Kg CO_2 eq in terms of GWP, 232.621MJ in PED and 6.291×10-5Kg sb eq in ADP. Hence, by multiplying the number of shoes produced in China, negative environmental influences from shoe making industry were also dramatic. According to further contribution rate of all process, we found that materials such as the water-based binder and the plastic last used in manufacturing process accounted for the major reason. Overall, while considering the environmental effects from the shoe manufacturing process, we shall not ignore the environmental impact whilst producing the binder and the last. Moreover, by reducing binder usage or updating the shoe making technology, and recycling the last can be an efficient way to reduce the environmental effects from the shoe making industry.

KEY WORDS: shoe making process, life cycle assessment, polyurethane synthetic leather, pump shoes

EVALUAREA EFECTULUI PANTOFILOR CU TOC ASUPRA MEDIULUI DIN PERSPECTIVA PROCESULUI DE FABRICAȚIE

REZUMAT. China este cea mai mare țară producătoare de încălțăminte, precum și cea mai mare țară generatoare de deșeuri de la fabricarea încălțămintei. Pentru a realiza dezvoltarea durabilă în industria încălțămintei, ar trebui să acordăm atenție serioasă efectului acestora asupra mediului. Prin urmare, prin aplicarea protocolului de evaluare a ciclului de viață (LCA), ne-am propus să explorăm efectul procesului de fabricație a pantofilor cu toc clasici asupra mediului. Urmând instrucțiunile specificate în ISO 14010, am stabilit mai întâi obiectivul și domeniul de aplicare ale acestui studiu; apoi am colectat date de intrare și ieșire din linia de producție de pantofi a unei întreprinderi din Wenzhou, China; ulterior, am aplicat software-ul eFootprint pentru modelarea LCA; în cele din urmă, am ales trei indicatori LCA pentru analiză ulterioară: Potențialul de încălzire globală (GWP, kg CO_2 echivalent), Cererea de energie primară (PED, MJ) și Potențialul de epuizare abiotică (ADP, kg Sb echivalent). Rezultatele noastre arată că, în urma procesului de fabricare a unei perechi de pantofi cu toc, se vor emite 11,427 kg CO_2 echivalent în ceea ce privește GWP, 232,621MJ pentru PED și 6,291 × 10-5Kg sb echivalent pentru ADP. Prin urmare, prin multiplicarea numărului de perechi de pantofi produși în China, influențele negative asupra mediului din industria încălțămintei au fost, de asemenea, dramatice. Conform ratei suplimentare de contribuție a tuturor proceselor, am constatat că materialele precum liantul pe bază de apă și calapodul de plastic utilizate în procesul de fabricație au reprezentat motivul principal. În general, luând în considerare efectele asupra mediului generate de procesul de fabricație a încălțămintei, nu vom ignora impactul asupra mediului în timpul fabricării liantului și calapodului. Mai mult, reducerea utilizării liantului sau actualizarea tehnologiei de fabricare a încălțămintei și reciclarea calapoadelor pot reprezenta o modalitate eficientă de a reduce efectele asupra mediului din industria încălțămintei.

CUVINTE CHEIE: procesul de fabricare a încălțămintei, evaluarea ciclului de viață, piele sintetică poliuretanică, pantofi cu toc

ÉVALUATION DE L›EFFET DU PROCESSUS DE FABRICATION DE CHAUSSURES À TALON HAUT SUR L'ENVIRONNEMENT

RÉSUMÉ. La Chine est le plus grand pays producteur de chaussures, ainsi que le plus grand pays générateur de déchets de chaussures. Afin de parvenir à un développement durable dans l'industrie de la chaussure, nous devons prêter une attention particulière à leurs effets sur l'environnement. Par conséquent, en appliquant le protocole d'analyse du cycle de vie (ACV), nous avons entrepris d'explorer l'effet du processus de fabrication des chaussures à talons hauts classiques sur l'environnement. En suivant les instructions spécifiées dans l'ISO 14010, nous avons d'abord établi l'objet et la portée de cette étude ; puis nous avons collecté des données d'entrée et de sortie de la chaîne de production de chaussures d'une entreprise de Wenzhou, en Chine ; par la suite, on a appliqué le logiciel eFootprint pour la modélisation ACV ; enfin, on a choisi trois indicateurs ACV pour une analyse plus approfondie : Le potentiel de réchauffement global (GWP, kg CO_2 équivalent), la demande en énergie primaire (PED, MJ) et le potentiel d'épuisement abiotique (ADP, kg Sb équivalent). Nos résultats montrent que, suite au processus de fabrication d'une paire de chaussures à talons, 11,427 kg CO_2 équivalent seront émis en termes de GWP, 232,621MJ pour PED et 6,291 × 10-5Kg sb équivalent pour ADP. Par conséquent, en multipliant le nombre de paires de chaussures produites en Chine, les influences environnementales négatives de l'industrie de la chaussure ont également été dramatiques. Selon le taux de contribution supplémentaire de tous les processus, nous avons constaté que les matériaux tels que le liant à base d'eau et la forme en plastique utilisés dans le processus

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de fabrication étaient la principale raison. De manière générale, compte tenu des effets environnementaux générés par le processus de fabrication de la chaussure, nous n'ignorerons pas l'impact environnemental lors de la fabrication du liant et de la forme. De plus, la réduction de l'utilisation de liants ou l'amélioration de la technologie de fabrication des chaussures et le recyclage des formes peuvent être un moyen efficace de réduire les effets environnementaux de l'industrie de la chaussure.
MOTS-CLÉS : processus de fabrication de chaussures, l'analyse du cycle de vie, cuir synthétique polyuréthane, chaussures à talons hauts

INTRODUCTION

China is the largest shoe producer, trader and consumer in the world, and its annual production, exports and consumption of shoes counted for 60%, 70% and 20% of the world individually [1]. Shoe-making process mainly includes three kinds of pollution: solid waste [2], dust pollution and volatile organic compounds (VOC) [3-6], where binders are the major source responsible for VOC emission in the manufacturing process. Although consumption of binder per pair shoe is 40g, by counting the amount of production which is over two billion pairs [7], more than 80,000t binder is consumed in footwear industry in China. Based on this fact, Chinese environmental authorities have listed the footwear industry as "severe pollution and high environmental risk" product inventory since 2017 [8-9]. Meanwhile, China promised in the Paris Agreement to reduce the carbon dioxide emissions per unit of China's GDP by 60% to 65% from 2005 by 2030. Therefore, it is necessary to evaluate the environmental effect of the shoe-making process, so as that we can optimize the production process, reduce waste emissions and finally achieve the goal of sustainable development.

In the strategical viewpoint, by means of life cycle assessment (LCA), researchers could quantitatively comprehend the environmental effect in terms of consumption of resources and energy as well as the emitted environmental load [10] for varied industry areas. Currently, a number of research studies has been conducted. Mila *et al*. [12] studied the LCA of women's leather shoes from cattle raising to abandonment, and then they found solid waste and cattle raising processes were the biggest environmental impacts sectors. Meanwhile, Barling [13] further approved that the animal raising was the main process contributing to higher environmental impact when manufacturing a pair of women's leather shoes. Afterwards, Cheah *et al*. [11] evaluated the carbon footprint of a pair of running shoes made of synthetic materials and they showed 14±2.7 Kg carbon dioxide equivalent emission in the production process. Further, Li Rui [14] assessed the LCA of three types of adhesive shoes and two module shoes in Fujian and Shanxi areas in China. They analysed the major polluting part or process of each kind of shoe, based on which they provided suggestions to enterprise how to reduce pollutant generation. Additionally, Serweta *et al*. [15] calculated the carbon footprint of seven outdoor shoes and they also provided suggestions for optimizing the manufacturing the process. Zhang June [2] investigated the recycling of used shoes and recommended disassembling, shredding and reusing to dispose, rather than simple incineration. Although the above studies focused on LCA in footwear industry, limitations still existed. (1) Polyurethane (PU), as a widely used material, was rarely reported in its evaluation on environmental impact; (2) Since a great part of shoe-making is the assembling process, we are still lacking knowledge about how the assembling process is affecting the environment.

Therefore, the aim of this study was to assess the LCA of a pair of pump shoes, and then to figure out the main environmental impacts in the shoe-making process. According to the literature, we can assume that adhesive materials, as well as plastic related components would have a heavy influence on the environment.

METHOD

Drawing lessons from the structure in principles of ISO 14010, we decide to use four steps leading to a complete LCA process: objective and scope determination, inventory analysis, impact assessment and interpretation of results. In this study, we chose the pump shoe as the target, one pair as the unit, since it was the most classical shoe style for ladies and is prone to become the criteria for other footwear styles. The pump was 60mm heel-height and made of PU material as shown in Figure 1. All the original data below came from the average of three times manual measurement in a large-

scale factory that cooperated with us. In this evaluation, the process of shoe-manufacturing follows the one employed in this factory.

Figure 1. Basic Pump Shoe

Objective and Scope Determination

The objective is first set to assess the environmental impact of manufacturing a pair of pump shoes and then to identify the critical process while the shoe is manufactured. Besides, we will provide some advice according to our conclusion in this study for the factory to make it more environmentally friendly.

As for the scope determination, since shoe-making is a process of assembling a number of components with the help of electricity, other factors such as upstream materials producing process were not considered. Further, the scope of this study was defined as input, assembling and output sections. The input included raw material and electrical energy consumed in processing machinery; while the assembling parts covered main materials, such as the heel, the midsole, the outsole, the last and other materials used in manufacturing process (OMMP). The output would consider the shoes and the waste. The system's boundary was shown in Figure 2.

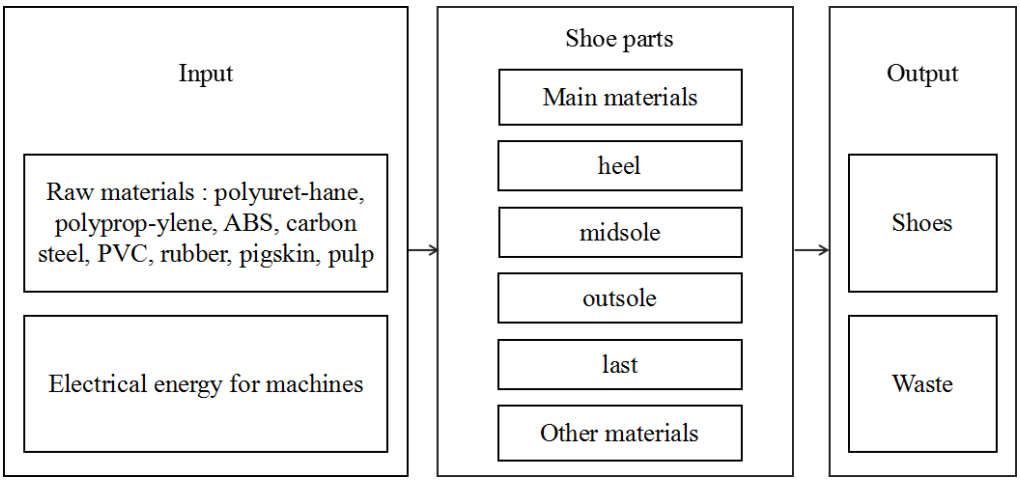

Figure 2. System Boundary of pump shoes

Inventory Analysis

LCI (life cycle inventory) refers to a listed target which required data collection process. According to the field data collection, we obtained all the necessary data for further modeling and they were shown in Table 1.

Table 1: LCA inventory data

Name	Material Name	Material Weight	Unit
PU	Polyurethane	44.2	g
Vamp lining	Pigskin	16.8	g
Front cap	Polyethylene	9.2	g
Back cap	Polyethylene	29.8	g
Heel	ABS	112	g
Mid sole	Pulp	24	g
Shank	Iron	40	g
Injection filler	Polypropylene	64	g

Name	Material Name	Material Weight	Unit
Single-layer sole	Polyunsaturate	84	g
Last	PVC	1104	g
Water-based binder	Polyurethane	46	g
Solvent binder	Polyurethane	30	g
Nail for heel	Carbon steel	2.8	g
Insole	Pigskin	4	g
Electricity	Electricity	0.1	kWh

Impact Assessment

We applied eFootprint software (IKE Environmental Technology Co., Ltd, China) for impact assessment. eFootprint is an online platform for LCA data reporting and analysis. It can be used to build life cycle models of various products and it includes the databases which satisfies most LCA modeling, such as China life cycle core database (CLCD), EU LCA database. Prior to modeling procedure, we determined that there is no by-products and renewable energy consumption in this study, so we would ignore the issues of waste regeneration. Meanwhile, materials whose weight accounted for less than 1% quantity of the production were filtered out.

This model refers to the cradle-to-gate procedure and a pair of shoes is considered as the basic unit. The upstream data of raw materials were from CLCD China ECER 0.8.1 and Ecoinvent database. The specific modeling and analysis processes were shown in Figure 3.

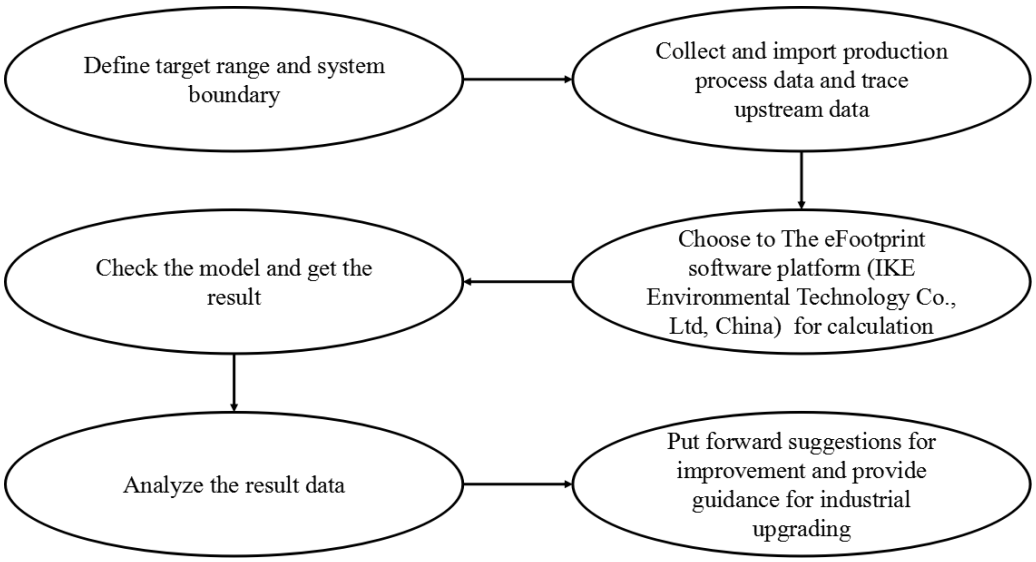

Figure 3. Flow chart of modeling and analysis

Interpretation of Results

In this study, we adopted three kinds of highlighted indexes: GWP, PED and ADP. GWP implies the strength of greenhouse gases using carbon dioxide (CO_2) as a benchmark; PED summaries the net increment of energy consumption; ADP indicates the non-biological consumption using Stibium (Sb) as a benchmark. Moreover, contribution rate of inventory data was also assessed. This indicator refers to the change of the index caused by a change rate of inventory data. By assessing the contribution rate of inventory in eFootprint, we could deeply comprehend our LCA results.

RESULTS AND DISCUSSIONS

Overall Environmental Impact Analysis

The main environmental impact types of the shoes were chosen as GWP, PED, and ADP.

GWP (total carbon footprint) of the shoes is 11.427 kg CO_2 eq, PED is 232.621 MJ, and ADP is 6.291×10-5 kg Sb eq.

Analysis of Environmental Impact of Each Manufacturing Section of the Shoes

The contribution rate of inventory data was shown in Figures 4-6.

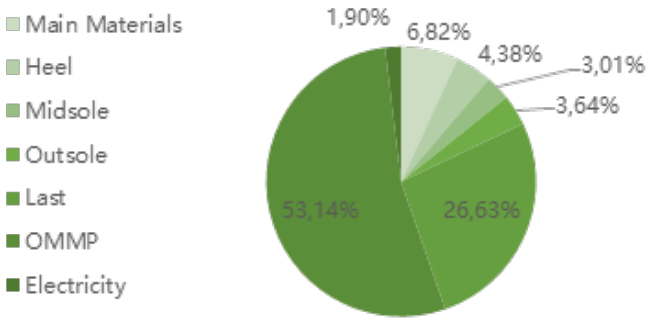

Figure 4. List contribution rate of PED (MJ)

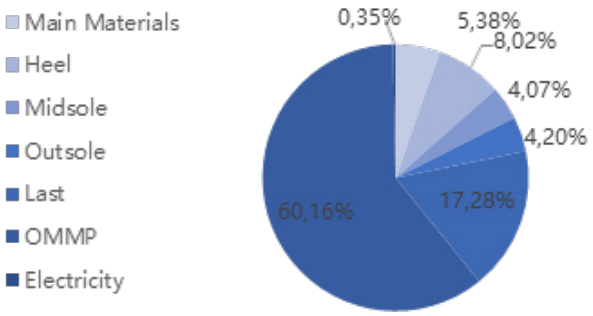

Figure 5. List contribution rate of ADP (kg Sb eq)

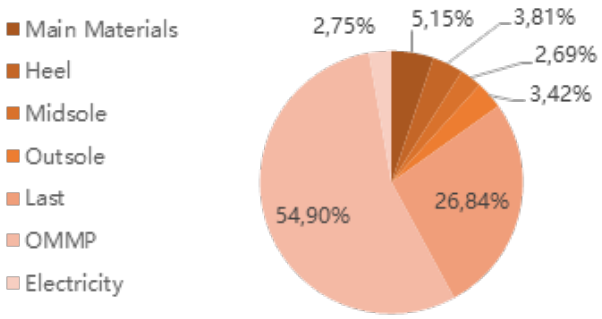

Figure 6. List contribution rate of GWP (kg CO_2 eq)

It could be seen from these figures that the shoes had a negative impact on the environment in general. The components assembled in the manufacturing process had the greatest negative impact on the environment, accounting for more than 50% of the three indexes. The last accounted for about 20%, while other parts had less impact.

By reviewing the major contributions, we found that OMMP contributed the most.

Within OMMP, water-based binder was the reason (Table 2).

Table 2: Contribution of other materials used in manufacturing process to LCA results

Part name	PED (MJ)	ADP (Kg SB eq)	GWP (Kg CO_2 eq)
Water-based binder	46.43	52.28	47.93
Solvent-based binder	6.58	7.41	6.79
Accessories	0.12	0.47	0.18

Discussions

In this study, we first assessed the LCA of a pair of pump shoes and found significant influences on environment; further, by contribution rate of all inventory, we highlighted that the key pollution factors were the water-based binder, solvent binder and the last. Our findings established a basis of LCA for women's shoes manufacturing process.

It was interesting that the adhesive materials, especially the water-based binder, used in the manufacturing process are a factor that contributed a lot to the LCA results. It might be postulated that adhesive materials easily emit VOCs. Naldzhiev *et al*. [16] found that polyurethane products might cause negative health effects at high concentrations, such as dizziness, eye irritation, skin irritation and pulmonary irritation. At present, a large amount of binder is used in footwear industry. Therefore, it is urged to reduce the use of adhesive materials or use an alternative technology to replace them.

Moreover, our outcomes also showed that the last was another contributor. Njati *et al*. [17] indicated that PVC products might increase the risk of lead poisoning due to its usual heavy metal additives. But in general mass production, shoe lasts are normally recycled or produced using recycling materials. Therefore, although the last contributed a significant portion to each environmental index, its actual influence on the environment was much lower. Additionally, according to improving the re-utilization of materials, we can reduce the impact of the last on the environment.

Although we finished the calculation and analysis of LCA method, there were limitations in our study inevitably: (1) Due to the limited tools, some materials could only be replaced by similar materials, such as synthetic leather material is a kind of complex material. But in this study, it was only considered as its main material polyurethane for calculation, which was a certain deviation from the actual, but still had a good direction guidance ability. We will improve the conditions of the study to carry out more detailed calculation of the various materials. (2) Our study only analyzed the environmental impact of the shoes, but it lacked the comparative analysis between the various production processes. Based on this study, the later research can establish models of other kinds of craft shoe-making and carry on the comparative analysis to find out the more environmentally-friendly process. Furthermore, some theoretical guidance should be made to upgrade shoe-making enterprise and even the whole industry.

According to our research above, we developed a protocol for footwear industry, such as how to collect the field data during the shoe making process and how to calibrate those data for LCA analysis. Secondly, we focused on pump shoes, which is a basic model in fashion shoes. Furthermore, according to this basic model, we could compare how the design or style in other fashion shoes affected the LCA results and then to develop a method to predict the LCA of other fashion shoes by means of simulation. The last one is that we used sourcing data of LCA from local database, which made the LCA results be more coordinated.

CONCLUSIONS

Overall, by LCA method, we quantitatively evaluated the environmental impact of the manufacturing process of women's single shoes. We can further summarize that while considering the environmental effects from the shoe manufacturing process, we shall not ignore the environmental impact whilst producing the

binder and the last. Moreover, reducing binder usage or updating the shoe making technology, and recycling the last can be an efficient way to reduce the environmental effects from the shoe making industry.

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Conflicts of Interest Statement

There are no conflicts of interest with other authors and institutions. No subjects or animals were included in this study. Neither participants nor informed consent were included in the study.

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ANALYSIS OF VARIATION OF THE SKIN SUBSTANCE WITH THE APPLICATION OF DIFFERENT ACIDS IN THE PICKLE STAGE IN ECUADORIAN SERRANO BOVINE LEATHERS

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ANALYSIS OF VARIATION OF THE SKIN SUBSTANCE WITH THE APPLICATION OF DIFFERENT ACIDS IN THE PICKLE STAGE IN ECUADORIAN SERRANO BOVINE LEATHERS

ABSTRACT. A chemical analysis was carried out to determine the content of skin substance in different leather samples prepared using several acids in the pickling stage. Ecuadorian bovine skin was utilized. It went through the tanning processes until reaching the pickling stage in which three treatments employing sulfuric acid, formic acid and oxalic acid, respectively, were applied. Later, tanning was applied, wet blue samples were obtained and their contents of skin substance were measured by means of AST D2868-17 rules. Results were verified through a statistical analysis using Infostat software. After post tanning stages a dyed leather was obtained upon which physical tests of tension resistance, elongation percent and lastometry as well as sensorial essays of feeling, softness and swelling were executed. The treatments produce results of skin substance from every leather area, that is, head, loin and backside. It is found that the sulfuric acid pickling features the highest content of skin substance (72.63%) followed by the formic acid pickling (70.94%) and the oxalic acid pickling which has the lowest amount of skin substance (65.04%). In order to validate the results, a statistical analysis was performed which confirms the chemical analysis. To ratify which one was the best treatment, a comparison based on the properties of each acid was made. The formic acid was confirmed as the most appropriate since it differentiates from the sulfuric acid due to the skin substance content by complying with the required parameters of elongation (15.89%), and softness/swelling (4%). On the other hand, oxalic acid produced lesser quality results.
KEY WORDS: skin substance, type of acid, pickling, physical analysis, sensory analysis

DETERMINAREA VARIAȚIEI SUBSTANȚEI DERMICE LA APLICAREA DIFERIȚILOR ACIZI ÎN ETAPA DE PICLARE A PIEILOR BOVINE SERRANO ECUADORIENE

REZUMAT. S-a efectuat o analiză chimică pentru a determina conținutul de substanță dermică în diferite probe de piele preparate folosind mai mulți acizi în etapa de piclare. S-a utilizat piele bovină ecuadoriană, care a fost prelucrată până la etapa de piclare în care au fost aplicate trei tratamente cu acid sulfuric, acid formic, respectiv acid oxalic. Ulterior, s-a aplicat tăbăcirea, s-au obținut probe de piele wet blue și s-a măsurat conținutul de substanță dermică utilizând AST D2868-17. Rezultatele au fost verificate printr-o analiză statistică utilizând software-ul Infostat. După etapele ulterioare tăbăcirii s-a obținut o piele vopsită pe care s-au executat teste fizice pentru determinarea rezistenței la rupere, procentului de alungire și gradului de întindere, precum și teste senzoriale de tușeu, moliciune și gonflare. Rezultatele privind conținutul de substanță dermică în urma tratamentelor sunt obținute pentru fiecare zonă a pielii, adică zona capului, cruponul și șira spinării. S-a constatat că piclarea cu acid sulfuric generează cel mai mare conținut de substanță dermică (72,63%), urmată de piclarea cu acid formic (70,94%) și piclarea cu acid oxalic, care generează cea mai mică cantitate de substanță dermică (65,04%). Pentru a valida rezultatele, s-a efectuat o analiză statistică care confirmă analiza chimică. Pentru a confirma cel mai bun tratament, s-a făcut o comparație bazată pe proprietățile fiecărui acid. Acidul formic a fost confirmat ca fiind cel mai potrivit, deoarece se diferențiază de acidul sulfuric datorită conținutului de substanță dermică prin respectarea parametrilor necesari de alungire (15,89%) și moliciune/ gonflare (4%). Pe de altă parte, acidul oxalic a produs rezultate de calitate mai scăzută.
CUVINTE CHEIE: substanță dermică, tip de acid, piclare, analiză fizică, analiză senzorială

DÉTERMINATION DE LA VARIATION DE LA SUBSTANCE DERMIQUE EN APPLIQUANT DE DIFFÉRENTS ACIDES DANS L'ÉTAPE DE PICKLAGE DE LA PEAU BOVINE SERRANO ÉQUATORIENNE

RÉSUMÉ. Une analyse chimique a été effectuée pour déterminer la teneur en substance dermique dans divers échantillons de peau préparés à l'aide de plusieurs acides au stade du picklage. On a utilisé de la peau bovine équatorienne, qui a été traitée jusqu'à l'étape de picklage au cours de laquelle trois traitements ont été appliqués avec de l'acide sulfurique, de l'acide formique et de l'acide oxalique, respectivement. Par la suite, on a appliqué le tannage pour obtenir des échantillons de peau wet blue et la teneur en substance dermique a été mesurée à l'aide de l'AST D2868-17. Les résultats ont été vérifiés par une analyse statistique à l'aide du logiciel Infostat. Après les étapes de post-tannage, un cuir teint a été obtenu sur lequel des tests physiques ont été effectués pour déterminer la résistance à la rupture, le pourcentage d'allongement et le degré d'étirement, ainsi que des tests sensoriels de toucher, de douceur et de gonflement. Les résultats concernant la teneur en substance

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dermique après les traitements sont obtenus pour chaque zone de la peau, à savoir le collet, le croupon et le dosset. Le picklage à l'acide sulfurique a généré la teneur en substance dermique la plus élevée (72,63%), suivi par le picklage à l'acide formique (70,94 %) et le picklage à l'acide oxalique, qui a généré la plus faible quantité de substance dermique (65,04 %). Pour valider les résultats, une analyse statistique a été réalisée confirmant l'analyse chimique. Pour confirmer le meilleur traitement, une comparaison a été faite sur la base des propriétés de chaque acide. L'acide formique a été confirmé comme le plus approprié, car il diffère de l'acide sulfurique en raison de la teneur en substance dermique en observant les paramètres nécessaires d'allongement (15,89 %) et de douceur/gonflement (4 %). D'autre part, l'acide oxalique a produit des résultats de moins bonne qualité.
MOTS CLÉS : substance dermique, type d'acide, picklage, analyse physique, analyse sensorielle

INTRODUCTION

The existence of leather stems from prehistory which evidences that men employed animal skins to protect themselves from cold, dress for battle, and cover objects [1]. Currently, the industry of tanning handles the transformation of skin into leather for clothing, shoes, and tapestry manufacturing, among other applications [2].

In Ecuador, leather industry began to reach its peak during the 1970s when it turned from a handcrafted to an industrial endeavor. Around 900.000 cattle skins are processed in slaughterhouses per year, and approximately 40 percent of them are destined to leather production. The Andean region stands out for this kind of production that concentrates in Tungurahua, Azuay and Pichincha provinces. A competition has been established between formal and informal companies dedicated to tanning [3].

The complexity that surrounds the acquisition of high-quality leather from raw material to elaborated leathers causes Ecuadorian leather to lack a high-quality level. These aspects have forced the tanning companies and researchers to experimentally investigate the leather processing in order to produce data and findings that could help to understand and improve its quality [4].

Transformation of skin into leather runs through different stages from raw materials reception until the leather finishing stage. One of the most important steps in leather tanning is pickling since it prepares the skin with the optimal pH of 3-4 so the tanning agents could achieve a good penetration into the skin structure [5]. During pickling an acid is used as the main reagent. This process works with strong, weak, and organic acids such as sulphuric, formic, acetic, lactic, oxalic, and hydrochloric acid. To avoid an excess of acidity and eliminate any lime residuals, a salt, commonly sodium chloride, is added. Depending on the type of leather intended to be obtained or client requirements, a single acid or the combination of several acids is utilized [6].

In recent decades, some investigations have been conducted to find new alternatives, sustainability and cost-effectiveness. These efforts include product variation in several process stages, usage of different kinds of skin and technology innovation. When a reagent is changed in any of the process stages, physical, sensorial and statistical analyses are applied. But scarce evidence is available at national level regarding the chemical analysis of leathers. Hence, this kind of research is relevant to get deeper understanding of the influence of a particular reagent on the variation of certain leather parameters, such as the skin substance.

The content of skin substance is one of the chemical analyses performed on leather, and it is obtained multiplying the content of nitrogen by a factor of 5.62 [7-8]. This parameter is calculated in several stages of the leather processing from the first type of leather, either wet blue or wet white, to the finished product [9]. For the determination of skin substance, a specific standard (ASTM D2868-17) exists. This one utilizes the Kjeldahl method to calculate the value of this parameter. The standard indicates the 5.62 factor, however such figure can have a 3% variation of based on the region, breed, sex, age, etc. [10]. There is no straightforward methodology to calculate the skin substance; despite this fact, the analysts work with dried, either shredded or pulverized, leather [11].

The use of a statistical analysis is relevant to verify the results. Software package Infostat is an application found in the Windows operating systems which features descriptive statistics, graphic methods, and advanced techniques of statistical modeling and multivariate analysis to analyze experimental results allowing it to generate hypothesis and compare its results to chemical, physical, sensorial, economic and social essays [12]. In leather research, in order

to guaranty and verify leather quality it is common to use physical and sensorial analyses. Regarding the physical ones, tension, tearing, elongation percent, lastometry, thickness and flower break, among others, stand out. These measurements are performed using appropriate instruments. This is applicable to finished and semi-finished leathers [13]. Sensorial analyses are carried out by qualified, experienced people. This measurement uses a one to five scale, five means outstanding, four meaning very good, three good, two average and one equals bad. These essays comprise parameters such as touch, softness, fullness, finesse, brightness and color. Sense organs like sight, olfaction and touch are utilized [14].

EXPERIMENTAL

Materials and Methods

Materials

In this investigation, a laboratory-scale drum capable of holding 10 skin strips, a macro Kjeldhal instrument, a dryer, a pH meter, an elastometer, and several other materials for each step of the process (pH paper, thermometer, volumetric flasks, kjeldahl flasks, pipette, burette, digestion tubes and analytical scale) were utilized.

Methods

A research methodology based on evidencing how the skin substance varies with the application of several treatments during one of the production stages is carried out. Data were generated and results were obtained by applying an experimental procedure which details from raw material characterization, passing through the tanning process, making emphasis in the pickling stage with the acid changes, until performing the chemical, physical and sensorial essays.

Experimental Design

A research methodology based on evidencing how the skin substance varies with the application of several treatments during one of the production stages is carried out. Data were generated and results were obtained by applying an experimental procedure which details from raw material characterization, passing through the tanning process, making emphasis in the pickling stage with the acid changes, until performing the chemical, physical and sensorial essays.

Characterization of Raw Materials

Ecuadorean Andean cattle skin is employed, in this case, cow skin. One skin strip is used for each treatment, that is, three strips for each of the experimental treatments.

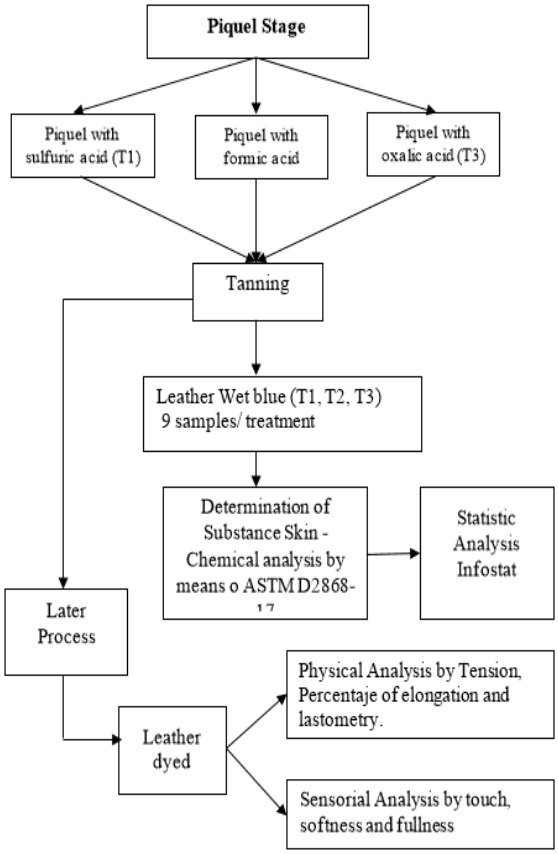

Figure 1. Experimental Design

Stage of Tanning: Pickling

Pickling is the stage under investigation. In such process, one of the reactants is changed to determine the content of skin substance, in this case the type of acid. At industrial level, a combination of acids is employed, but in this research three acids are individually applied which produce different values in each of the treatments. The following acids are applied with 6% of salt in relation to weight: the first treatment (T1) operates with sulfuric acid as a strong inorganic acid; the second treatment operates with formic acid as a weak organic acid; and the third one utilizes oxalic acid as a dicarboxylic organic acid. The acid concentration depends on the pH obtained during the deliming, for all the treatments a pH of approximately 3 is obtained.

Table 1: Stages of pre-tanning

PRE-TANNING STAGES		
Soaking		
Liming and lime		
Deliming and bating		
	Pickling	
Pickling with sulfuric acid (T1)	Pickling with formic acid (T2)	Pickling with oxalic acid (T3)

The next stage, tanning, is the one in which the skin turns to leather through the application of tanning agents [15-16]. Chrome salts are used to obtain the first type of leather known as wet blue and the determination of the content of skin substance for each of the treatments follows.

Chemical Analysis – Determination of the Content of Skin Substance by means of ASTM D2868-17 Norm

In order to calculate the content of skin substance, a drying of the sample to be analyzed is carried out first. The sample is subjected to a temperature of 102°C during a lapse of 4 to 8 hours until a constant weight is obtained [17]. The whole skin of the animal is divided in two strips, and each strip is divided in three main zones of the skin, that is, head, trunk and backside. Three samples are taken from each skin zone getting a total of nine samples for each treatment. The skin and leather always produce different results on each one of the zones; two skin samples that give the same results will never be found. This is the reason why a different strip is used for each treatment and three samples are considered for each zone.

The ASTM-D2868-17 standard, describes the Determination of nitrogen and skin substance in leather, blue leather (wet blue) and white leather (wet white) through the Kjeldahl method, that consist in a digestion, distillation and titration or volumetric analysis.

Determination of the Percentage of Chromium in Leathers

The chromium content in tanned leathers is a primary test within leather research, for this analysis we worked with the technique Chromium absorption in leather of the SIRAC (Environmental Reference System for the Colombian Tannery Sector), which mentions the percentage chromium oxide Cr_2O_2 absorbed by tanned leather with a high degree of accuracy; three samples were taken for each area of the skin, head, back and butt with a total of nine samples for each acid used, used as samples in the same way as wet blue.

Statistical Analysis

From the values obtained for the content of skin substance in the different zones of each treatment, a statistical study can be applied using the software package Infostat by running an analysis of variance on the results.

Table 2: Determination of skin substance by means of ASTM D1868-17 standard

	Chemical Analysis	
T1	Head zone: 3 samples Center zone: 3 samples Butt zone: 3 samples	ASTM-D2868-17, *Nitrogen and Substance Skin Content Leather in leathers, blue leather (wet blue) and white leather (white leather)*
T2	Head zone: 3 samples Center zone: 3 samples Butt zone: 3 samples	
T3	Head zone: 3 samples Center zone: 3 samples Butt zone: 3 samples	

Table 3: Determination of the Percentage of Chromium in leathers by means of SIRAC

	Chemical Analysis	
T1	Head zone: 3 samples Center zone: 3 samples Butt zone: 3 samples	SIRAC (Environmental Reference System for the Colombian Tannery Sector), *Determination of the Percentage of Chromium in leathers*
T2	Head zone: 3 samples Center zone: 3 samples Butt zone: 3 samples	
T3	Head zone: 3 samples Center zone: 3 samples Butt zone: 3 samples	

Table 4: Statistical analysis

T1	Head: 3 results Loin: 3 results Rear: 3 results	Analysis of variance using the Infostat software (Substance Skin Content)
T2	Head: 3 results Loin: 3 results Rear: 3 results	
T3	Head: 3 results Loin: 3 results Rear: 3 results	

Physical and Sensorial Analyses

A variety of physical and sensorial parameters exist. The essays that customarily are carried out on leather were applied. Specifically, physical essays of lastometry by means of INEN 555 standard [18], percent of elongation and tension using the ISO 3376 standard [19]. Regarding the sensorial analysis, the majority of parameters work with grades from 1 to 5. Touch, softness, and fullness essays are applied along all the zones of the skin strip. The results from both physical and sensorial analyses verify the results of chemical essays and provide a comparison among all the obtained values.

Table 5: Physical analysis

Physical analysis		
T1	Dyed leather band	• Test Lastometry
T2	Dyed leather band	• Test Percentage of elongation
T3	Dyed leather band	• Test of Tension

Table 6: Sensorial analysis

Sensorial analysis		
T1	Dyed leather band	• Test Touch
T2	Dyed leather band	• Test Softness
T3	Dyed leather band	• Test Fullness

RESULTS AND DISCUSSIONS

Table 6 depicts the characterization of raw materials. Skin of cows from the Andean region was chosen because this region comprises the main leather production at national level. This type of skin is the most commercial and it is utilized by leather companies all over the country.

Table 7: Characterization of raw materials

Type	Sex	Size	Appearance	Weight
Ecuadorian serrano bovine skin (Beef)	Female	Small	Medium hard skin, two-colored coat, skin with a healthy surface, no skin damage	Skins between 5 to 6 kg.

Pickling Stage

Pickling is the stage prior to tanning, in which the sulfuric, formic and oxalic acids adequately prepare the skin so it reacts correctly to the tanning agents; in Figures 2, 3 and 4 show the variation of time versus the pH of each treatment.

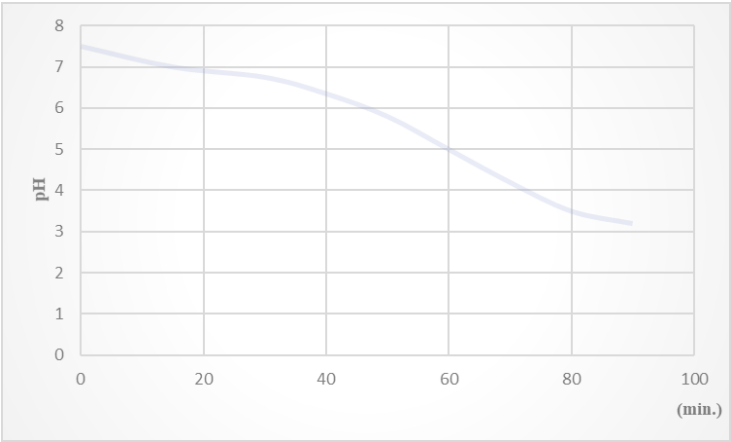

Figure 2. Pickling – Sulfuric Acid Curve (T1)

Figure 2 evidences that pickling with sulfuric acid requires approximately 90 minutes to reach a pH of 3 and it consumes around 1.25% of the acid in regard to the pelt weight. At industrial level, the pickling takes an average time of 2, 4, and 6 hours. In our case, time is shorter because we work at laboratory scale and employ a small amount of skin. The mechanical action has proven to be important during all the stages.

Sulfuric acid is a diprotic, strong, inorganic acid. The pH was monitored at 15 and 20 minutes, the pH decreasing was evidenced since the skin has different zones. This causes every added agent to react differently in each, these zones are head, center and butt.

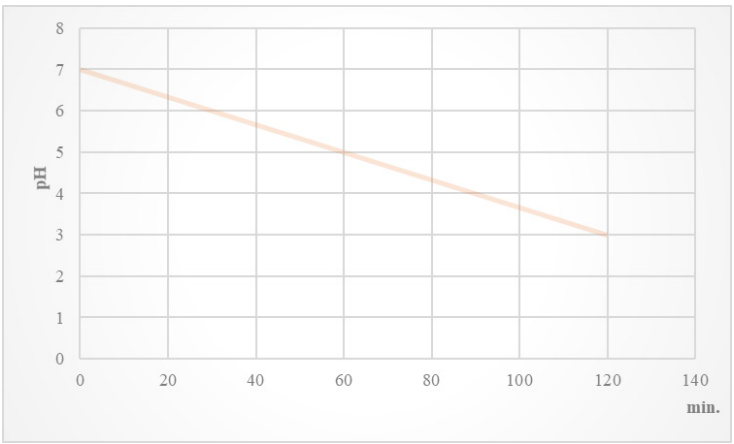

Figure 3. Formic acid pickling curve (T2)

Figure 3 shows the addition of formic acid (T2). This one is more regular regarding time, being measured in intervals of 15 minutes. It evidences a pH/time curve that is more uniform; the effect of the reagent was more effective, this weak organic acid behaves as a masking agent, preventing the release of substances such as chromium salt from the internal structure of the skin: the collagen.

It provides a good level of penetration having a higher reaction along all the skin zones. The approximate time was 120 minutes and a consumption of 2% regarding to the gut weight was obtained. Such time can vary depending on the mechanical action and equipment.

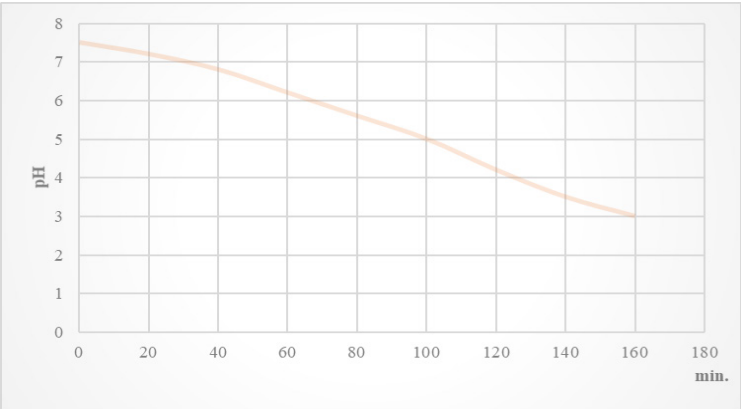

Figure 4. Pickling curve with oxalic acid (T3)

Figure 4 shows the results for treatment T3, which employs oxalic acid. This is a dicarboxylic acid that releases two hydrogen ions per molecule and it is a lyotropic agent capable of producing swelling, it can also generate changes in the internal structure of the skin due to the presence of carboxylo and amino ions. The penetration level is rather shallow, the acid reacts superficially with the skin producing a higher time (160 minutes) and 3.25 percent of acid consumption. From these results it is deduced that such treatment is deficient.

Determination of Skin Substance

After the pickling, tanning is carried out, this stage produces wet blue samples for each treatment. They were dried applying the INEN-565 standard. In order to determine the content of nitrogen and skin substance, the ASTM-D2868-17 standard was applied. This one allows to calculate such parameters both in wet blue and other leathers, it is emphasized that a 4% chromium salt was used in relation to weight in all the tests. Table 7 depicts the results for skin substance in each leather zone, a total of 9 results for each treatment. It was specified that results for samples 1, 2 and 3 correspond to the head zone, results 4, 5, and 6 to the trunk zone, and results 7, 8, and to the backside zone. It is evidenced that the skin content is irregular for each leather zone as well as for each treatment. In the case of T1, the norm produces an average result of 72.6296 % for skin substance content which is the highest. For T2, a skin substance content of 70.9446% is obtained, hence this one ranks second. Finally, T3 produces a content of 65.0440% which is far inferior to the rest, therefore this treatment is the one with less skin substance content.

Table 8: Skin substance results for each treatment

	Pickling with sulfuric acid	Pickling with formic acid	Pickling with oxalic acid
1	69.4603	73.7332	67.7032
2	71.3064	71.0598	64.3845
3	70.1241	72.1305	65.3914
4	74.5949	70.7324	67.8155
5	76.6506	71.3571	64.0792
6	76.1898	72.1540	65.4690
7	71.0060	68.5360	66.3406
8	71.5702	69.9500	61.6577
9	72.7644	68.8479	62.3208
AVERAGE	72.6296	70.9446	65.0440

Table 7 proves that the results from samples 1, 2 and 3 correspond to the head zone, those from samples 4, 5, 6 correspond to the trunk zone, and those from samples 7, 8 and 9 correspond to the backside zone. It is verified that the skin substance content is irregular in each zone and each treatment as well.

Regarding T1, the norm produces an average value of 72.63% for skin substance content, therefore this the treatment that produces the highest skin substance content. T2 places itself second with 70.9446%, and T3 – which utilizes oxalic acid – with an average value of 65.0440% is the treatment with the lowest value of all.

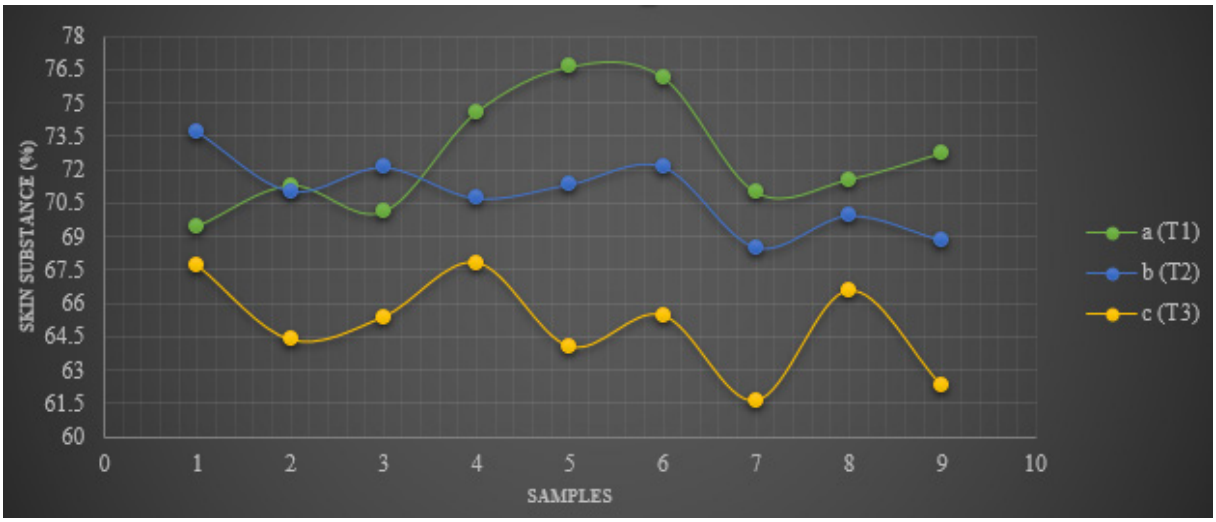

Figure 5. Curves of skin substance for (a) Pickling with sulfuric acid, (b) Pickling with formic acid, and (c) Pickling with oxalic acid

Figure 5 depicts the relation skin substance versus treatment for the 9 samples of each treatment. ASTM D2868-17 standard points out a reference value of 72.93% for the average substance skin content. The sulfuric acid pickling (T1) produces significantly higher values since this one is a strong inorganic acid that gives a primary and a secondary ionization which generates a gradual reaction with the amino and carboxyl bonds of collagen. In this way, skin consumption is prevented and an average value of 72,6296% is reached. This result is the closest one to the reference set by the standard. Examination of the curve shows a higher skin substance content for the trunk zone. This zone is hardest and hence the most difficult to penetrate. Head and backside zones produce similar values, the treatment with formic acid (T2) produces a significant skin substance content of 70.9446% which is close to the T1 value and the norm standard. This acid is optimum because of its properties, such as being a reduction agent and its good level of penetration in the skin; furthermore, it is a masking agent that reacts with chromium salts helping the tanning to penetrate more effectively and avoiding its detaching from the collagen structure. The results from the head, trunk and backside zones display similar values, giving rise to a more uniform curve that evidences the level of penetration of this acid is effective along the whole skin. The pickling with oxalic acid produced the lowest content of skin substance since this is a strong, dicarboxylic, organic acid, unstable when subjected to heating which leads to its decomposition in CO_2, CO and H_2O. A deficient reaction between the acid and the collagen structure is achieved. Hence, this treatment should be discarded because of its low effectiveness of penetration as well as the deficiency to work in an individual way, stressing that this treatment gives results very distant from those of the other ones and the reference set by the standard.

The reference value established by the standard does not surpass the other results. This will vary with the region, sex, race and other characteristics that make skin or leather investigation differ. Regarding quality, the skin

substance is not a quality index but a control one. This index serves as a reference for leather conservation, tanning standard and a datum of interest for tanners, as well as a reference for physical or sensorial analysis. All these results provide a standard to verify quality along with the physical and sensorial essays performed with the different treatments.

Chromium Percentage Analysis in Leathers

Additionally, within the chemical analysis, the percentage of Cr_2O_3 consumed in each of the treatments of each acid was determined in order to make a comparison with the skin substance analysis, mentioning that the T1, treatment with sulfuric acid had a good penetration of chromium in the fibers of the head, back and butt areas with an average value of approximately 2,001%, showing a light blue color in the flower area and in its thickness an almost uniform color, for the T2 with formic acid as expected, it was the best treatment due to the properties that this acid presents, especially that of allowing a good penetration of chromium in the structure of the skin with an average value of 2,913% approaching the 3-5% interval, which are values that are daily present in leathers mentioning that for a leather to be of quality it should not be less than 2.5% according to the SIRAC technique, corroborating the results of skin substance which is evidenced as the best treatment and an optimal acid to continue working on a daily basis within the tanning industry; on the other hand, the T3 being with oxalic acid, presented a simply superficial penetration with an average of approximately 1,140% due to the properties of this acid that it is advisable to work it in a combined way, finally comparing these results with the substance analysis they position the treatments in a hierarchy similarly.

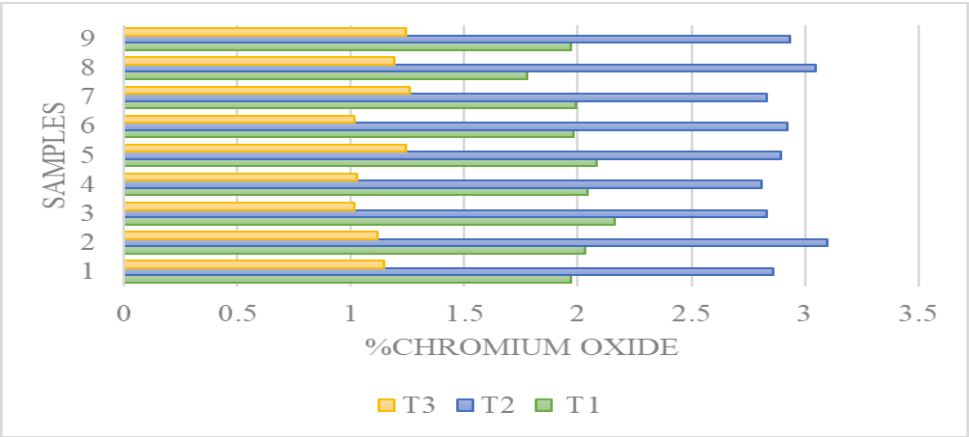

Figure 6. Percentage of Chromium results for each treatment T1, T2 and T3

Table 9: Percentage of Chromium results for each treatment

	Pickling with sulfuric acid	Pickling with formic acid	Pickling with oxalic acid
1	1.9685	2.8575	1.143
2	2.032	3.0988	1.1176
3	2.159	2.8321	1.016
4	2.0447	2.8067	1.0287
5	2.0828	2.8956	1.2446
6	1.9812	2.921	1.016
7	1.9939	2.8321	1.2573
8	1.778	3.048	1.1938
9	1.9685	2.9337	1.2446
AVERAGE	2.0009	2.9139	1.1401

Analysis of Variance

An analysis of variance was applied to the data from the chemical essays to corroborate the results, the software package InfoStat was utilized. Table 8 shows the average results of skin substance when treatments T1 and T2 are compared. These values are similar between them and close to the reference value set by the standard which is in accord with the results of the chemical analysis. A careful look to the table allows to group T1 and T2 together because of the closeness of their results. T3 pertains to a different group since its results are significantly different from those of T1 and T2. Hence, the pickling treatments with sulfuric acid and formic acid feature optimum properties for the tanning process. However, they differ in regard to their individual properties. As showed, each treatment worked on nine samples to produce skin substance results that rank in decreasing order. Figure 6 verify this finding by comparing the average values of each treatment with the results from the chemical analysis.

Table 10: Analysis of variance

	Treatment	Average	n	E.E.	Type A	Type B
1	T1	72.63	9	0.73	A	
2	T2	70.94	9	0.73	A	
3	T3	65.02	9	0.73		B

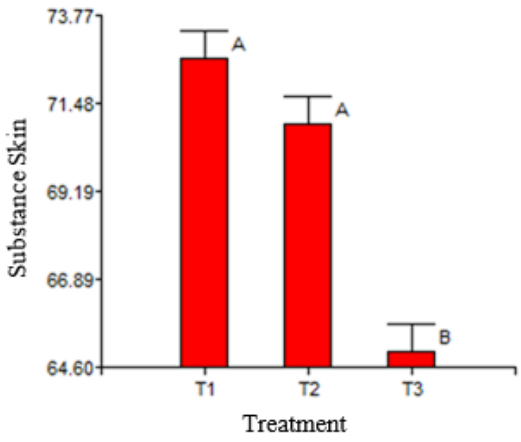

Figure 7. Statistical analysis

Physical Analysis

Tear Strength

This technique measures the resistance to breaking of the grain along with the process of gradually stretching a leather specimen until the final rupture of its fibrillar chains. The procedure is based on the AENOR standard which states that all leather samples should surpass the reference value of 1000 N/cm^2. For T1 a value of 1485.2 N/cm^2 was achieved, T2 produced a value of 1154.2 N/cm^2, and T3 gave a value of 1228.1 N/cm^2. As it is observed, T1 produces the highest value. These results can be explained from the fact that the dyed leather did not pass through all the finishing procedures, such as stretching and softening which are influential during the application of a physical analysis.

Table 11: Physical analysis

Treatment	Tear strength (N/cm^2)	Percentage of Elongation (%)	Lastometry (mm)
T1 (pickling with sulfuric acid)	1485	10.71	24.88
T2 (pickling with formic acid)	1154	15.89	11.27
T3 (pickling with oxalic acid)	1228	8.80	68.66

Percentage of Elongation

It is based on the INEN 1061 or ISO-3376 standards. It states that the value of reference of elongation percentage for leather is a value between 40 to 80%. Treatment T2 produces an elongation percentage of 15.89% which is the highest of all; T2 follows with an elongation percentage of 10.71%, while T3 gives a result of 8.80%. From these data, it is observed that framing T2 as the closest to the established treatment parameters, discarding T3 with a relatively low value; these results are not up to standard based on leather finishing conditions.

Lastometry

The INEN 555 standard rules this parameter. It states that the lowest reference value which is accepted for lastometry is 7.20 mm. T1 achieves a value 24.88 mm, T2 produces a value of 11.27 mm, and T3 gives a value of 68.66 mm. All treatments comply with the reference value, but it is observed that T3 provides a parameter which is significantly higher than those of the rest. This could be explained by the fact that oxalic acid is not recommended to be used individually and because of its properties. Regarding the results from T1 and T2, they are closer to each other, the observed difference could be attributed to the distinctive properties of sulfuric and formic acids.

Sensorial Analysis

For sensorial analysis, a grading scale of 1 to 5 points is applied. Scores are registered by qualified, highly experienced persons. Figure 7 evidences that formic acid pickling (T2) obtained the highest score in touch, featuring a higher sensitivity and softness at the fingertips contact. Regarding softness and fullness, this leather has a flexible appearance; it also shows a steady color, tanning and dyeing across the whole leather surface since formic acid has a good level of penetration. On the other hand, the oxalic acid pickling produced poor results in all sensorial parameters, causing flaws in the leather.

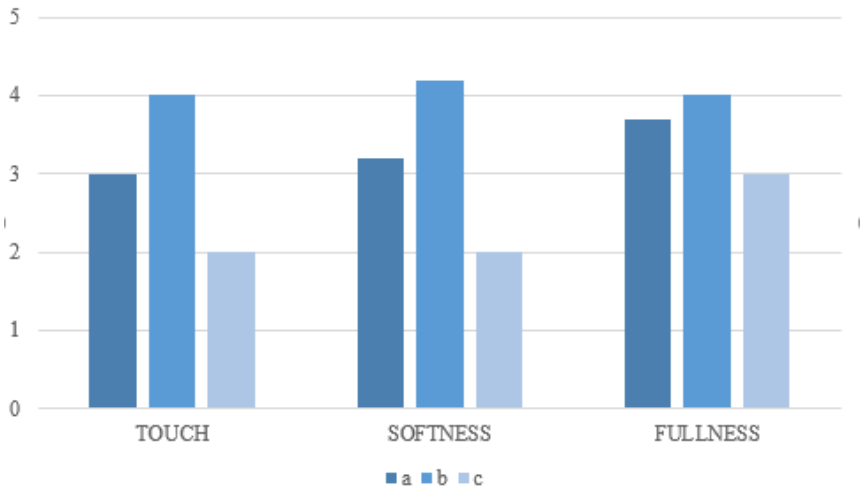

Figure 7. Sensorial analyses of: (a) Sulfuric acid pickling, (b) Formic acid pickling, (c) Oxalic acid pickling

CONCLUSIONS

A chemical analysis was applied to all the treatments, the sulfuric acid pickling (T1) produced the highest content of skin substance (72.63%) which is close to the reference value of ASTM D2868-17 standard (72.93%). The formic acid pickling (T2) produced the second closest result (70.94%) which, in turn, is also quite close to the reference value. On the other hand, the oxalic acid pickling (T3) produced a lower result (65.56%). The content of skin substance is a parameter that serves as a reference for the tanning industry which is further verified jointly corroborating the chromium oxide content by statistical, physical and sensorial analyses.

Analysis of variance corroborated the results from the chemical analysis. It confirmed that sulfuric acid pickling (T1) and formic acid pickling (T2) produced the highest values of skin substance content. It also evidenced that these results are significantly better than the one produced by oxalic acid pickling (T3).

Regarding tension analysis, T1 produced the highest value (1485 N/cm^2). T2 produced the highest elongation value (15.89%), and T3 gave the highest lastometry result (68.67 mm). Sensorial analyses brought about high scores for formic acid pickling (T2) with 4 and 4.5 points. This means that T2 complies with the majority of physical and sensorial parameters, and it places itself in second place regarding the content of skin substance. Therefore, T2 is considered the best treatment since it uses a reducing, masking agent and shows a good level of penetration in the skin fibers. Conversely, the oxalic acid pickling (T3) give rise to poor results which are explained by the inadequate properties of the agent it utilizes.

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INFLUENCE OF SOLAR RADIATION INSOLATION PRECIPITATION ON HYDROPHOBIZED LEATHER FOR SHOE UPPERS

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INFLUENCE OF SOLAR RADIATION INSOLATION PRECIPITATION ON HYDROPHOBIZED LEATHER FOR SHOE UPPERS

ABSTRACT. The influence of solar radiation and precipitation on leather samples for the upper part of footwear, treated with water-repellent compounds, was determined and the process of their destruction in natural atmospheric conditions was determined. The study of the effect of solar radiation on natural skin has not been sufficiently studied. In connection with the above, the test was carried out on experimental hydrophobized and initial (control) leather samples in an open area to determine the insolation of solar radiation and precipitation on the skin for the upper shoes. During the tests, a systematic examination of the exposed samples was carried out for 1-6 months, sampling for physico-mechanical and other tests was recorded by meteorological conditions. After that, the samples were subjected to organoleptic evaluation, physical-mechanical and chemical-analytical analyses, as well as structural studies. It was visually determined that, depending on the variant of hydrophobization used, fibrillar collagen formations change in different ways. After atmospheric insolation acts on the control sample, its fibrillar structure changes sharply, numerous micro cracks appear, located mainly perpendicular to the fiber axis, and clearly defined dark zones are found between the fibrils. Fibril outlines become indistinct, numerous torn ends are observed. However, such changes are not observed for hydrophobized samples. Significant changes in physical and mechanical properties are observed in the first and fourth months of natural aging. In the hydrophobized sample, the rate of change in hydrothermal destruction and the appearance of cracks in the face layer subjected to aging in an open area, is always lower compared to the control sample.

KEY WORDS: hydrothermal destruction, hydrophobization, insolation of solar radiation, destruction, fibrillar structure

INFLUENȚA RADIAȚIEI SOLARE ȘI PRECIPITAȚIILOR ASUPRA PIELII HIDROFOBIZATE PENTRU FEȚE DE ÎNCĂLȚĂMINTE

REZUMAT. S-a determinat influența radiației solare și a precipitațiilor asupra probelor de piele pentru fețe de încălțăminte, tratate cu compuși hidrofugi, precum și procesul de distrugere a acestora în condiții atmosferice naturale. Efectul radiației solare asupra pielii naturale nu a fost suficient studiat până acum. În legătură cu cele de mai sus, prezentul studiu a fost efectuat pe probe experimentale de piele hidrofobizată și în stare inițială (martor) într-o zonă deschisă pentru a determina influența radiației solare și a precipitațiilor asupra pielii pentru fețe de încălțăminte. În timpul testelor, s-a efectuat o examinare sistematică a probelor expuse timp de 1-6 luni, s-au prelevat probe pentru teste fizico-mecanice și alte teste în funcție de condițiile meteorologice. După aceea, probele au fost supuse evaluării organoleptice, analizelor fizico-mecanice și chimice, precum și analizelor structurale. S-a determinat vizual că, în funcție de varianta de hidrofobizare utilizată, formațiunile de colagen fibrilar se schimbă în moduri diferite. După acțiunea radiației solare și a atmosferei asupra probei martor, structura fibrilară a acesteia se schimbă brusc, apar numeroase microfisuri, situate în principal perpendicular pe axa fibrelor și se constată zone întunecate clar definite între fibrile. Contururile fibrilelor devin indistincte, se observă numeroase capete rupte. Cu toate acestea, astfel de modificări nu se observă în cazul probelor hidrofobizate. Modificări semnificative ale proprietăților fizice și mecanice sunt observate în prima și a patra lună de îmbătrânire naturală. În cazul probei hidrofobizate, rata de modificare în ceea ce privește deteriorarea hidrotermică și apariția fisurilor în stratul de suprafață al probei supuse îmbătrânirii într-o zonă deschisă, este întotdeauna mai mică comparativ cu proba martor.

CUVINTE CHEIE: deteriorarea hidrotermică, hidrofobizare, radiație solară, distrugere, structură fibrilară

L'INFLUENCE DU RAYONNEMENT SOLAIRE ET DES PRÉCIPITATIONS SUR LE CUIR HYDROPHOBE POUR LES TIGES CHAUSSURE

RÉSUMÉ. L'influence du rayonnement solaire et des précipitations sur les échantillons de cuir pour les tiges de chaussures, traitées avec des composés hydrofuges, ainsi que le processus de leur destruction dans des conditions atmosphériques naturelles ont été déterminés. L'effet du rayonnement solaire sur le cuir n'a pas été suffisamment étudié jusqu'à présent. Dans le cadre de ce qui précède, la présente étude a été réalisée sur des échantillons expérimentaux de cuir hydrophobe et initiale (témoin) dans une zone ouverte pour déterminer l'influence du rayonnement solaire et des précipitations sur le cuir pour les tiges de chaussures. Au cours des tests, un examen systématique des échantillons exposés a été effectué pendant 1 à 6 mois, des échantillons ont été prélevés pour des tests physico-mécaniques et d'autres tests en fonction des conditions météorologiques. Après cela, les échantillons ont été soumis à une évaluation organoleptique, à des analyses physico-mécaniques et chimiques, ainsi qu'à des analyses structurelles. Il a été déterminé visuellement que, selon la variante hydrophobe utilisée, les formations de collagène fibrillaire changent de différentes manières. Après l'action du rayonnement solaire atmosphérique sur l'échantillon témoin, sa structure fibrillaire change brutalement, de nombreuses microfissures apparaissent, situées principalement perpendiculairement à l'axe des fibres et il existe des zones sombres bien définies entre les fibres. Les contours des fibrilles deviennent indistincts, de nombreuses extrémités cassées sont observées. Cependant, de tels changements ne sont pas observés dans le cas d'échantillons hydrophobes. Des changements importants dans les propriétés physiques et mécaniques sont observés au cours des premier et quatrième mois du vieillissement naturel. Dans le cas de l'échantillon hydrophobe, la vitesse d'évolution des dommages hydrothermaux et l'apparition de fissures dans la couche superficielle de l'échantillon soumis au vieillissement en zone ouverte est toujours plus faible par rapport à l'échantillon témoin.

MOTS CLÉS : dommages hydrothermaux, hydrophobie, rayonnement solaire, destruction, structure fibrillaire

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INTRODUCTION

Significant studies have investigated the effect of solar radiation on collagen-based materials [1-3]. Nalyanya *et al*. [4] have reported an investigation on the effect of artificial ultraviolet radiation on the viscoelastic and dynamic viscosity of both pickled and tanned leathers. However, to our knowledge, there appears no documented investigation into the effect of unfiltered solar radiation on the mechanical properties of bovine leather. Therefore, this study presents the results on effects of natural solar radiations on the viscoelastic properties of bovine leather using thermal and dynamic mechanical analyses. This investigation also reports the effects of oscillation frequency and furnace temperature on the viscoelastic properties of leather. The study also makes a comparison of the effect of solar radiation on tanned leather and pickled leather to explore the effect of chrome-tanning on the solar radiation absorption of bovine leather.

It is well known that the Republic of Uzbekistan is located in Central Asia and has a favorable economic as well as strategic location.

About 300 sunny days and less than 300 ml of rainfall are observed annually in Uzbekistan. The continental climate is expressed in sharp fluctuations in temperature day and night, in summer and winter. In summer, the average temperature exceeds 35°C, and on some days, it is even higher than 45°C. Heat is relative.

The average annual rainfall in the plains is about 90-580 mm, and in the mountains about 460-910 mm [5-6]. In the summer, the sun does not leave the sky for 300-330 hours per month in the north and 380-390 hours in the south. The largest solar radiation is observed on the flat territory of the Republic of Uzbekistan (annual amount of 6400 MJ/m^2) and is slightly reduced in the foothills, very easy to carry thanks to low humidity.

Cloudiness reduces the total radiation flux, and with continuous cloudiness direct radiation is absent. The regional potential of total solar energy can be characterized by the average annual value of solar radiation per 1m^2 (cm^2) of horizontal surface.

To assess the duration of the flow of solar energy, a total indicator is used - the annual amount of sunshine. For Uzbekistan, it is 2815-2880. It may be noted that the effect of solar radiation on natural skin has not been sufficiently studied.

EXPERIMENTAL PART

When performing the work, the following were used: acrylic emulsion A-1, polyvinyl ethinyl dihydroxychlorosilane, industrial oil IA-20, penetrator and widely used polyethylhydrosiloxane. Based on them, a composition of water repellents was prepared in various initial ratios. Water repellents were prepared by sequentially mixing the above materials at a temperature of 20–22°C for 3-4 hours [7-8].

Studies of structural, physico-mechanical and physico-chemical properties, electron microscopy methods, and standard methods for assessing the properties of the materials were used.

Objects of Study

Polymethylsiloxane Liquids (PMS-100, PMS-200) are transparent, chemically inert liquids. They are a mixture of polymers of linear structure $(CH_3)_3Si$ [—$OSi(CH_3)_2$]n, where n = 3-700. Density at a temperature of 20°C was in the range of 0.98-0.99 g/cm^3, boiling point 300°C, pour point 62-64°C.

A Surfactant Preparation (OP-10) (a mixture of ethoxylated dialkylphenols), CnH_{2n+1} C_6H_4O $(C_2H_4O)_m$ H, where n = 9-10, m = 10-12, is a light yellow oily paste, the pH of the aqueous solution is 7-8. The clarification of the aqueous solution occurred at a temperature of 90°C [9].

Acrylic Emulsion №1 is an aqueous dispersion of polymethyl acrylate, plasticized during the polymerization with a small amount of dibutyl phthalate [10-11].

Polyvinylethinyldihydroxychlorosilane. In a four-necked flask with a volume of 500ml,

equipped with a mechanical stirrer with a shutter, a thermometer, a dropping funnel and a reflux condenser, 103.78 ml (74 g 1.0 mol) of ethyl ether (or 88.73 ml (78 g 1.0 mol) of benzene). Then, 53.29 ml silicon tetrachloride were poured with stirring (85g 0.5 mol). After that, the temperature was raised to 60°C and 68.42 ml vinyl ethynyl magnesium bromide was added portionwise (77.5 g 0.5 mol) for 45-50 minutes. Then, with vigorous stirring, the temperature was raised to 70°C, the reaction continued for another 4.0-5.0 hours. After time, the stirrer was stopped, allowed to cool for 2.0 hours and cooled to 10.0 ± 2.0°C.

Then, in small quantities, the reaction mixture was transferred to a separatory funnel, washed several times with double-distilled water (until chlorine ions appeared in the washing water, with a breakdown with silver nitrate) to remove magnesium chloride.

Ethyl ether solvent was distilled off by vacuum distillation at a temperature of 35.6°C (or benzene at 80.1°C), using a vacuum pump, with a pressure for ethyl ether of 1.8-2.0, and in the case of benzene, 5.0-5.2 mm.

The resulting vinyl ethynyl trichlorosilane was introduced into the sump and 81.63 ml was released from there. Intermediate of 182.57 ml was added to the mixer with stirring of vinylethynyl trichlorosilane, water, for 2.0 hours at a temperature of 146 ± 5.0°C for the purpose of hydrolysis of the intermediate.

The hydrolysis of vinyl ethynyl dihydroxychlorosilane was done with 182.565 ml water for 2.0 hours in a temperature range of 146 ± 5.0°C.

Then the target product of vinyl ethynyl dihydroxychlorosilane was subjected to distillation, and the product was obtained PVEDGOHS with ethyl ether 75.46 ml (58%) in the case of benzene 70.60 ml (58%) [12].

Experimental Technique

Methodology for the Preparation and Use of Water Repellents

Production Technology. Water repellents were prepared by sequentially mixing the starting materials at various ratios (wt.%) As an experimental option: acrylic emulsion-20% 40-70, polyvinylethinyldihydrosichlorosilane-80% 2-12, industrial oil, IA-20 12-53, penetrator 4-6 and control polyethylhydrosiloxane (GKZh-94) 100 at a temperature of 20–22°C for 3-4 hours.

Technology Application. Application by plush brush: not diluted, or diluted in a 1:3 ratio. Spraying: diluted in an aqueous medium in a ratio of 1:2 is sprayed in 1-2 passes from a distance of 20-30 cm. It should be noted that the action of the hydrophobizing composition occurs immediately after the complete evaporation of the solvent. Liquid formulations do not change the tone of dyed skin.

Methodology for Studying the Properties of Water Repellents

Determination of Skin Steam. The steam capacity of the skin was estimated by the amount of moisture absorbed by the sample, in % of the mass of an absolutely dry sample:

$$P = \frac{a-b}{b} \cdot 100, \qquad (1)$$

where, a is the mass of the sample after absorption of moisture, g; b is the mass of an absolutely dry sample, g [11].

Determination of Breathability. Breathability is determined on the basis of Interstate standard GOST 938.18-70. This standard applies to all types of skin and establishes a method for determining breathability. A device was used to determine breathability.

The breathability of the skin and skin tissue of the fur characterizes their ability to pass air at a pressure difference on both sides of the test sample.

The air permeability index, $cm^3/(cm^2 \bullet h)$, is the air volume in cubic centimeters passing through 1 cm^2 of the test sample for 1 h with a pressure difference on both sides of the sample equal to 9.81 MPa. The results of the absolute breathability test B_a, s, were calculated by the formula:

$$B_a = t - t_0 \qquad (2)$$

where t is the time taken to pass 100 cm^3 of air, s; t_0 is the outflow time of 100 cm^3 of water from the device without a sample, s.

The final result was calculated as the arithmetic mean of two definitions. Relative

breathability was found by the formula: B_0=V•3600/S, B_a, where V is the volume of air passing through the sample (according to the test conditions it is equal to 100 cm^3); S is the working area of the sample, equal to 10 cm^2; B_a - absolute breathability, s. [12].

Water Permeability Tests in Static Conditions. Water resistance and permeability under static conditions are determined on the basis of Interstate standard GOST 938.21-71. This standard applies to all types of leathers and establishes a method for determining water resistance and permeability when testing leather samples in static conditions. Water permeability is characterized by the amount of water passing through a wet sample. Water permeability and permeability of skin samples were determined on a PVS-2 device.

To test the sample, 2 ml of water was passed through it (provided that it would take no more than 2 hours), after which the water level was noted on the graduated tube of the device with an absolute error of 0.05 ml and the time was recorded on the counter. Then, 5 ml of water was passed through the sample and its level in the tube and time were noted a second time. The water level and time were used to calculate the amount of water that passed through the sample for the corresponding time. When testing denser samples, first left under water pressure for 2 hours (during this time no more than 2 ml of water should pass through the sample), after which the water level in the tube and time were noted. Then the level was noted after 2 hours. If an insignificant amount of water passed through the sample in 2 hours, then the tests continued for another 2 hours. At least two determinations were made with each sample, the difference between them did not exceed 10% of the average value. The test shall be carried out at a temperature of 20 ± 2.0°C.

Water permeability, ml/(sm^2•h), calculated by the formula:

$$B = \frac{V \cdot 60}{t \cdot S} \qquad (3)$$

where, V is the amount of water passing through the sample during the test, ml; t is the test time, s; S is the sample area, cm^2 [9].

Determination of Vapor Permeability. Vapor permeability is determined on the basis of Interstate standard GOST 938.17-70. This standard applies to all types of skin and establishes a method for determining vapor permeability. The following equipment and reagents are used to determine vapor permeability: technical scales in accordance with Interstate standard GOST 24104-2001; desiccators according to Interstate standard GOST 25336-82 with an inner diameter of 250mm; metal glasses 45mm high and 55mm in diameter.

Vapor permeability is the ability of the skin to pass water vapor. Vapor permeability is one of the most important indicators used to assess the hygienic properties of the skin. Vapor permeability is expressed in milligrams of moisture passing through 1 cm^2 of sample area in 1 h, or as a percentage of the mass of water vapor passing through the test sample to the mass of water evaporated from an open surface under the same conditions.

Vapor permeability was determined in special metal cups on round samples with a diameter of 55 mm; the diameter of the working part of the sample is 36 mm.

The relative vapor permeability P_0, %, was calculated by the formula:

$$P_0 = \frac{q \cdot 100}{q_1} \qquad (4)$$

where, q is the decrease in mass of the glass with the contents after 6 hours of testing, g; q_1 is the arithmetic mean of the decrease in the mass of control glasses with water, g.

In the case of vapor permeability of the samples, *P* must be expressed in milligrams of moisture passing through the unit area of the sample per unit time, then the calculation was performed according to the formula:

$$P_0 = \frac{q}{t\pi r^2} \qquad (5)$$

where, q is the decrease in mass of the glass with the contents, mg; t is the duration of the experiment, h; πr^2 is the working area of the sample, cm^2. The arithmetic average of the test results of two samples taken from the same sample was taken as the test results [12].

Determination of Hygroscopicity. Hygroscopicity also characterizes the ability of the skin to absorb water vapor from the surrounding air. The hygroscopicity of the samples was determined by increasing the mass of the sample, maintained at a relative

humidity of 100% for 16 hours, and expressed as a percentage of the initial mass of the sample.

Tests are carried out on samples with dimensions of 50 × 50 mm.

Samples aged under normal atmospheric conditions were weighed on an analytical balance with an absolute error of 0.001 g and placed in a desiccator above water so that they had free air access.

The relative humidity above the water in the desiccator was 100%. After 16 hours in a desiccator, the samples were weighed and the hygroscopicity *G*, %, was calculated by the mass gain referred to the mass of the air-dry sample:

$$G = \frac{q_1 - q_2}{q} \cdot 100 \qquad (6)$$

where, q_1 is the mass of the sample moistened in a desiccator, g; q_2 is the mass of the same sample in the air-dry state, g [9].

RESULTS AND DISCUSSION

During the tests, a systematic examination of the exposed samples was carried out, sampling for physico-mechanical and other tests, while meteorological conditions were recorded.

The control and experimental hydrophobized samples were taken at certain intervals during their stay in atmospheric conditions (1-6 months). Figure 1 shows the corresponding photographs [14-15].

Figure 1. Photographs of experimental and control hydrophobized samples produced during (a-January, b-June) 6 months of their stay in atmospheric conditions

The studies were carried out on 5 longitudinal and 5 transverse control and experimental samples of chrome tanned leather for upper shoes.

It should be noted that when examining the skin (Fig. 2) after exposure to harsh climatic factors, changes in their color, structure and the appearance of micro cracks were noticed.

The results of microscopic studies showed that the characteristic properties of the leather for the upper of chrome tanning shoes are reflected in their structure. The results of microscopic studies showed that the characteristic properties of the leather for the upper of chrome tanning shoes are reflected in their structure.

It was visually determined that, depending on the variant of hydrophobization used, fibrillar collagen formations change in different ways.

After atmospheric insolation acts on the control sample, its fibrillar structure changes sharply, numerous micro cracks appear, located mainly perpendicular to the fiber axis, and clearly defined dark zones are found between the fibrils. The contours of the fibrils become indistinct, there are numerous torn ends.

However, such changes are not observed for hydrophobized samples. In the control variant, an increase in the number of cracks was noted and the surface becomes rough.

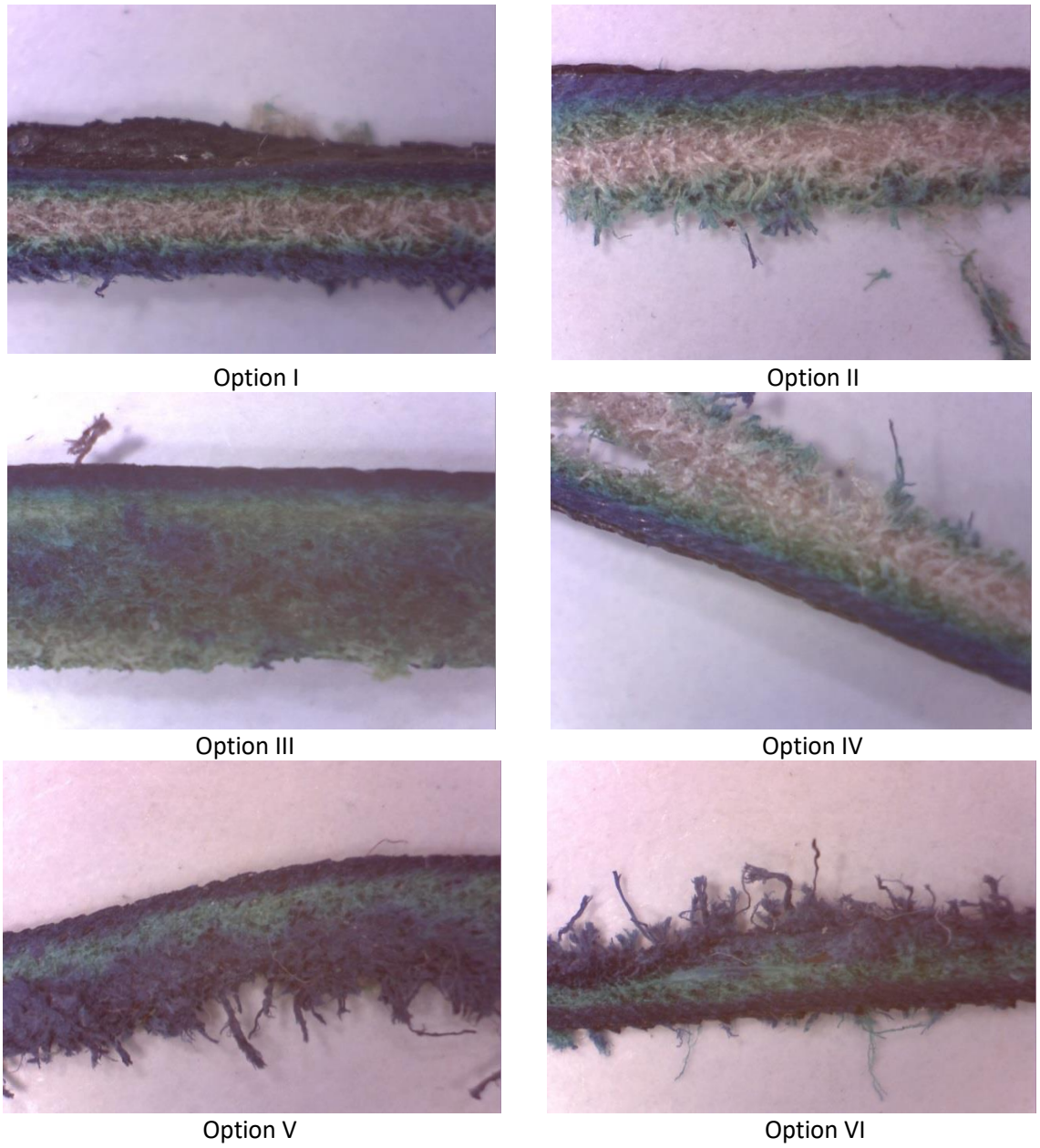

Figure 2. Microscopic photographs of experimental (I-IV) and control (V) skin samples (Magnification × 200 times)

It must be emphasized that the process of destruction of the surface of the skin proceeds mainly under the influence of the above photochemical effects caused by ultraviolet rays [16-17].

The test results further show that the longer the insolation of solar radiation with alternating precipitation lasts, the more the breaking stress and the hydrothermal degradation of chrome tanned leather for the upper of the shoe decrease. It was determined that the hydrothermal degradation of the skin and the tensile stress change according to a certain regularity: a decrease in hydrothermal degradation and a weakening of the tensile stress. As a result of exposure to natural factors, the skin gradually loses its strength properties [18-19].

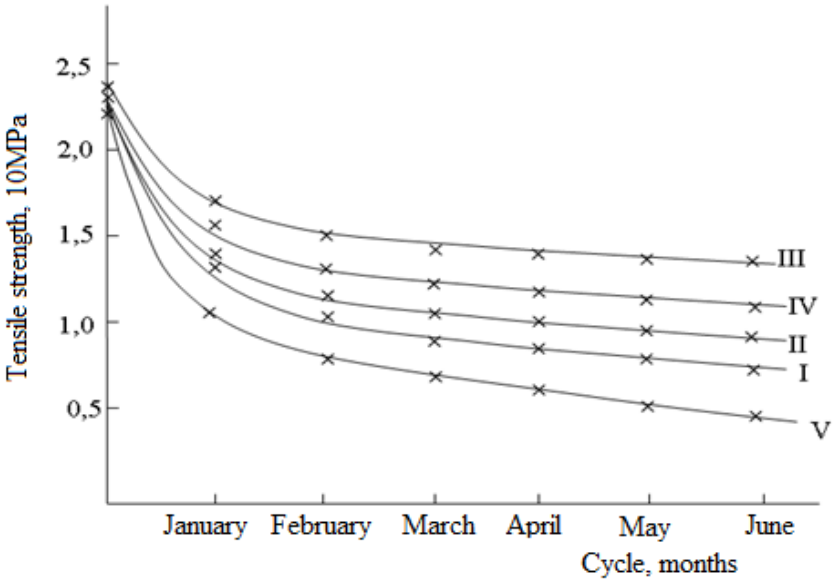

Figure 3. The dependence of the tensile strength of the skin treated with various options of water repellents on the duration of exposure climatic factors: I-IV experimental and V control skin sample

An intensive change is also observed in the case of aging under the direct influence of solar radiation and precipitation. In Fig. 3. curves of the tensile strength of skin samples treated with water repellents on the duration of exposure to climatic factors are presented: I-IV experimental and V control skin samples.

As revealed, in the control V version, the tensile strength decreases sharply in comparison with I-IV experimental versions of hydrophobized samples. Moreover, in all cases, the maximum decrease from 2.20 to 2.65 *MPa*, the tensile strength drops 1.64-0.75 *MPa* from January to March. Further, in the following months, the value of this indicator will be in the range of 0.42-193 *MPa*. In these cases, maximum strength is observed for the III - hydrophobized skin sample. Among environmental factors, solar radiation has a significant effect on the properties of leathers for chrome tanned shoe uppers. It speeds up the aging process. In Fig. 3. the change in elongation of I-V skin samples is shown, both initial and modified using hydrophobic composite materials.

From the results obtained, a strong decline in elongation of the samples was observed in the first four months. It should be noted that the III experimental skin sample has a maximum elongation of six months compared with other samples, and the minimum as expected for V control sample. Their difference, i.e. elongation is about 10%, which once again confirms the high hydrophobizing ability of the studied objects for resistance to environmental factors.

In studies, the influence of atmospheric effects on the facial surface of the skin and on hydrothermal stability was simultaneously studied. With a few exceptions, it was found that natural aging, along with mechanical and physical properties, reproduces well the changes in such indicators as the appearance of cracks in the face layer under tension, and hydrothermal stability.

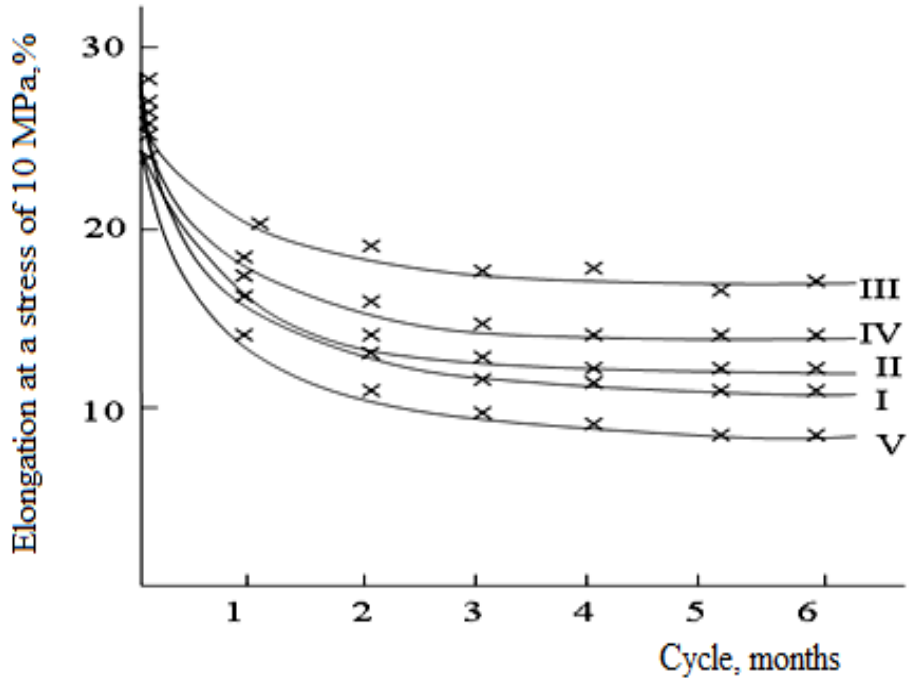

Figure 4. Change in skin lengthening for treated with various variants of water repellents on the duration of exposure to climatic factors: I-IV experimental and V control sample of the skin

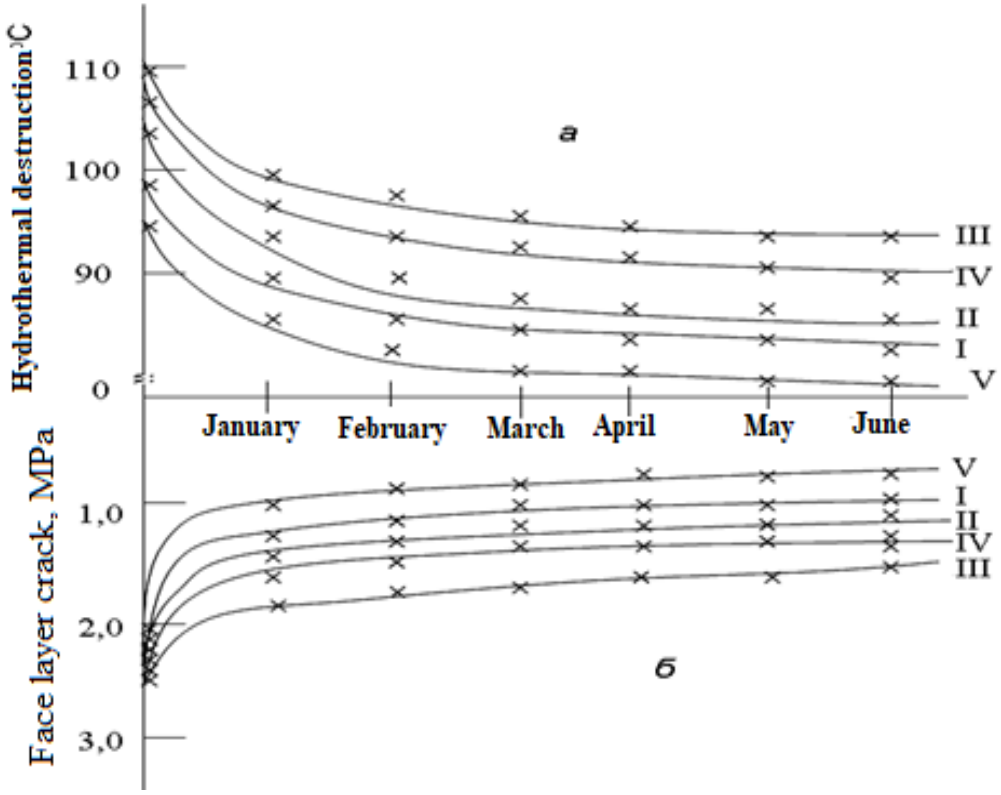

Figure 5. Kinetic dependences of hydrothermal destruction (a), and the appearance of cracks in the facial layer of the skin (b) treated with various variants of water repellents on the duration of exposure to climatic factors: I-IV experimental and V control skin samples

Fig. 5. kinetic dependences of hydrothermal destruction (a), the appearance of cracks in the facial layer of the skin (b) treated with various types of water repellents on the duration of exposure to climatic factors are given: I-IV experimental and V control skin samples.

The results of the kinetic dependences of hydrothermal destruction and the appearance of cracks in the facial layer of the skin treated differently with the help of water repellents on the duration of exposure to climatic factors and the control skin sample are corrected to a certain extent with previously obtained data.

Significant changes in physical and mechanical properties are observed in the first and fourth months of natural aging. In the third sample, the rate of change in hydrothermal destruction and the appearance of cracks in the face layer subjected to aging in an open area, is always lower compared to the control sample. It also seemed very important to study the chemical composition of experimental hydrophobized and control skin samples. In Table 1 the results of chemical analysis of experimental and control hydrophobized skin samples are presented [20].

Table 1: Chemical analysis of experimental and control hydrophobized leather samples

		Options					
		Experienced					
	Indicator	I	II	III	IV	V	Control Interstate standard GOST 338-81
Content, %:	Chromium oxide	3.2	3.4	3.6	3.7	2.8	n/l 4.3
	Silica	2.3	2.4	2.6	2.8	2.4	n/l 1.8
	Ash	1.5	1.8	2.0	2.2	2.4	n/m 3.3
	Substances extracted with organic solvents	10.5	11.7	11.5	12.3	10.2	10-13
	Water washed common	2.3	2.4	2.4	2.6	3.4	n/l 4.2
	Fatty substances	34.3	26.1	28.9	26.6	20.4	n/l 23.4
	The number of products, %	25.5	31.9	41.9	29.3	26.4	n/l 36.7

From the data of table 1, as can be seen, with an increase in the content of polyvinyl ethyl dihydroxychlorosilane in the experimental variants, the contents of chromium oxide and silicon dioxide increase accordingly [21-22]. You can also notice a slight increase in the relative content of ash and substances extracted with organic solvents. A change in the components of the skin leads to a change in the number of products. In experimental skins, the product number the average for all options was 32,15%, which is within 20% more compared to the control. It also seemed very important to carry out the spectroscopic study of the interaction of hydrophobizing compositions with collagen.

The aim of this work is to study by IR spectroscopy the nature of the bonds of the studied hydrophobizing composites with the main skin protein, collagen. Measurements of IR spectra were carried out on a Specord 75IR spectrophotometer made in Germany [23-24].

Collagen was used as a model. The object of the study was a film obtained from a 4% collagen solution, hardened by immersion in a solution of tanning chromium compounds with a basicity of 45% and a Cr_2O_3 concentration of 100g/l for 1 hour, then followed by drying and rinsing. After obtaining the film, its absorption spectrum in the IR region was determined and subjected to treatment with the investigated hydrophobizing agents: a hydrophobizing composition based on PVEDHOHS, an emulsion of polyethylhydrosiloxane and collagen.

IR spectra of the studied preparations were recorded using high-resistivity silicon wafers as a substrate. The spectrum of the organosilicon liquid of polyethylhydrosiloxane was recorded using a sample in the form of a layer between plates on NaCl.

The manifestation of the hydrophobic properties of the hydrophobizing composition is based on the hydrolysis reaction of the chromium

complex of stearic acid. Moreover, the molecules of the hydrolyzed substance, reacting with each other, form difficultly soluble high-molecular products that are firmly held by the material.

Comparison of the spectra of the initial and treated PVEDOHS with collagen and polyethylhydrosiloxane with collagen, Fig. 6-7.

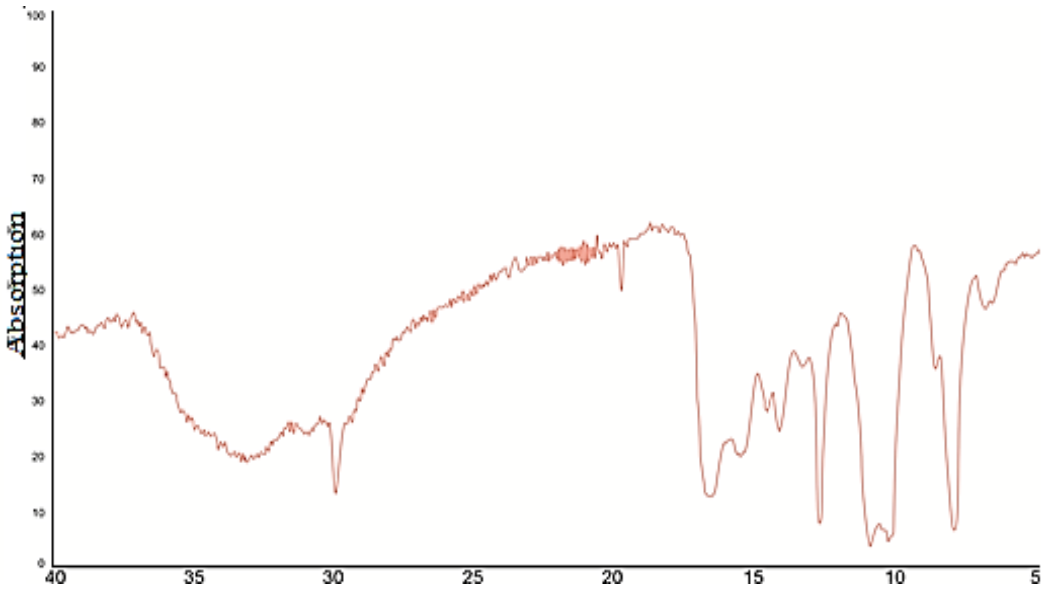

Figure 6. Spectrum III version of the prototype

In the range of 3500-3055 cm^{-1}, a stretching vibration of OH and NH groups by hydrogen bonding appears, Figure 6. Stretching vibration (Vk) of CH, CH_2 groups appears in the range of 2990 and 3090 cm^{-1}. Carbonyl group (C=O) Amide I appears in the 1660 cm^{-1} region. The deformation NH-bond appears at 1550 cm^{-1}. The deformation CH, CH_2 appears in the region of 1450 and 1410 cm^{-1} and in the OH group. The absorption band of $Si(CH_3)$ appears in the region of 1270 cm^{-1}, Si-O bonds with an open chain appear in the region of 1090-1025 cm^{-1}, and $Si(CH_3)$ bonds appear at 800-790 cm^{-1}. Carbonyl group (C=O) Amide I appears in the region of 1650 cm^{-1}. The deformation NH-bond appears at 1530 cm^{-1}.

Deformation CH, CH_2 appears in the region of 1450 and 1400 cm^{-1} and in the OH group. The absorption band of $Si(CH_3)$ appears in the region of 1270 cm^{-1}, Si-O bonds with an open chain appear in the region of 1090-1010 cm^{-1}, and $Si(CH_3)$ bonds appear at 790-780 cm^{-1}.

In the range of 3600-3100 cm^{-1}, a stretching vibration of OH and NH groups appears by bonded hydrogen bonds.

Stretching vibration (Vk) of CH, CH_2 groups appears in the region of 2980 and 3100 cm^{-1}.

When comparing the IR spectra of collagen treated with polyethylhydrosiloxane and collagen in the presence of a zirconium salt, one can see insignificant absorption bands at 2160 and 830 cm^{-1}, characteristic of stretching and bending vibrations of the Si-H bond, as well as an expansion of the absorption band in the region of 3380-3280 cm^{-1}, which can be explained by the adsorption of silicone both on the collagen surface due to the forces of intermolecular attraction between the polar collagen groups and the Si-O dipole, and on the catalyst surface. The possibility of the formation of hydrogen bonds with the amino groups of collagen with the participation of the Si-H – groups of polyethylhydrosiloxane is not excluded (Fig. 7).

The IR spectrum of the original collagen shows all absorption bands characteristic of collagen, since the constituent of collagen is proteins and amino acid residues.

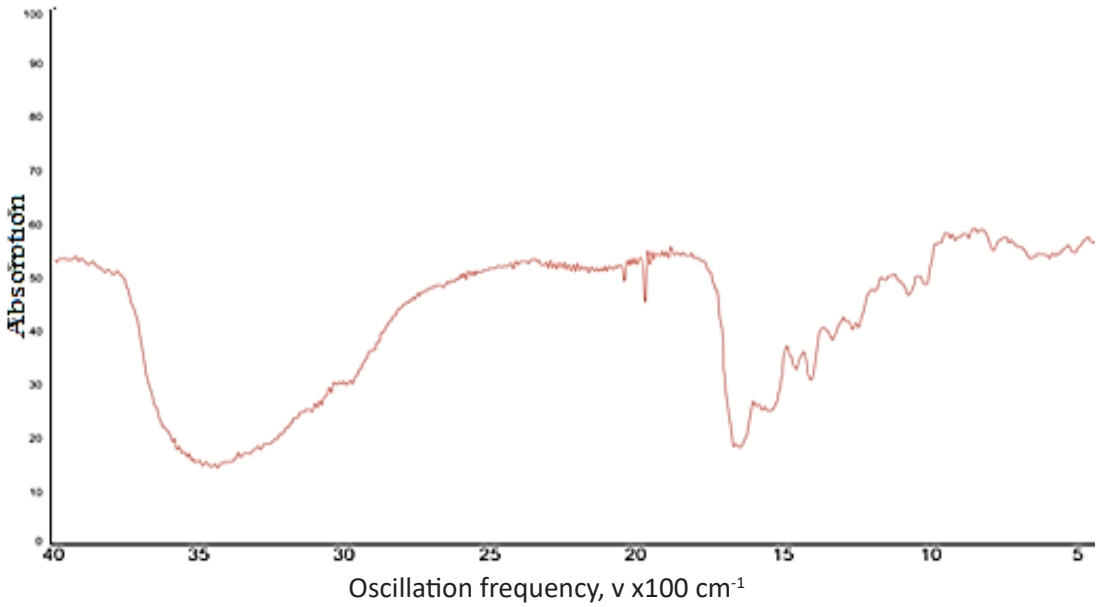

Figure 7. VI-variant, the original sample of collagen

Thus, we can conclude that a comparison of the spectra of the initial and processed collagen with PVEDOHS shown in Fig. 6-7 shows a significant broadening of the absorption band in the region of 3500-3100 cm^{-1} and a noticeable increase in the intensity of the CH, CH_2 group at 2980 cm^{-1}.

In accordance with the blurring and broadening of the bands of stretching vibrations of hydroxyl groups in this region, this suggests the presence of a hydrogen bond between the OH groups of the hydrolyzed complex and the functional NH- groups of collagen. However, the interaction of the chromium complex with the amino groups of collagen is also possible with the formation of strong covalent bonds between the nitrogen and chromium atoms.

When studying the IR spectra of PVEDHOCS, a certain shift of the absorption band was observed, sometimes it shifts somewhat towards lower frequencies. The presence of absorption bands at 1400, 1375, 1235 cm^{-1} corresponds to the C-C bond. The shift of the band in the region of 3460, 3400, 3280 cm^{-1} corresponds to the stretching vibrations of OH groups.

In this case, the characteristic bands for the ethylene bond are found in the frequency range 1600, 1530 cm^{-1}; an absorption band is present in the spectra of the PVEDOHS compound. At 600, 550 cm^{-1}, a band characteristic of Si-Cl is observed.

Absorption bands in the frequency range 1650, 1550 and 1450, 1414 cm^{-1} remain unchanged from the IR spectra of collagen treated with PVEDGOHS. This is characteristic of the COOH groups of collagen, indicating that during the adsorption of the complex, it can decompose into water-insoluble basic chromium stearate and water-soluble chromyl chloride, which has a tanning effect.

That the organosilicon liquid polyethylhydrosiloxane in the form of an emulsion is fixed on collagen only through the forces of a sorption nature and does not form strong covalent chemical bonds with collagen.

It was found that the spectrum of processed collagen does not differ in any way from the spectrum of untreated collagen, which leads to the conclusion that there is no noticeable chemical interaction between polyethylhydrosiloxane and collagen under these conditions.

CONCLUSIONS

The results of the study carried out in the IR spectrum give reason to believe that the effect of hydrophobization, in the case of using various composites, is due to the interaction of the hydrophobizator with the functional groups of collagen, a certain orientation of hydrocarbon radicals, the formation of a water-repellent film, as well as a combination of these processes.

Conducting comprehensive studies on the aging process has established that when exposed to chrome skins, the effects of sunlight, oxygen, temperature, air humidity and precipitation jointly affect them.

It is known that aging of polymers under the action of sunlight is a photochemical process. In this case, the polymer molecules, first absorbing a quantum of energy of the corresponding wavelength of light, goes into a highly excited state. After that, either the molecule gives up energy in the form of a light quantum, or spends its energy on the oxidation and destruction reactions. This explains the greatest decrease in breaking stress and breaking load when exposed to solar radiation on the control samples.

Based on this, it can be concluded that hydrophobizing compositions based on polyvinylethinyldihydroxychlorosilane, especially the III experimental version, are the most effective.

The obtained results of the experiments clearly demonstrated that insolation of solar energies and precipitation cause a complex of physicochemical transformations. Such processes occur at a fairly high speed under the influence of oxygen, ozone and other gases, as well as solar radiation, heat and humidity. The nature of the ongoing processes is significantly affected by hydrophobic compounds containing in skin products. Thus, aging and skin destruction processes are prevented.

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THE USE OF NON-CHROME MINERAL TANNING MATERIALS AS A PREFERABLE ENVIRONMENTALLY FRIENDLY TANNING MATERIAL

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THE USE OF NON-CHROME MINERAL TANNING MATERIALS AS A PREFERABLE ENVIRONMENTALLY FRIENDLY TANNING MATERIAL

ABSTRACT. Mineral chrome tanning agent is the most widely used tanning agent for various types of leather articles, given its various advantages. Besides its many advantages, there is a negative side to chrome tanneries, namely the presence of waste disposal that is harmful to the environment. Therefore, this study aims to determine the quality of mineral tanning materials other than chrome (aluminium and titanium) as a substitute for leather tanning (free of chrome). The research raw materials were 12 pieces of pickled goatskin. The chemicals used are aluminium tanning agent (Novaltan Al), titanium tanning agent, salt (NaCl), Peramit MLN, Derminol OCS, MgO, $NaHCO_3$, BCG indicator, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, Acid dyestuff, formic acid, Sincal DR and anti-fungal. The method used is to carry out the tanning process using aluminium tanning agents with levels of 2%, 4%, and 6% Al_2O_3, continued the combination between aluminium and titanium tanning agent. The results obtained were analyzed for the cross-sectional and content of the leather using the EDX method, a shrinkage temperature (Ts) test, and physical quality of crust skin. The results showed that the higher the Al_2O_3 content, the more Al content in the leather, but the lower the wrinkle temperature of the leather. Meanwhile, the longer the processing time, the aluminium content in the skin increases. The use of aluminium and titanium tanning agent can improve the physical quality of the skin, both in terms of tensile strength and skin softness. The conclusion that can be drawn is the use of 2% free of chrome (aluminium) tanning material can produce Ts of 71°C. The physical quality of the crust skin from aluminium and titanium mineral tanning agents is better than the single-use of aluminium.

KEY WORDS: free of chrome, mineral tanning agent, aluminium, titanium

UTILIZAREA AGENȚILOR TANANȚI MINERALI FĂRĂ CROM CA MATERIALE DE TĂBĂCIRE PRIETENOASE CU MEDIUL

REZUMAT. Agentul de tăbăcire pe bază de crom este cel mai utilizat agent tanant pentru diferite tipuri de articole din piele, având în vedere avantajele multiple ale acestuia. Pe lângă numeroasele sale avantaje, există un neajuns pentru tăbăcăriile care folosesc crom, și anume necesitatea de a elimina deșeurile nocive pentru mediu. Prin urmare, acest studiu își propune să determine calitatea materialelor de tăbăcire minerale, altele decât cromul (aluminiu și titan), ca înlocuitori pentru tăbăcirea pielii (fără crom). Materiile prime folosite în cercetare au fost 12 bucăți de piele de capră piclată. Substanțele chimice utilizate au fost: un agent de tăbăcire pe bază de aluminiu (Novaltan Al), un agent de tăbăcire pe bază de titan, sare (NaCl), Peramit MLN, Derminol OCS, MgO, $NaHCO_3$, indicator BCG, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, colorant acid, acid formic, Sincal DR și agent antifungic. Metoda utilizată este realizarea procesului de tăbăcire folosind agenți pe bază de aluminiu cu conținut de Al_2O_3 în proporții de 2%, 4% și 6%, continuându-se cu o tăbăcire combinată cu agenți pe bază de aluminiu și titan. S-au analizat pieile obținute pentru a determina conținutul de aluminiu în secțiune transversală folosind metoda EDX, temperatura de contracție (Ts) și calitatea fizică a pielii crust. Rezultatele au arătat că, cu cât este mai mare conținutul de Al_2O_3, cu atât este mai mare conținutul de Al în piele, dar cu atât este mai scăzută temperatura de contracție. Pe de altă parte, cu cât timpul de prelucrare este mai mare, conținutul de aluminiu din piele crește. Utilizarea agentului de tăbăcire din aluminiu și titan poate îmbunătăți calitatea fizică a pielii, atât în ceea ce privește rezistența la tracțiune, cât și moliciunea pielii. Concluzia care poate fi trasă este că utilizarea agenților tananți fără crom (aluminiu) în proporție de 2% poate conduce la obținerea Ts de 71°C. Calitatea fizică a pielii crust tăbăcită combinat cu agenți pe bază de aluminiu și titan este mai bună decât în cazul utilizării simple a aluminiului.

CUVINTE CHEIE: fără crom, agent de tăbăcire mineral, aluminiu, titan

L'UTILISATION DES AGENTS DE TANNAGE MINÉRAUX SANS CHROME COMME MATÉRIAUX DE TANNAGE RESPECTUEUX DE L'ENVIRONNEMENT

RÉSUMÉ. L'agent tannant au chrome est l'agent tannant le plus utilisé pour divers types de maroquinerie, compte tenu de ses nombreux avantages. Outre ses nombreux avantages, les tanneries qui utilisent du chrome présentent un inconvénient, à savoir la nécessité d'éliminer les déchets nocifs pour l'environnement. Par conséquent, cette étude vise à déterminer la qualité des matériaux de tannage minéraux, autres que le chrome (aluminium et titane), en tant que substituts pour le tannage du cuir (sans chrome). Les matières premières utilisées dans la recherche étaient 12 pièces de peau de chèvre piclée. Les produits chimiques utilisés étaient : un agent tannant à base d'aluminium (Novaltan Al), un agent tannant à base de titane, sel (NaCl), Peramite MLN, Derminol OCS, MgO, $NaHCO_3$, indicateur BCG, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, colorant acide, acide formique, Sincal DR et agent antifongique. La méthode utilisée consiste à réaliser le procédé de tannage à l'aide d'agents à base d'aluminium contenant de l'Al_2O_3 dans des proportions de 2%, 4% et 6%, en poursuivant par un tannage combiné avec des agents à base d'aluminium et de titane. Les cuirs obtenus ont été analysés pour déterminer la teneur en aluminium en section transversale par la méthode EDX, la température de retrait (Ts) et la qualité physique du cuir en croûte. Les résultats ont montré que plus la teneur en Al_2O_3 est élevée, plus la teneur en Al dans la peau est élevée, mais plus la température de retrait est basse. D'autre part, plus le temps de traitement est long, plus la teneur en aluminium du cuir est élevée. L'utilisation d'agent tannant à l'aluminium et au titane peut améliorer la qualité physique de la peau, tant en termes de résistance à la traction que de douceur de la peau. La conclusion que l'on peut en tirer est que l'utilisation d'agents tannants sans chrome (aluminium) dans la proportion

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de 2% peut conduire à une Ts de 71°C. La qualité physique du cuir en croûte tanné aux agents à base d'aluminium et de titane est meilleure qu'avec la simple utilisation de l'aluminium.
MOTS CLÉS : sans chrome, agent tannant minéral, aluminium, titane

INTRODUCTION

Leather tanning is an industry that needs special attention given to the many challenges it faces. The thing that needs to be seen further is about environmental sustainability for the next life of mankind. Without paying attention to environmental sustainability, the production processes of various industries will only focus on profit alone.

Environmental sustainability can be achieved if every aspect of life is considered without damaging the environment. Tanning is an industry that faces the perception that it contributes to environmental damage, namely the large waste produced and the irreversible raw materials used. Therefore, it is important to try to replace tanning materials with materials that are more environmentally friendly. Furthermore, the materials used so far are mostly hazardous to health or carcinogenic substances. If this material is used continuously for a long period of time it can endanger the health of tanners as well as those who use leather products.

The tanning materials that have been used include chrome, vegetable, aldehyde, and others. There should be an effort to try other tanning materials that are still acceptable to consumers and still have good quality (according to standards). Chromium is one of the most important environmental problems related to leather tanning. The most commonly used leather tanning process is chrome tanning. This implies the presence of chromium in both liquid waste and leather waste. Leather waste must be disposed of in landfills which causes a large environmental impact and high costs [1]. The negative impact of this chrome tanning agent is when Cr (III) changes to Cr (VI). Although there is a solution to reduce Cr (VI), that is, adding a vegetable tanning agent which can reduce the formation of Cr (VI) [2]. However, solutions and studies of other mineral substances in leather tanning are still needed.

Other minerals that can be used for tanning are aluminium and titanium. Aluminium is a mineral tanning material that can be used and developed further as a tanning material that is more environmentally friendly than chrome. Aluminium as a tanning material has a Ts value of 65°C. The function of this tanning is influenced by the ligand which is combined with the metal tanning material. Aluminium tanning agent has good results but not the aluminium tanning agent by itself. Therefore, it is necessary to further study the use of aluminium as a substitute for chrome tanning. Aluminium and titanium produce white leather.

The other material example which can produce white leather is formalin. However, formalin is a toxic material that is harmful to the environment and health. Formalin can be used as a tanning agent because it contains formaldehyde. Formaldehyde is one of the simple aldehyde tanning agents [3].

The aluminium-silica tanning process produces white leather with standards that meet the automotive upholstery industry. The strong white and cationic properties make it easy to create vibrant colors. Leather processed in this way is free from chromium, aldehydes, and organic solvents [4]. Wet white skin is somewhat less stable than wet blue skin on UVA rays, because of the tendency to break the polypeptide bonds in existing cases [5].

Wet white tanning with basic ingredients from vegetable tanning agents and Laponite nanoclay produces leather with physical quality that meets standards for furniture leather, with no harmful ingredients, Cr (VI), and free from detectable formaldehyde. This system can reduce the global warming potential and human toxicity potential compared to conventional tanning processes, without using a chrome tanning agent [6].

The effect of the presence of aluminium (III) in chromium tanning has been shown to increase the rate of chromium fixation, with an effect analogous to catalysis. It can be seen that pretreatment with aluminium has a positive effect on chrome content. The reaction between carboxyl collagen and aluminium (III) is fast [7].

Aluminium salt has the advantage of being abundant and cheap. However aluminium is only loosely bound to collagen, so the reaction is opposite when the skin is wetted and in an acidic environment, for this reason, this process is considered pseudo tanning and is called pseudo tanning rather than tanning [8].

Basic aquo ions can interact electrostatically via water ligands or form complexes, which are more electrovalent than covalent. Because it is known that aluminium (III) does not form a stable complex. Therefore, the bonds between the collagen and the matrix can be broken down hydrothermally, but the aluminium core environment will not change much. Therefore, it can be concluded that the aluminium-based matrix involves water that can be broken down, which allows shrinkage, i.e. the electrostatic interaction with the carboxyl collagen is far enough away to allow this to occur, but the aluminium (III) core does not change its magnetic field. In contrast, covalent skin between carboxyl collagen and chromium (III) is a direct interaction, which cannot be broken down under shrinkage conditions. Therefore, the shrink transition cannot involve breaking metal collagen bonds, so the process must involve breaking hydrogen bonds in helix three, causing them to break down, and in the linked matrix around helix three [7]. The suspended solid content in aluminium tanning wastewater is lower than conventional chrome tanning wastewater and combined tanning wastewater. This may be due to the different amounts of tanning materials, resulting in the immobilization of large amounts of collagen in the tanning material, the remaining tanning material cannot penetrate the collagen fibers, so there is more suspended solids content [9].

Aluminium can be used as a pre-tanning material. If it is used as a pre-tanning material, it can be continued with tanning using 30% mimosa vegetable tanning, which can produce a temperature of 94.54°C [10]. Besides the increasing use of Al_2O_3, the higher the level of shrinkage temperature. However, the higher the Al_2O_3, the more it causes grain coarseness [11]. On the other hand, titanium (IV) salts have a similar affinity for collagen as aluminium (III), in part due to some similarities in properties, such as the acidity of the ion and the tendency to hydrolyze and to precipitate as the pH is raised above 3. The interaction with collagen carboxyls is similarly electrovalent, rather than covalent. However, one difference is the greater filling effect of Ti (IV) salts, due to the polymeric nature of the salts, which produces softer leather. The weak chemical interaction with collagen results in shrinkage temperatures of 75-80°C [7].

EXPERIMENTAL

Materials and Methods

Instruments

Drum trial, bucket, baumemeter, knife, thickness gauge, measuring frame, set-out knife, and tilt table.

Materials

12 pieces of pickled goatskins, with an area of 7 sq ft, thickness 0.7 - 0.75 mm.

The chemicals used are aluminium tanning agent (Novaltan Al), titanium tanning agent, salt (NaCl), Peramit MLN, Derminol OCS, MgO, $NaHCO_3$, BCG indicator, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, Acid dyestuff, formic acid, Sincal DR and anti-fungal.

Technology Process

The research was conducted by carrying out a tanning process using aluminium and titanium tanning as a substitute for chrome tanning agent. The tanning process was carried out with 3 kinds of Al_2O_3 content, namely, 2%, 4%, and 6%, and also the use of aluminium mixed with titanium (2:1).

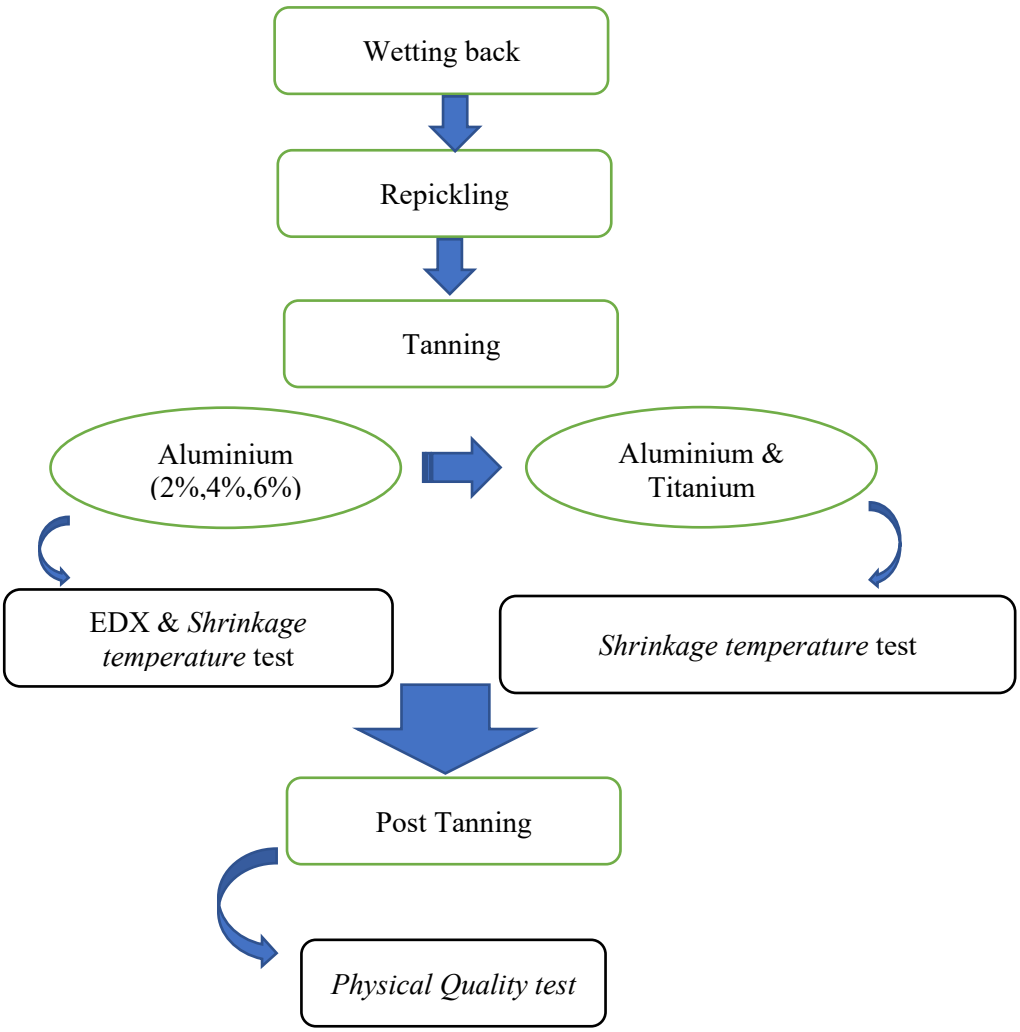


Figure 1. Research flow chart

Data Analysis

Shrinkage temperature test (Ts)

Shrinkage temperature test is a test to determine the temperature when the skin first wrinkles/shrinks. The test is carried out by cutting a skin sample and placing it in heated water. Furthermore, it is observed at what temperature the skin starts to wrinkle. The results of Ts of each treatment obtained were compared with the one-way ANOVA test. The best results of Ts then mix with titanium tanning agent.

Analysis of the Content of the Tanning Agent in the Skin

The content of aluminium tanning agent in wet white leather was then tested using the EDX (Energy-Dispersive Xray Spectroscopy) test (based on differences in concentration variations, followed by a function of time).

Physical Quality Test

The resulting crust skin was tested for tensile strength, and a test for softness using a softness meter.

RESULTS AND DISCUSSIONS

The global rise in pollution is increasingly demanding for the development of producing good quality leather that is friendly to the environment. One of the things that can be used is the use of chrome-free tanning materials. The mineral tanning material class that can be studied in more depth as a

substitute for chrome are aluminium and titanium.

Effect of Aluminium Concentration on Aluminium Levels in the Skin

Of the total amount of aluminium used in the tanning stage, some of the aluminium tanning agents will react with skin collagen and part will be carried away to the waste. After basification of aluminium compounds at the end of the tanning process with magnesium oxide, a reaction occurs between the aluminium complex and the collagen protein in which the aluminium binds directly to the carboxylate groups of collagen [12], as shown in Figure 2 and Figure 3.

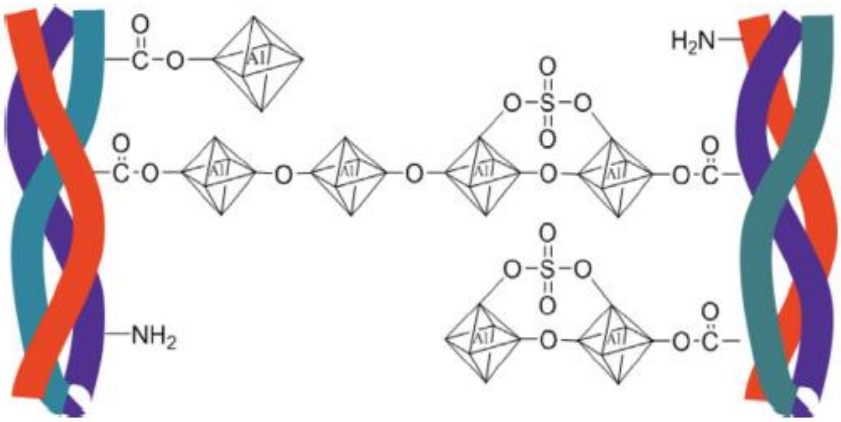


Figure 2. Representative of the bonding of aluminium tanning agents with skin collagen [13]

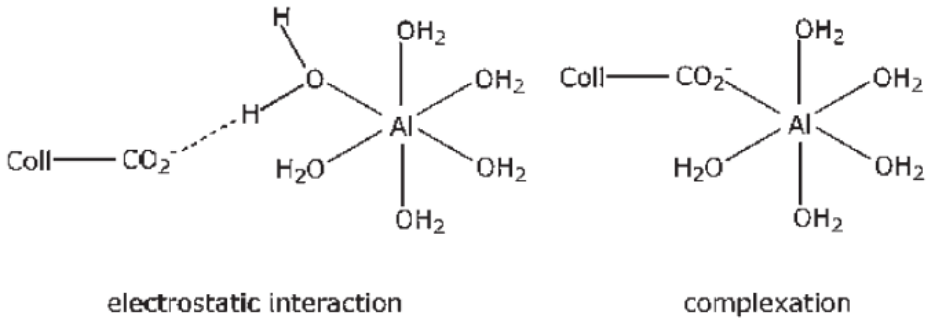


Figure 3. Interaction of Al and collagen [7]

Table 1: EDX skin results with varying concentrations of aluminium

Element	Al 2% (mass %)	Al 4% (mass %)	Al 6% (mass %)
C	43.17	48.86	45.02
N	11.07	15.06	17.35
O	34.50	25.37	32.03
Na	1.29	4.19	1.40
Mg	0.16	0.19	0.27
S	3.34	0.27	0.30
Cl	2.50	5.14	1.98
Ca	3.18	-	-
Cr	-	-	-
Al	0.79	0.93	1.64

The EDX data in Table 1 presents that the main constituent elements of the skin, whether tanned with chrome or aluminium tanning materials, are carbon, nitrogen, and oxygen which are elements commonly found in living things and are the main constituent elements of amino acids and lipids. Meanwhile, other elements, namely sodium (Na), magnesium (Mg), sulfur (S), calcium (Ca), and chloride (Cl) were also detected to be the constituent of the

skin. These elements are naturally present in the skin as mineral salts, but can also come from chemicals used in the leather tanning process such as pickling, unhairing, liming, basification, and others.

Based on Table 1, it is also seen that the aluminium content in leather at a concentration of Al_2O_3 is 2%, 4%, and 6%. The higher the number of Al_2O_3 used, the higher the aluminium content in the skin. This shows that the aluminium used is still acceptable on the skin with the increasing amount of Al_2O_3 used. The more aluminium content in the skin it is expected that the more aluminium will be bound to the carboxylate group of the skin, so that the tanning will be better.

Cross-section of Wet White Skin

Figure 4 is a picture of goatskin before and after the wet white tanning process is carried out. It can be seen in the picture that the result of aluminium tanning and mixed aluminium and titanium is skin that is evenly white or so-called wet white, which is different from the skin from chrome tanning agent which produces wet blue skin.

a. Pickled skin

b. Wet white aluminium

c. Wet white aluminium & titanium

Figure 4. Goatskins

Effect of Tanning Time on Aluminium Levels in the Skin

Table 2 describes that the longer the processing time, the higher the aluminium content in the skin. This shows that the processing time is important to achieve the target of penetration of the tanning material into the skin. The process of tanning and complex formation is not an instant reaction. The rate of reaction changes with pH conditions and process temperature [7]. Good control of the quality of the tannery requires adherence to the established temperature, pH, and time relationships.

Table 2: The level of aluminium in the skin based on the processing time

*Tanning time (hour)	Aluminium in the skin (%)
1	0.53
4	1.00
7	1.09
10	1.04

*concentration Al = 2 %

The shrinkage temperature of wet white TVT increased with the length of tanning time and remained stable after 3 hours of tanning [14]. Therefore, the optimal tanning duration is set to be 4-5 hours. This shows the importance of processing time to reach mature skin and a certain wrinkle temperature.

Shrinkage Temperature (Ts) of Wet White Tanning Agent

Table 3: Results of mean pH and shrinkage temperature (Ts)

Tanning agent	%	Pickled skin		Wet white	
		pH	Ts (°C)	pH	Ts (°C)
Aluminium	2	2.5	42	3.9	71
	4	2.5	43	3.9	69
	6	2.5	43	3.8	68
Aluminium : Titanium	2 : 1	2.5	43	4.5	73

Based on Table 3, it can be seen that the shrinkage temperature of wet white is lower than that of wet blue because chrome tanned leather still has the highest Ts value (±100°C). Even the shrinkage temperature between exhausted and conventional tanning chrome has different results. The shrinkage temperature for skin with an exhausted tanning system has higher heat resistance than others [15]. There is a difference in the temperature of the pickled skin wrinkle with the wet white aluminium skin. After the skin was tanned, there was an increase in the temperature of the wrinkle (shrinkage temperature). Pickled skin has an initial pH of 2.5 then after aluminium tanning, the pH is 3.8 - 3.9. The increase in pH is in line with the increase in the wrinkle temperature of the skin from pickled skin to wet white skin. According to Li [14], it is clear that the wrinkle temperature of wet white increases with increasing pH. When the pH of the tanning is higher, a shrinkage temperature of around 90°C is reached, which indicates strong tanning ability. The number of carboxylate groups on the collagen side chain increases with increasing pH, which supports the equalization of the carboxylate groups with aluminium.

Goatskin that is tanned with aluminium tanning material can produce wet white leather with a shrinkage temperature of ± 70°C. This Ts is lower than chrome tanning which is capable of up to 100 or 120°C. However, the maximum performance of a tannery Ts is not a benchmark, the benchmark is what the final result of the leather product will be made of, requiring high heat resistance. So that with the performance of Ts 71°C, 69°C, 68°C, and also 73°C from a mix of aluminium and titanium, it is still acceptable or it is said that the skin is tanned ripe. The combination tanning agent between aluminium and titanium can reach higher Ts. Based on the results of shrinkage temperature testing, it can be seen that the higher the Al_2O_3 content used for tanning, the lower the Ts achieved. Based on these results, it can be said that although the aluminium content in the skin increases with the addition of Al_2O_3 used (Table 1), it does not mean that the higher the aluminium binds to the carboxylate. There is an indication that the aluminium in the skin is only penetrated and has not been bonded. This is following that if the tanning material is too excessive, it is feared that there will be aluminium in the collagen structure but it is not chemically bound to the collagen protein carboxylate group (appears as dissolved aluminium in the skin) [12]. So as a result, if the aluminium does not bind to the skin, the Ts obtained will be low.

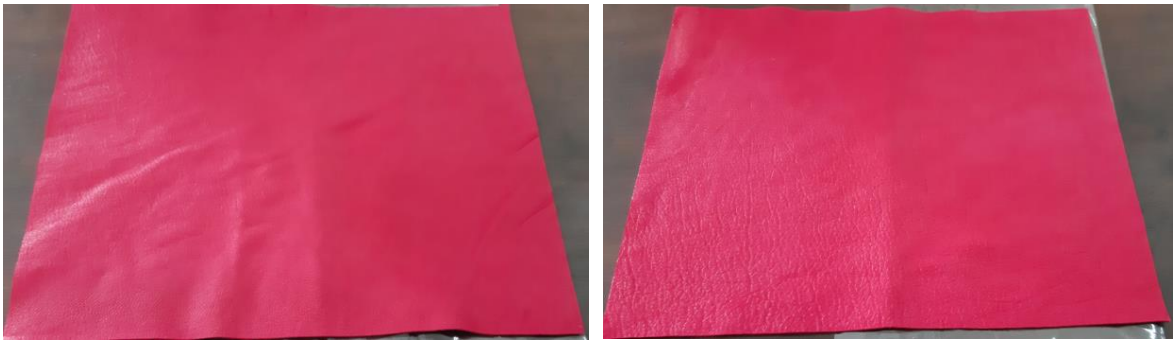
Table 4: ANOVA Ts test results on the three variations of Al_2O_3

Variable	Content of Al_2O_3			*P* value
	2%	4%	6%	
Ts (°C)	70.67 ± 0.58	69 ± 1	67.67± 10.58	0.008

The value of the shrinkage temperature changes with alterations in the amount of tanning material used. Based on the results in Table 4, it shows these changes, then when tested by ANOVA (Table 4) it can be seen that the results of Ts (shrinkage temperature) at the variation of 2%, 4%, and 6% have a significant difference ($p < 0.05$). This indicates that the use of tanning agents affects the yield of Ts obtained from aluminium tanning agents.

Although the results obtained are inversely proportional. If there is no bonding with the collagen carboxylate group, the wrinkle temperature (Ts) will be low. This indicates that the increase in the amount of tanning material used for tanning does not result in an increasing number of wrinkles. The use of a 2% aluminium tanning agent is capable of tanning the skin with an average performance of Ts 71°C.

After analyzing the quality of the tanning leather, then the leather with the percentage of 2% Al_2O_3 and the mix between aluminium and titanium was carried out post tanning process to produce crust dyed leather. The part of the crust dyed skin that has been cut is shown in Figure 5.



a. Aluminium b. Aluminium & Titanium

Figure 5. Crust dyed skin

Based on Figure 5, it can be seen that leather tanned using aluminium and titanium has good color evenness. This shows that this mineral tanning material also has good color quality results when used for colored leather products. The results of the physical quality of the crust, both tensile strength and flexural strength, are shown in Table 5.

Table 5: Physical quality of crust dyed skin

Tensile strength (N/mm)		Softness (mm)	
Aluminium	Aluminium & Titanium	Aluminium	Aluminium & Titanium
17.61	25.05	3.9	4.5
16.59	50.91	3.5	3.75
13.15	50.88	3.4	3.3

Based on Table 5, it can be seen that the leather produced from mineral tanning materials other than chrome can produce physical qualities that can be compared with certain articles. The use of aluminium and titanium tanning materials simultaneously in the tanning process can improve the physical quality of the skin, both in terms of tensile strength and skin softness. This can be used as a consideration for the use of other mineral tanning materials other than chrome to produce leather. The use of titanium (IV) tanning material has advantages such as having a shrinkage temperature of Ts = 76.1°C and chromium-free waste production. In addition, it can also improve the quality of non-allergenic products because titanium (IV) salt is harmless and does not cause problems for sensitive skin or mucous membranes [16].

CONCLUSIONS

Aluminium and titanium tanning agents are proven to be able to be used for tanning skin, by penetration of the tanning agent into the skin and achieving the desired wrinkle temperature. The higher the Al_2O_3 used, the higher the aluminium content in the skin. The higher the Al_2O_3 used, the lower the shrinkage temperature (Ts) obtained, this is related to the bond between the tanning material and skin collagen, not only penetrated in the skin.

The use of Al_2O_3 2% can be used for tanning with a shrinkage temperature (Ts) of 71°C. The physical quality of the crust skin from mixed aluminium and titanium mineral tanning agents is better than the single-use of aluminium, as a driving force for chrome-free tanning agents.

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STUDY ON THE RELATIONSHIP BETWEEN THE TOE-OUT GAIT AND FOOT HALLUX VALGUS IN THE ELDERLY CHINESE

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STUDY ON THE RELATIONSHIP BETWEEN THE TOE-OUT GAIT AND FOOT HALLUX VALGUS IN THE ELDERLY CHINESE

ABSTRACT. The study selects 50 senior people at the age of more than 60 and 30 young people at the age of 18-26 as test group and control group respectively, including people with mild foot disease, such as flat feet, pes cavus and hallux valgus. Questionnaire survey of effective data volume and observation are used to understand common problems of the foot in the elderly, collect shape photos of the foot in senior people, and subjectively analyze their foot shape and gait characteristics. Footscan plate plantar pressure test system and Kistler 3D force platform are used to objectively analyze plantar pressure distribution and gait characteristics of subjects. According to study results: Toe-out gait causes the plantar pressure to move to the forefoot, therefore, the forefoot is the part with the highest risk of injury of foot in toe-out gait, especially the first toe, causing hallux valgus and various foot problems. The toe-out gait causes increase of gait cycle, slow walking speed, poor buffer effect, and may bring pain in feet and lower extremities, thus affecting the dynamic characteristics of the entire lower limb.

KEY WORDS: the elderly, toe-out gait, foot hallux valgus

STUDIU PRIVIND RELAȚIA DINTRE MERSUL CU PICIOARELE ÎN EVERSIE ȘI HALLUX VALGUS LA POPULAȚIA CHINEZĂ VÂRSTNICĂ

REZUMAT. Studiul selectează 50 de persoane cu vârsta de peste 60 de ani și 30 de tineri cu vârsta cuprinsă între 18 și 26 de ani ca grup de testare, respectiv, grup martor, incluzând persoanele cu afecțiuni ușoare ale piciorului, cum ar fi piciorul plat, pes cavus și hallux valgus. Chestionarul privind volumul efectiv de date și observarea sunt utilizate pentru a înțelege problemele comune ale piciorului la vârstnici, pentru a colecta fotografii ale formei piciorului la persoanele în vârstă și pentru a analiza subiectiv forma piciorului și caracteristicile mersului. Sistemul de testare a presiunii plantare Footscan și platforma de forță Kistler 3D sunt utilizate pentru a analiza obiectiv distribuția presiunii plantare și caracteristicile mersului subiecților. Conform rezultatelor studiului, mersul cu picioarele în eversie determină deplasarea presiunii plantare către antepicior, prin urmare, antepiciorul este partea cu cel mai mare risc de rănire în mersul cu picioarele în eversie, în special degetul mare, provocând hallux valgus și diverse probleme la picioare. Mersul cu picioarele în eversie determină creșterea ciclului de mers, conduce la o viteză de mers lentă, are un efect slab de absorbție a șocului și poate cauza dureri ale labei piciorului și ale extremităților inferioare, afectând astfel caracteristicile dinamice ale întregului membru inferior.

CUVINTE CHEIE: vârstnici, mers cu picioarele în eversie, hallux valgus

ÉTUDE SUR LA RELATION ENTRE LA DÉMARCHE EN ROTATION EXTERNE ET L'HALLUX VALGUS DU PIED CHEZ LES PERSONNES ÂGÉES CHINOISES

RÉSUMÉ. L'étude sélectionne 50 personnes âgées de plus de 60 ans et 30 jeunes âgés de 18 à 26 ans comme groupe test et groupe témoin respectivement, y compris des personnes atteintes d'une maladie du pied bénigne, comme les pieds plats, le pied creux et l'hallux valgus. L'enquête par questionnaire sur le volume de données et l'observation sont utilisées pour comprendre les problèmes courants du pied chez les personnes âgées, collecter des photos de la forme du pied chez les personnes âgées et analyser subjectivement la forme du pied et les caractéristiques de la démarche. Le système de test de pression plantaire Footscan et la plate-forme de force Kistler 3D sont utilisés pour analyser objectivement la distribution de la pression plantaire et les caractéristiques de la marche des sujets. D'après les résultats de l'étude, la démarche en rotation externe provoque un déplacement de la pression plantaire vers l'avant-pied, par conséquent, l'avant-pied est la partie présentant le plus grand risque de blessure lors de la démarche en rotation externe, en particulier le gros orteil, provoquant un hallux valgus et divers problèmes pour le pied. La démarche en rotation externe augmente le cycle de marche, conduit à une vitesse de marche lente, a un faible effet d'absorption des chocs et peut provoquer des douleurs au pied et aux extrémités inférieurs, affectant ainsi les caractéristiques dynamiques de l'ensemble entier du membre inférieur.

MOTS CLÉS : personnes âgées, démarche en rotation externe, hallux valgus du pied

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INTRODUCTION

With aging of the world, problems of the elderly are increasing. The elderly are more susceptible to fracture during fall due to osteoporosis and brittleness increase. Statistically, more than 40% of the elderly easily fall with age [1]. Foot problems are related to the balance and stability of the elderly, playing an important role in preventing falling injury and improving living quality of the elderly [2]. Foot problems of the elderly are diverse and complex, and it is difficult to find the root cause, therefore, the study on the foot of the elderly lacks theoretical support.

Toe-out gait is one of the more common gait abnormalities [3]. Toe-out gait not only slows down the step, but also causes injury after long-term accumulation in the case that instep and forefoot are vulnerable to fatigue for larger impact on tibia when amount and intensity of exercise are greater [4]. Foot hallux valgus is a common morphological lesion, and foot hallux valgus malformation or pain manifests itself [5]. The incidence rate is high in the elderly, and normal walking is affected in severe cases. Li Fengling [6] selected 10 subjects with normal feet and 10 subjects with slight hallux valgus feet as control group and hallux valgus group. According to results, the lateral side of the forefoot becomes the main support mode, causing that ankle joint extends in case of touchdown, knee joint retracts, and hip joint turns outward. Su Honglun [7] *et al*. introduce the concept of transverse arch and hallux valgus, analyze biomechanical change, and obtain the relationship between hallux valgus and collapse of transverse arch. Wei Mengtian [8] *et al*. study the young men with toe-out gait. According to results, both the peak value and pressure time of toe-out gait in medial side and lateral side as well the third toe increase, and the time to reach the peak value in each area of the foot increases. According to some studies [9], foot impulse of toe-out gait decreases compared with the normal gait in forefoot and arch of foot. Gestel L.V. [10] *et al*. make a study on whether to change the foot load of toe-out gait through the plate pressure system. According to results, conscious change of gait can reduce the load of the foot area.

At present, neither domestic nor overseas studies draw a consistent conclusion in terms of plantar pressure distribution characteristics. In addition, studies on toe-out gait and hallux valgus make an analysis on mechanical changes based on focus on mechanics and morphological characteristics, but do not explore relevance. Therefore, causes of results are unknown, which is adverse to drawing a systematic conclusion. Therefore, the exploration on morphological and mechanical changes of toe-out gait and hallux valgus of the elderly and the analysis on its relevance are of great significance. Meanwhile, it provides data support for the study on the foot function, guarantee for the improvement of living quality of the elderly, and better theoretical research support for the development of shoes for the elderly.

EXPERIMENTAL

Experiment Equipment

Plate Plantar Pressure Test

The study adopts Belgian plate plantar pressure test system Footscan, with measurement frequency of 125 - 300 Hz, with 4,096 sensors with specification of 0.5 cm*0.7 cm.

3D Force Platform

In this study, Switzerland Kistler 3D force platform is used. 12 physical sensors of quartz crystal are placed on the four corners of the 3D force platform. 3 sensors for each corner are sensitive to the z, x and y-axis forces respectively. By combining the 3D force of four corners, the total 3D force and direction, as well as acting point and torque can be calculated. The plantar pressure test plate and 3D force platform are shown in Figure 1 from left to right.

Figure 1. Experimental equipment

Experimental Objects and Plans

Questionnaire Survey

Xi'an was selected as the study site for the questionnaire survey, 1,000 (500 male and 500 female) senior people at the age of 60 - 95 in Henan, Hebei, Jiangsu, Sichuan and other places were selected. The questionnaires were about the shoes and boots for the elderly. 1,000 questionnaires were distributed and 800 valid questionnaires were recovered. Seven views of the feet of the elderly were collected and the gait of the elderly was captured on video by digital high-definition cameras.

Mechanical Test

50 (25 male and 25 female) senior people at the age of more than 60 and 30 (15 male and 15 female) young people at the age of 18-26 were selected as test and control group, respectively, including people with mild foot disease, such as flat feet, pes cavus and hallux valgus. The subjects were healthy, with regular exercise habits; there had been no operation on foot and no other injury on lower limb in half a year; before the test, the subjects were informed of the test process, and all the subjects signed the informed consent form. During the test, the subjects were required to walk barefoot naturally with their normal gait [11], and the whole process was repeated three times. In order to ensure that the independent test is not affected by many factors, the interval of each test shall not be less than 1 min.

The plantar is divided into 10 regions according to the analysis process, as shown in Figure 2: Different zones are distinguished by different color blocks and acronyms. T1 represents the first toe, T2-5 represents the second to fifth toes, M1-M5 represents the first to the fifth metatarsophalangeal joints, MF represents the midfoot, HM represents the medial part of the heel, and HL represents the lateral part of the heel.

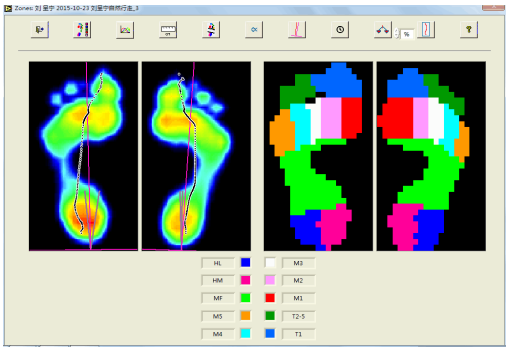

Figure 2. Regional distribution of plantar pressure

Methods

The study is mainly divided into two parts: survey and experiment. The survey study is mainly to obtain the proportion of common foot problems of the elderly through questionnaire survey and collection of foot shape and gait information. The experiment study mainly carries out biomechanical measurement of exercise [12]. Through the plate plantar pressure test and 3D force platform, parameter data of plantar pressure distribution and foot stability of the elderly is obtained, and data results are processed and analyzed to draw a condition of relevance between toe-out gait and foot hallux valgus of the elderly. The technical route of study is shown in Figure 3.

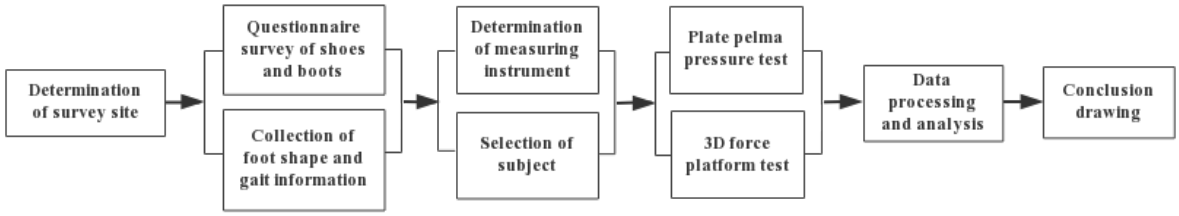

Figure 3. Research Technology Roadmap

RESULTS AND DISCUSSIONS

Survey Results of Common Foot Problems in the Elderly

The foot deformation of the elderly mainly includes the changes of forefoot, such as hallux valgus, claw toe, overlapping toe, and arch of foot. The survey results show that 15% of the elderly have claw toe, 19% of the elderly have overlapping toe, 14% of the elderly have toe adhesion, and 47% of the elderly have hallux valgus; the gait results show that 18% of the elderly shamble from side to side while walking, 20% of the elderly walk with weak legs and slow gait; 5% of the elderly have foot pain or numbness while walking, and 36% of the elderly walk in toe-out gait. Resurvey of the elderly with toe-out gait shows that 80% of the elderly have hallux valgus from the 36% of the people with toe-out gait. The summarized results are shown in Figure 4.

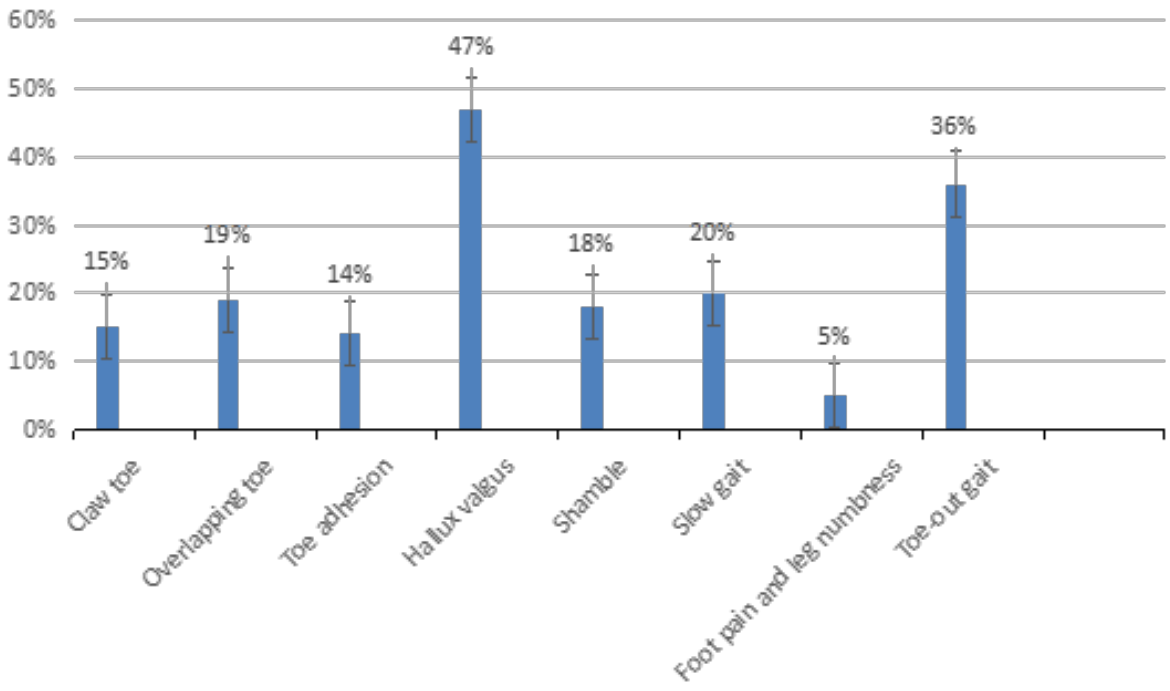

Figure 4. Survey results of common foot problems in the elderly

Plantar Mechanical Results of the Elderly

Results of Pressure Distribution in Each Plantar Zone through Plate Plantar Pressure Test

Data of peak pressure in each plantar zone in the elderly group and the young group is shown in Table 1.

Table 1: Peak pressure in each plantar zone (x±s)

Zone	Elderly male	Young male	Elderly female
T1	8.86 (±4.65)	8.93 (±4.32)	7.82 (±4.59)
T2-5	3.29 (±2.41)	3.01 (±2.63)	3.51 (±2.98)
M1	7.81 (±4.23)	10.34 (±4.3)	7.46 (±3.97)
M2	14.63 (±6.10)	16.92 (±4.15)	17.58 (±6.19)
M3	16.92 (±7.56)	18.03 (±5.34)	18.57 (±6.53)
M4	11.45 (±6.08)	10.79 (±5.68)	12.94 (±6.15)
M5	6.87 (±3.54)	5.04 (±3.17)	8.07 (±5.94)
MF	4.55 (±1.96)	3.16 (±2.12)	4.23 (±2.21)
HM	12.19 (±5.13)	14.29 (±5.01)	11.86 (±5.02)
HL	11.63 (±4.29)	14.17 (±3.95)	12.23 (±3.79)

According to the results of peak pressure in each plantar zone, in T1 zone, the peak pressure of plantar in the elderly group is lower than that of the young group, while in T2-5 zone, the peak pressure of plantar in the elderly group is significantly higher than that of the young group, which may be related to the big toe of the elderly. In the elderly group, the maximum zone of peak pressure of plantar is M2 and M3, showing that the plantar pressure of the elderly shifts to lateral forefoot.

Results of Touchdown Area in Each Plantar Zone through Plate Plantar Pressure Test

Data of plantar touchdown area of each zone in the elderly group and the young group is shown in Table 2. As for the touchdown area of the midfoot, if it is 21%-28%, it is the normal arch of foot; if it is more than 28%, it is flat feet; if it is less than 21%, it is pes cavus.

Table 2: Plantar touchdown area of each zone (x±s)

Zone	Elderly male	Young male	Elderly female
T1	15.14 (±4.82)	16.40 (±4.18)	13.24 (±4.73)
T2-5	11.7 (±6.93)	15.73 (±7.75)	11.32 (±7.89)
M1	15.83 (±4.56)	15.42 (±3.34)	12.94 (±3.34)
M2	12.47 (±2.03)	12.67 (±1.89)	10.36 (±2.58)
M3	10.01 (±1.43)	10.35 (±1.36)	8.47 (±1.73)
M4	10.43 (±1.11)	10.54 (±1.23)	8.52 (±1.74)
M5	10.70 (±2.32)	11.07 (±2.14)	9.74 (±2.85)
MF	40.01 (±9.09)	38.71 (±7.55)	37.22 (±8.72)
HM	19.76 (±1.80)	19.43 (±1.58)	16.67 (±3.46)
HL	17.25 (±1.78)	16.72 (±1.71)	13.56 (±3.31)

According to the results of touchdown area in each plantar zone, in T1 zone, the male in the elderly group is less than that in the young group by 1.26 cm^2, and the female in the elderly group is less than that in the young group by 1.84 cm^2. The touchdown area of the first toe decreases, objectively showing that the proportion of hallux valgus in the elderly is relatively high. The MF touchdown area in the elderly group is larger than that in the young group, the male in the elderly group is less than that in the young group by 1.30 cm^2, and the female in the elderly group is less than that in the young group by 1.05 cm^2.

Classification Results of Foot Axis Angles through Plate Plantar Pressure Test

As for the foot axis angles, if it is 5-12°, it is normal walking gait; if it is less than 5°, it is toe-

in foot; if it is greater than 12°, it is toe-out foot [13]. Data of classification of foot axis angles is shown in Table 3.

Table 3: Classification of foot axis angles

Angle	Number of feet in elderly male	Number of feet in young male	Number of feet in elderly female	Number of feet in young female
＜5°	2	3	3	4
5°-12°	8	7	10	8
＞12°	15	5	12	3

According to the classification results of foot axis angles, the number with foot axis angles more than 12° is the majority in elderly group, showing that the elderly mostly walk in toe-out foot.

Time Phase Characteristics of Each Phase of Touchdown through Plate Plantar Pressure Test

The results of time phase show that except for the phase of heel touchdown, the time phases of other phases of gait cycle in the elderly group are significantly greater than that in the young group, as shown in Table 4.

Table 4: Data of single step timing ($\overline{X}$ ±s)

Time phase	Female			Male		
	Elderly female/ ms	Young female/ms	Sig. both sides	Elderly male/ms	Young male/ms	Sig. both sides
Heel touchdown	45.72 (±15.34)	55.46 (±23.20)	.002**	46.50 (±17.97)	53.15 (±16.17)	.014*
Forefoot touchdown	61.53 (±35.5)	52.42 (±25.04)	.020*	51.54 (±36.52)	35.28 (±21.78)	.000**
Whole foot touchdown	349.80 (±70.11)	274.46 (±75.11)	.000**	92.34 (±80.00)	293.62 (±63.70)	.004**
Forefoot off the ground	308.35 (±74.86)	273.79 (±47.79)	.000**	298.23 (±61.47)	279.97 (±46.93)	.040*
Whole gait cycle	767.02 (±65.56)	655.19 (±56.26)	.000**	787.53 (±50.49)	662.02 (±57.18)	.000*

Note: "*" and "**" refer to that they are significant in 0.05 level (both sides) and 0.01 level (both sides) respectively.

Time Phase Results of 3D Force Platform

Ts is the time of support phase before touchdown, Tb is the time of swing phase by single foot, and Tp is the time of the phase of kicking ground for pushing off. During movement, for each phase in single support gait cycle, the time phase of the elderly group is greater than that of the young group, as shown in Table 5.

Table 5: Single step timing and difference level ($\overline{X}$ ±s)

Time phase	Female			Male		
	Elderly female	Young female	Sig. both sides	Elderly male	Young male	Sig. both sides
Ts	0.72 (±0.21)	0.65 (±0.05)	.000**	0.8 (±0.14)	0.65 (±0.06)	.000**
Tb	0.35 (±0.11)	0.32 (±0.06)	.011*	0.4 (±0.09)	0.32 (±0.06)	.000**
Tp	0.37 (±0.13)	0.33 (±0.06)	.000**	0.4 (±0.08)	0.34 (±0.05)	.000**

Note: "*" and "**" refer to that they are significant in 0.05 level (both sides) and 0.01 level (both sides) respectively.

Study Results for Force Value in Z Direction of 3D Force Platform

Z direction refers to the direction that is perpendicular to the horizontal plane, and the T-test results of its mechanical indicators and independent samples of young people are shown in Table 6.

Table 6: T-test of each indicator in Z direction ($\overline{X}$ ±s)

Indicator	Female			Male		
	Elderly female	Young female	Sig. both sides	Elderly male	Young male	Sig. both sides
Fmax/N	544.83 (±211.26)	598.99 (±86.93)	.006**	719.86 (±109.29)	743.97 (±10.85)	.076
Tv/%ST	55.17 (±27.56)	69.28 (±16.18)	.000**	51.82 (±26.89)	52.61 (±5.24)	.073
Fsz/N	396.01 (±158.63)	414.46 (±52.72)	.189	518.09 (±76.13)	519.26 (±63.13)	.054
Vv/m/s	5.14 (±3.32)	5.05 (±0.31)	.641	6.36 (±1.11)	5.16 (±0.51)	.006**
Fbz/N	393.79 (±158.66)	415.49 (±60.49)	.134	521.69 (±82.94)	524.11 (±68.15)	.010*
Fpz/N	397.04 (±163.39)	411.41 (±58.43)	.327	516.23 (±80.95)	517.91 (±70.12)	.007**

Note: "*" and "**" refer to that they are significant in 0.05 level (both sides) and 0.01 level (both sides) respectively.

According to the results of force value in Z direction, the maximum force value Fmax in vertical direction, the average force value Fsz in support phase before touchdown, the average force value Fbz in vertical direction in swing phase and the average force value Fpz in vertical direction in the phase of kicking ground for pushing off of the elderly group are significantly reduced, especially in the elderly female.

Study Results for Force Value in Y Direction of 3D Force Platform

Y direction refers to the direction that is parallel to the walking direction, and the T-test results of its mechanical indicators and independent samples of young people are shown in Table 7.

Table 7: T-test of each indicator in Y direction ($\overline{X}$ ±s)

Indicator	Female			Male		
	Elderly female	Young female	Sig. both sides	Elderly male	Young male	Sig. both sides
Ta-pb/%ST	50.30 (±38.46)	51.55 (±35.48)	.807	47.38 (±36.58)	51.86 (±36.73)	.385
Va-pb/m/s	0.26 (±0.10)	0.25 (±0.74)	.752	0.33 (±0.10)	0.28 (±0.07)	.000**
Ta-pp/%ST	56.36 (±37.54)	47.06 (±35.32)	.073	49.67 (±36.17)	46.66 (±36.17)	.557
Va-pp/m/s	0.28 (±0.10)	0.248 (±0.06)	.002**	0.33 (±0.09)	0.30 (±0.07)	.009**

Note: "**" refers to that it is significant in 0.01 level (both sides)

According to the force value in Y direction, the time percentage for the occurrence of maximum force value Ta-pb in the elderly group is less than that in the young group, while the speed change in Y direction in swing phase Va-pb is large. It proves that the time of swing phase in the elderly group is short, and the stability of contralateral lower limb for supporting is poor, which makes the swing accelerate. In the phase of kicking ground for pushing off, the time percentage for the occurrence of maximum force value Ta-pp in Y direction in the elderly group increases, and the speed change Va-pp increases.

Study Results for Force Value in X Direction of 3D Force Platform

X direction refers to the direction that is perpendicular to the walking direction, and the T-test results of its mechanical indicators and independent samples of young people are shown in Table 8.

Table 8: T-test of each indicator in X direction ($\overline{X}$ ±s)

Indicator	Female			Male		
	Elderly female	Young female	Sig. both sides	Elderly male	Young male	Sig. both sides
Fmax(m-lm) /N	27.81 (±12.93)	21.81 (±10.65)	.001**	39.33 (±23.58)	39.06 (±17.0)	.919
Tm-lm/%ST	24.51 (±29.28)	28.27 (±25.33)	.342	26.71 (±30.15)	27.04 (±30.40)	.939
Fmax(m-ll) /N	30.80 (±15.49)	24.81 (±11.04)	.001**	41.86 (±28.13)	39.54 (±16.56)	.422
Tm-ll/%ST	33.96 (±32.49)	27.62 (±28.09)	.128	28.43 (±31.74)	27.76 (±30.47)	.879

Note: "*" and "**" refer to that they are significant in 0.05 level (both sides) and 0.01 level (both sides) respectively.

According to the force value results in X direction, the maximum force value Fmax (m-1m) in medial side of foot is significantly less than the maximum force value Fmax (m-11) in lateral side of foot, and the time Tm-1m for the occurrence of maximum force value in medial side of foot is less than the time Tm-11 for the occurrence of maximum force value in lateral side of foot.

Path of Center of Pressure (COP) of 3D Force Platform

The T-test results for path of COP in the elderly group and the young group as well as the independent samples are shown in Table 9.

Table 9: T-test of the data of COP ($\overline{X}$ ±s)

	Female			Male		
	Elderly female	Young female	Sig. both sides	Elderly male	Young male	Sig. both sides
Y/mm	62.35 (±24.64)	53.94 (±27.81)	.021**	77.53 (±30.98)	56.27 (±30.30)	.000**
X/mm	195.14 (±43.13)	187.57 (±49.02)	.236	246.00 (±52.19)	237.51 (±57.12)	.433

Note: "**" refers to that it is significant in 0.01 level (both sides)

According to the results for the path of COP, in Y direction, the crossing amplitude for the path of COP in the elderly group is greater than that in the young group, which is significantly different, indicating that the forward amplitude of the elderly is large, and the gait is unbalanced.

Experimental Analysis

Analysis I

The touchdown area and the peak plantar pressure of the elderly group in T1 zone reduces, while the plantar pressure in T2-T5 zones increases, causing the increase of pressure time integral in M2-M4 zones of the forefoot of the elderly group. Due to the hallux valgus caused by its bone deformity, the time phase in each phase increases, and the foot axis angles significantly increase. It can be concluded that the foot deformation directly affects the size change of each part of the foot, which causes the differences in its mechanical characteristics compared to young people. The force value of plantar pressure of the elderly is towards the outside, it may increase the feeling of fatigue in walking, and cause the flat feet in severe cases.

Analysis II

Due to the uneven plantar stress in walking caused by foot deformation, the time phase of each phase in walking in the elderly group is greater than that in the young group, and the foot axis angles significantly increase, which causes the toe-out gait. The survey results show that the toe-out gait in the elderly accounts for 36% of the respondents, which has also been indicated in the test indicators of 3D force platform, the value in X direction of the elderly group is greater than that of the young group. Because the foot of toe out is towards the outside when touching the ground during movement, the stride of each step will reduce compared to the normal touchdown stride when the step speed is certain, its force is not completely forward, while

the foot moves forward in the form of half of "X", "A" and "V", the strength of the person moving is broken down in this way, which slows down the step speed.

Analysis III

The time phase of each phase in the whole gait cycle of the elderly group increases, the other phases of the single support gait cycle of the 3D force platform significantly increase except that the time Ts of support phase before touchdown in the elderly group is significantly less than that in the young group, the maximum force value in medial side of foot is significantly less than the maximum force value in lateral side of foot, and the increase of gait cycle indicates that the walking speed of the elderly becomes slow, which indicates the gait characteristics of drag, weakness and slowness of the elderly. And the center of gravity of the foot of the elderly is towards the outside, Fmax, Fsz, Fbz and Fpz reduce, which proves that the elderly have difficulty in lifting foot, and the gait characteristic of foot weakness is directly connected with the foot deformation caused by hallux valgus indeed.

CONCLUSIONS

(1) Toe-out gait causes the plantar pressure to move to the forefoot, therefore, the forefoot is the part with the highest risk of injury of foot in toe-out gait, especially the first toe, causing hallux valgus and various foot problems.

(2) The toe-out gait causes increase of gait cycle, slow walking speed, poor buffer effect, and may bring pain in feet and lower extremities, thus affecting the dynamic characteristics of the entire lower limb.

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EUROPEAN RESEARCH AREA

COTANCE NEWSLETTERS

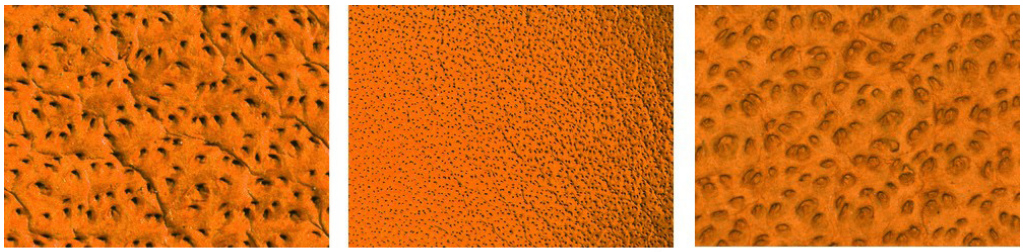
Starting with January 2019, the COTANCE Council will issue a monthly ***COTANCE Newsletter*** with the purpose of **promoting an improved image of leather** to relevant decision makers and domestic stakeholders including Members of the European and National Parliament, Governmental authorities, Ministerial officers, Customers of the leather industry, Brands, Retail chains, Relevant NGOs, Designers, etc. The monthly newsletters present topics that tell the truth about a controversial aspect or a fact that is not well known by the general public to bring about a better understanding of leather and the European leather industry, as well as a positive predisposition to legislate in favor of the leather industry. The newsletters are available in seven languages at https://www.euroleather.com/index.php/newsletter, and were also published in the 2019-2021 issues of *Leather and Footwear Journal*. Newsletter 7 is given below.

NEWS 7/2021

Aniline and Nubuck Leather – for anyone who loves the Exceptional

Real leather is available in different fine, refined and premium types. Here you can learn more about these some of the **premium and soft leathers**.

Aniline leather is pure real leather and the finest leather available. Although it is available in various colours, the surface is not coated. The natural characteristics of the hide are thereby preserved, and any natural characteristic, however small, such as the grains, remains visible. The result is an extremely soft and supple leather with a natural look. Only flawless hides are processed into aniline leather, which makes this type of leather extremely valuable and also expensive.



Aniline leather. Magnified 7x resp. about 30x. Leica MST5x-DCI/DFC450 camera. Credit: Wollsdorf Leather

Nubuck leather has a velvet-like finish. The leather is buffed, creating a soft, velvety and warm surface. It is highly breathable and able to wick away sweat, ensuring a high level of wearing comfort while maintaining the protective function for which leather is known. Nubuck is used in upholstered furniture, handbags, clothing, shoes, gloves and as automotive leather.

It's all about the right care!

Leather is subject to a natural ageing process. Just like good wine, it matures and gains its own unique character over time. Delicate natural leather can be kept beautiful for a long time when treated and cared for properly.

See our Newsletter 09/20 for 14 tips to take care of your favourite leather product!

edited by

COTANCE

in collaboration with

WKO INDUSTRIE
Textil · Bekleidung · Schuh · Leder

News Release from the IULTCS

09 August 2021

IULTCS to Support Leather Students to Virtually Attend XXXVI IULTCS Congress in Ethiopia

As the XXXVI IULTCS Congress approaches (03-05 November 2021) the Africa Leather and Leather Products Institute (ALLPI) is pleased to announce that there will be support available to enable 20 leather (or associated subject) students to attend the congress virtually. The support is being provided from a grant of US$2,000 that is being awarded by IULTCS. President, Dr Luis Zugno, stated "Despite the current difficulties with travelling it is vital that we encourage our future leather scientists and technologists to participate in these prestigious events as both presenters and attendees. IULTCS has provided the financial means for this to happen for 20 young people and I call on industry professionals to ensure likely candidates are aware of this opportunity."

To apply to attend, students should contact executive.director@allpi.int

XXXVI IULTCS Congress

The two leather congresses (XXXVI IULTCS and 5th World Leather Congress) are to be held in Addis Ababa on 01 – 05 November 2021 and are expected to leave delegates with great insights and informative actions that delegates could use in their respective institutions and/or enterprises.

Registration for the congresses has commenced and a new registration fee structure for remote registrations is in place – with the ability to 'upgrade' to in person attendance if travel restrictions allow. Abstract submission for the IULTCS Congress is open until 31 August 2021 – with the option to submit a remote paper, allowing current global research to be shared, even if the presenter cannot be in attendance.

The link **https://www.iultcs2021africa.org/home** will provide more information on registration and guidelines for submission of Abstracts.

There are also opportunities to support these high-profile, globally attended events by becoming sponsors, as it is critical to our industry that we continue to share our knowledge, research and best practice – various packages are available to suit all budgets so companies are encouraged to contact the organisers to see how they can best participate.

Summary Information:

5th World Leather Congress: 01 November 2021
XXXVI IULTCS Congress: 03 - 05 November 2021
Venue: Ethiopian Skylight Hotel, Addis Ababa, Ethiopia
Working Language: English
ALLPI Website: **https://www.allpi.int**

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News Release from the IULTCS

16 September 2021

Dr T Ramasami Announced as Recipient of the IULTCS Merit Award 2021

It is with great pleasure that IULTCS announces Dr Thirumalachari Ramasami has been chosen as the winner of the prestigious IULTCS Merit Award for Excellence in the Leather Industry. The IULTCS was founded for the purpose of encouraging the technology, chemistry and science of leather on a worldwide basis. It is therefore appropriate that we recognise the achievements of those of stature in our industry who have contributed significantly to our global understanding of the leather industry and its by-products. The IULTCS Merit Award is given biennially by the IULTCS Executive to an individual, whose past or current endeavours have had an extraordinary impact on our industry and provide an example for others to follow. Dr Ramasami fits this profile perfectly.

Dr T Ramasami is known for his significant contributions to the chemistry of chromium as a scientist and leadership to the Indian leather sector as a technologist and to science as a civil servant. Ramasami's investigations focussed on mechanistic chemistry, industrial applications of chromium salts and ecological solutions to industrial environmental problems. Some of his major research contributions include demonstration of anomalous reactivity of chromium(III), stabilisation of unusual oxidation states of chromium, mechanistic insights into chromium induced apoptosis, understanding host guest interactions in biomolecular systems and development of technologies for improved tanning systems.

He developed a "Unified theory of tanning" by probing molecular level understanding of tanning systems. More than 12 technologies developed by his group are in commercial exploitation and several of them have been developed from first principles without international equivalents. He has guided more than 30 students for their doctoral research and authored more than 237 research publications, eight chapters in books, and numerous general articles. He holds more than 40 patents. In recognition of his contributions to leather research he was invited to deliver the John Arthur Wilson Memorial Lecture.

The Merit Award will be presented to Dr Ramasami once travel restrictions allow.

News Release from the IULTCS

20 September 2021

IULTCS Young Leather Scientist Grant Programme 2022 Announced

The Executive Committee of the IULTCS is pleased to announce the 2022 grants to be awarded to two young scientists, under the age of 35, for research projects in the categories: Leather Research and Sustainability/Environment - to be conducted at a recognised institution in 2022.

"Leather Naturally is proud to continue sponsoring the Dr Mike Redwood Sustainability/ Environment grant with the monetary sum of €1,000 sponsorship" said Egbert Dikkers, Chairperson. "With Leather Naturally focussing on providing education to designers, brands and consumers, it was a logical step to sponsor this award named in honour of our founder Dr Mike Redwood."

2022 will be the eighth year of the grant, and in addition to Sustainability/Environment the IULTCS will provide the monetary sponsorship for a single sum of €1,500 grant to a Basic Leather Research project.

Michael Meyer, Chairman of the International Union of Research Commission (IUR) of IULTCS and Research Director at Freiberg (Germany) based FILK Leather Institute expressed his appreciation of the continued engagement: "We are very happy to announce the award for the 8th year. The detailed project results of previous winners are presented in their reports on the IULTCS web site. It is worthwhile reviewing these substantial and significant investigations. We very much value the contribution of Leather Naturally to our YLSG programme. It is a vital instrument to encourage young leather scientists to acquire awareness and become more connected to the established research community of our industry. We have seen the programme growing stronger over the past years. Last year´s awards resulted in numerous, ambitious applications with innovative ideas and sustainable technologies."

Application submissions for the 2022 YLSG programme open on 01 October 2021 and Luis Zugno, President of IULTCS, asks young research talents of the industry to file innovative and thought-provoking project ideas before the 30 November 2021 deadline.

Details of the eligibility requirements are available on the IULTCS website YSLG_application_ rules_and_procedure_2022.pdf (iultcs.org)

The IULTCS requests that readers of this announcement forward the information to those institutions and individuals who could benefit from the award.

SPRING AND AUTUMN FAIR TARGETS THE WELLBEING OF RETAILERS WITH RETAIL TRUST CHARITY & WELLBEING PARTNERSHIP AND ANNOUNCES FEMALE FOUNDERS INITIATIVE

Hyve Group is pleased to announce the Retail Trust as its Charity Partner for Spring and Autumn Fair for two years and Wellbeing Partner across all its Retail Shows in the UK comprising Spring Fair, Autumn Fair, Pure, Glee and Scoop, to provide dedicated support, awareness and fundraising for the retail sector.

The partnership will incorporate offsite volunteer days, team challenges, and onsite activity kicking off at Autumn Fair on the 5th – 8th September 2021 at NEC Birmingham. The partnership also sees the exciting launch of the Female Founders scheme that will offer free stands to six inspirational female founders.

Creating hope, health, and happiness for everyone in retail from 1832, the Retail Trust has been caring for, and protecting, the lives of people working in retail. Hyve Group plc's UK Retail division has already supported the Retail Trust's online wellbeing event 'For the four' in May, and in June employees volunteered to help get the Retail Trust's new online eBay fundraising shop up and running: sorting donated clothes, taking pictures, writing descriptions, and getting images online. All the money the online sales make will go towards running the Retail Trust's supported-living estates. The charity provides a much-needed safe haven and happy community where the over 55's can thrive, maintain their health and retain their independence.

During the 2-year Charity partnership, Hyve Group will take part in fundraising activities to raise awareness and funds for the Retail Trust. A dedicated Wellbeing section will launch on each of the event websites for Spring and Autumn Fair, Glee, Pure and Scoop. This will feature informative and supportive articles alongside videos that support the wellbeing of retailers and wholesalers alike.

Alongside this, the Retail Trust will also be supporting the Spring Fair Female Founders initiative. Launching at Autumn Fair 2021, Female Founders initiative is an exciting program created to champion and celebrate inspiring female entrepreneurs.

The initiative will support the growth of female founded retail businesses by offering six businesses a free stand at Spring Fair 2021, followed by 12 months of business mentoring with leading female entrepreneurs. The scheme will be announced and launched at Autumn Fair in September.

Managing Director, Retail & Fashion at Hyve Group plc, Julie Driscoll says; "We are absolutely thrilled to announce the Retail Trust as our Charity & Wellbeing Partner. Over the next two years we look forward to raising much needed funds and awareness, especially after the incredibly challenging year the retail sector and especially the independents have experienced. Through our shows we are entrenched in the retail industry and fully understand the importance of listening to and understanding its needs, offering support and advice, health, and wellbeing initiatives, as well as celebrating entrepreneurship."

A host of onsite wellbeing initiatives at Autumn Fair will be announced before the show but look set to include a Wellbeing lounge to allow attendees to escape the busy show floor and focus on their wellbeing, meditation sessions, and wellbeing content sessions providing information on the wellbeing services and training the Retail Trust offers as a charity.

Chief Executive of the Retail Trust, Chris Brook-Carter says: "The Retail Trust has been creating hope, health and happiness for everyone in retail for nearly 200 years, but our cause has never been more relevant. The financial aid we

provide to help people stay in their homes, feed their families, or make essential hospital visits has doubled to more than £900,000 in the last year, and we've run nearly 8,000 counselling sessions.

"This support simply wouldn't be possible without the donations the Trust receives and our valuable partnerships with organisations from across the retail industry. We're really looking forward to joining forces with Hyve Group over the next two years as we work together to continue to raise awareness and provide vital help to those who need it."

Find out more at https://www.autumnfair.com/wellness-hub

AUTUMNFAIR

5-8 SEPTEMBER 2021
NEC BIRMINGHAM

AUTUMN FAIR LAUNCHES REMOTE EXHIBITING AND WELCOMES 30 INTERNATIONAL SUPPLIERS TO SHANDONG PAVILION

Autumn Fair, the leading marketplace for home, gift and fashion taking place from the 5th – 8th September at NEC Birmingham, has launched a first of its kind 'Remote Exhibiting' package created to provide a solution to international travel challenges and enable leading international suppliers to showcase their products to Autumn Fair buyers.

With stands built, set up and staffed on behalf of the exhibitors by staff based in the UK, September's Autumn Fair will welcome the Shandong Pavilion, showcasing products from 30 suppliers from China's Shandong Province. Shandong's regional GDP totalled at 7.3129 trillion yuan in 2020, ranking third in China. It is an important manufacturing base in China with a deep industrial heritage focusing on consumer products, and the Shandong Pavilion at Autumn Fair will stage the largest collection of Chinese manufacturers offering a wide range of home, gift, and fashion collections.

Stuart Thomas, Head of Global Partnerships, Hyve Group plc says; "We are delighted to be working with Shandong Province to showcase a brilliant range of high-quality manufacturers at Autumn Fair. For UK retailers looking to source from China, Remote Exhibiting ensures we continue to deliver this and enables our international community to carry on doing business at our UK shows. The package allows products to be showcased to buyers, with no travel from the exhibitors."

Visitors to the Shandong Pavilion will be able to see, touch and experience products in person, while virtual sales meetings allow buyers to speak directly to the suppliers. Follow up is made quick and easy with CRM leads that include

notes tailored to each stand visitor.

Cao Guoping, Director of European & American Affairs Division of Shandong Provincial Department of Commerce, has been committed to developing economic and trade cooperation between Shandong and European countries for many years. He says; "Shandong features close economic and trade exchanges with the United Kingdom. The 'Made in Shandong' initiative strives to create products with lean materials, exquisite design, fine production, and meticulous service. A total of 30 consumer goods companies were invited to participate in this exhibition, involving household items like furniture, mirrors, carpets, straw and willow weaving, artificial flowers, and handkerchiefs, gifts such as greeting cards, chocolates, and fashion accessories, exquisite accessories of craft ornaments and glass handicrafts. We welcome British retailers to contact us and purchase Shandong-made products."

Shandong Pavilion remote exhibitor **Ms. Zhang Jing, Manager of Jinan Hualin International Trade Co. Ltd** says; "Our company has specialised in the production of furniture, wooden hangers, and various brushes since 2005. Our company obtained the FSC certificate in 2012 and passed the BSCI in 2020. Though unable to participate in person due to impact of COVID-19 epidemic, we will show our products to British buyers through remote display as part of the Shandong Pavilion organised by Department of Commerce of Shandong Province. We are eager to showcase high-quality products to British buyers and welcome more European buyers to contact us."

Bao Shuangyan, Manager of Laizhou More Than Chocolate Co. Ltd adds: "As part of the Shandong Pavilion organised by Department of Commerce of Shandong Province, we hope to display our finest products to buyers and expand sales channels. We have cost-effective daily consumption products suitable for UK and European markets, and mid-end to high-end gift products developed for various festivals. We are confident in our products and welcome new buyers and partners from the UK and European markets."

For further information on Remote Exhibiting visit https://www.autumnfair.com/remote-exhibiting-at-autumn-fair-2021, and to discover the Shandong Pavilion remote exhibitors and others from China with UK representatives take a look at https://tinyurl.com/ws7b2xn7.

NATIONAL AND INTERNATIONAL EVENTS

7TH WORLD CONGRESS ON RECENT ADVANCES IN NANOTECHNOLOGY (RAN 2022) 04-06 APRIL 2022, LISBON, PORTUGAL

RAN is aimed to become one of the leading international annual congresses in the field of nanotechnology. The congress is composed of 2 conferences. While each conference consists of an individual and separate theme, the 2 conferences share considerable overlap, which prompted the organization of this congress.

ICNNFC'22 - 7th International Conference on **Nanomaterials, Nanodevices, Fabrication and Characterization**

NDDTE'22 - 7th International Conference on **Nanomedicine, Drug Delivery, and Tissue Engineering**

This congress will provide excellent opportunities to the scientists, researchers, industrial engineers, and university students to present their research achievements and to develop new collaborations and partnerships with experts in the field.

Paper Submission Deadline: **October 08, 2021**

Notification to Authors: **November 05, 2021**

Early-Bird Registration Deadline: **November 30, 2021**

More information: https://rancongress.com/

6TH INTERNATIONAL CONFERENCE OF THEORETICAL AND APPLIED NANOSCIENCE AND NANOTECHNOLOGY (TANN'22) 02-04 JUNE 2022, NIAGARA FALLS, CANADA

The 6th International Conference of Theoretical and Applied Nanoscience and Nanotechnology (TANN'22) aims to become the leading annual conference in fields related to nanoscience and nanotechnology. The goal of TANN'21 is to gather scholars from all over the world to present advances in the fields of nanoscience and nanotechnology and to foster an environment conducive to exchanging ideas and information. This conference will also provide an ideal environment to develop new collaborations and meet experts on the fundamentals, applications, and products of the mentioned fields.

TANN is an acronym for **T**heoretical and **A**pplied **N**anoscience and **N**anotechnology.

Topics for TANN'22 include, but are not limited, to the following:

- Nanobiomechanics
- Nanobiotechnologies
- Nanocatalysis
- Nanoelectronics
- Nano-Graphene
- Nanomaterials, Nanodevices: Fabrication, Characterization and Application
- Nanomedical Applications: Drug Delivery, and Tissue Engineering
- Nanotechnology and Agriculture
- Nanotechnology and Energy
- Nanotechnology and Environment
- Societal aspects of Nanotechnology: Ethics, Risk Assessment, Standardization

Extended Paper Submission Deadline: **Nov. 26, 2021**
Extended Notification to Authors: **Jan. 14, 2022**
Extended Early-Bird Registration Deadline: **Feb. 11, 2022**

More information: https://tannconference.com

8TH WORLD CONGRESS ON NEW TECHNOLOGIES (NEWTECH'22)
03-05 AUGUST 2022, PRAGUE, CZECH REPUBLIC

NewTech is aimed to become one of the leading international annual congresses in the fields of new technologies. The congress is composed of 4 conferences. While each conference consists of an individual and separate theme, the conferences share considerable overlap, which prompted the organization of this congress.

- **ICNFA'22** - 13th International Conference on **Nanotechnology: Fundamentals and Applications**
- **ICEPR'22** - 12th International Conference on **Environmental Pollution and Remediation**
- **ICBB'22** - 8th International Conference on **Biotechnology and Bioengineering**
- **ICERT'22** - 6th International Conference on **Energy Research and Technology**

This New Technologies Congress 2022 will provide excellent opportunities to the scientists, researchers, industrial engineers, and university students to present their research achievements and to develop new collaborations and partnerships with experts in the field.

Paper Submission Deadline: **January 7, 2022**
Notification to Authors Deadline: **February 25, 2022**
Early-Bird Registration Deadline: **March 11, 2022**

More information: https://newtechcongress.com

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Presentation of Papers

The scientific papers should be presented for publishing in English only. The text of the article should be clear and precise, as short as possible to make it understandable. As a rule, the paper should not exceed fifteen pages, including figures, drawings and tables. The paper should be divided into heads and chapters in a logical sequence. Manuscripts must meet high scientific and technical standards. All manuscripts must be typewritten using MS Office facilities, single spaced on white A4 standard paper (210 x 297 mm) in 11-point Times New Roman (TNR) font.

Paper Format

Title. Title (Centered, 12 pt. TNR font) should be short and informative. It should describe the contents fully but concisely without the use of abbreviations.
Authors. The complete, unabbreviated names should be given (Centered, 10 pt. TNR font), along with the affiliation (institution), city, country and email address (Centered, 9 pt. TNR font). The author to whom the correspondence should be addressed should be indicated, as well as email and full postal address.
Abstract: A short abstract in a single paragraph of no more than 200-250 words must accompany each manuscript (8 pt. TNR font). The abstract should briefly describe the content and results of the paper and should not contain any references.
Keywords. Authors should give 3-5 keywords.

Text

Introduction. Should include the aims of the study and results from previous notable studies.
Materials and Methods. Experimental methods should be described clearly and briefly.
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Conclusions. The general results of the research are discussed in this section.
Acknowledgements. Should be as short as possible.
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Diagrams, Figures and Photographs should be constructed so as to be easy to understand and should be named "Figures"; their titles should be given below the Figure itself. The figures should be placed immediately near (after or before) the reference that is being made to them in the text. Figures should be referred to by numbers, and not by the expressions "below" or "above". The number of figures should be kept to minimum (maximum 10 figures per paper).
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Formulas, Equations and Chemical Reactions should be numbered by Arabic numbers in round brackets, in order of appearance, and should be centered. The literal part of formulas should be in Italics. Formulas should be referred to by Arabic numbers in round brackets.
Nomenclature. Should be adequate and consistent throughout the paper, should conform as much as possible to the rules for Chemistry nomenclature. It is preferable to use the name of the substances instead of the chemical formulas in the text.
References should be numbered consecutively throughout the paper in order of citation in square brackets; the references should list recent literature also. Footnotes are not allowed. If the cited literature is in other language than English, the English translation of the title should be provided, followed by the original language in round brackets. Example: Handbook of Chemical Engineer (in Romanian), vol. 2, Technical Press, Bucharest, 1951, 87.
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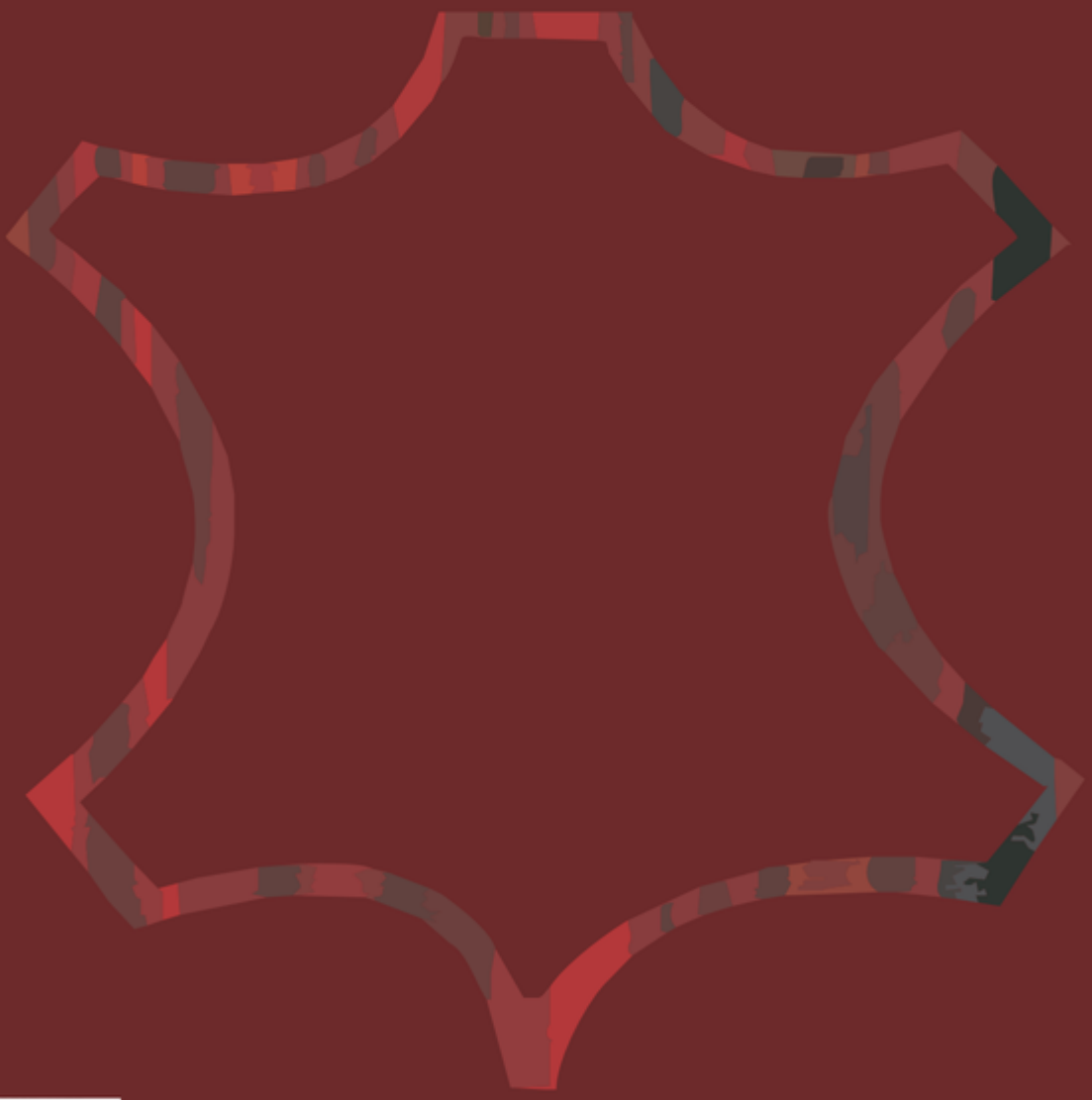

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