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DEVICE FOR DETERMINING PERMEABILITY OF TANNING LIQUID

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Abstract: An important problem in the field of improving and developing equipment for determining the filtration properties of porous materials (in the example of skin products) is solved in the article. The importance of this study lies in the experimental determination of the permeability coefficient of the porous material. The filtration capacity of the hide samples and the coatings of the working rolls made of LASCH and BM cloths was experimentally determined in the article under industrial conditions. The results of the study of the filtration capacity of the skin product samples in the areas under consideration will make it possible to fulfill the requirements for the high-quality processing of skin materials. It was determined that the highest value of the filtration coefficient was observed in the "belly" section of the hide, the smallest value - in the "shoulder" section, and the average value - in the "butt" section, which is explained by the density of the structure of collagen fibers and pores; as the "belly" has a looser structure, the "shoulder" – the densest, and the "butt "is between them. The highest value of the filtration coefficient is observed with the LASCH cloths, and the smallest – with the BM cloth, which depends on the density of the structure of the considered cloth and the size of their pores. The LASCH cloth is made of polymer threads, while the BM cloth consists mainly of natural wool fibers and, to a lesser extent, of synthetic threads. A critical analysis of the results of an experimental study showed that the filtration capacity of a skin product decreases with an increase in the pressure of the tanning liquid.
Key words: filtration capacity, skin product, moisture-wicking cloth, collagen fibers.

1. INTRODUCTION

Knowing the structure of the skin and its parameters during machining operations makes it possible to correctly design technological devices and machines for skin processing. Namely, when removing excess fluid from chrome-plated leather, due to the non-homogeneous structure, the residual moisture will be non-uniform over its entire area. After liquid treatment, raw hides usually contain up to 80% fluid. To ensure the uniformity of residual moisture in all sections of the hide, it is necessary to maintain a constant pressure on the working bodies during the pressing operation. After pressing, depending on the purpose of the finished leather, the residual moisture in the raw material should be from 45 to 60 percent.

Therefore, based on this, it is necessary to create squeezing devices that allow solving these problems, for example, to develop devices with composite working bodies. Composite working bodies make it possible to copy the non-uniform thickness and surface of chrome-plated leather.

Consequently, approximately equal uniformity of the removed fluid from the entire area of the skin is ensured in a percentage ratio. At that, each composite working body has an elastic coating of cloth, which also makes it possible to significantly compensate for the uniformity of the fluid removed from the chrome-plated skin. All measures aimed at improving the quality of the technological operation of squeezing fluid from chrome-plated skins directly affect the results of subsequent operations. This is especially reflected in the operations of planing and splitting chrome-plated hides. To do this, it is necessary to experimentally investigate the non-homogeneous structure of the hide, and, based on its results, select scientifically based parameters of all technological operations.

The PKF-01 compression-filtration apparatus for determining the clay filtration coefficient is known, made by BIOLIGHT, Russia (ISO 25884) [1]. There is also device MT 166 (ISO 5633-84), for measuring the water resistance of paper made by "Metrotex" - a manufacturer of testing equipment in Russia [2].

During the operation of these devices for filtration, there may be a gradual clogging of the filter elements with mechanical impurities [1, 2]. When these devices are used repeatedly, the characteristics of the test samples will be variable.

One of the factors determining the efficiency of fluid squeezing from wet skin products and increasing the intensity of squeezing is the coefficient of filtration in the skin sections and in LASCH and BM cloths (moisture-wicking materials). To meet the requirements for high quality processing of skin materials, it is necessary to determine the filtration capacity of the skin product in its topographic sections and of the LASCH and BM cloths [3–5]. The cloth of the LASCH and BM brands is used in the tannery for covering the squeezing rollers in the form of stockings and a conveyor belt. The authors have conducted experiments to determine the filtration properties of skin products after chrome tanning and the features of LASCH and BM cloths [6–9].

For a mathematical description of the process of fluid removal from material in roller squeezing machines, the material is considered a two-phase medium consisting of solid particles and a liquid that fills the pores between them. The solid phase of the material (leather, fabric, etc.) consists of fibers. Liquid consists of bound and free water. Bound water has a certain structure. Its molecules are oriented and retained at the surface of fibers with considerable force. A film is formed around the fibers, and it constitutes a unit with solid particles. The thinner the film of bound water, the greater its viscosity. When a load is applied, film water deforms along with the fibers. Therefore, film water can be attributed to a solid skeleton.

Free water filling the pores between the fibers transmits hydrostatic pressure, moves through the pores under the pressure difference, and is filtered.

In the calculation model, the compressibility of the fibers of the material is ignored. The fluid is considered incompressible. The solid phase of the model forms a skeleton, which serves as the basis of the raw skin material. The porosity of the material is a variable value. Water filtration in the accepted design model obeys the Darcy law. In the mathematical description of the processes of compaction of multiphase systems, including two-phase systems, the following concepts should be known:

Rheological equation of state of each phase of the system (liquid, fiber);

The interaction pattern of individual phases;

Change in the ratio of phases per unit volume of the material.

The intensity of the change in the ratio of liquid and solid particles per unit volume depends on the direction of movement of one phase relative to the other. Therefore, for a multiphase medium, there cannot be a single rheological equation of state. The equation of state is a physical law, the upper one for each point of the medium, depending on the geometry of the deformable area. If we assume the existence of a single rheological equation, then it should also reflect the geometry of the compacted area.

The form of the equation of state is determined experimentally under conditions of phase non-interaction. For a two-phase system, two equations of state for each phase of the component reflect the patterns of shape change and volumetric deformation.

In soil mechanics, there is a direction - the theory of volumetric compression with a linearly deformed soil skeleton, where the process of soil consolidation is accompanied by the emergence of interaction forces between two phases of soil (skeleton and pore water) in the form of body forces due to pressures in the pore fluid. The study of multiphase soils is based on the filtration theory of consolidation, created in 1925 by C. Terzaghi and developed by N.M. Gersevanov, V.A. Florin, N.A. Tsitovich and others. According to this theory, the following is assumed in the rheological equations of state: the pore fluid is an ideal gaseous component if it exists. It obeys the Boyle-Mariotte law and Henry's solubility law, the skeleton is instantly deformable and obeys only the compression curve. The compression curve is understood as the relationship between porosity and effective compressive stresses without the possibility of lateral expansion.

According to this theory, the soil phases are considered separate, autonomous systems. It is believed that pore pressure does not cause autonomous systems and any additional deformations in the skeleton. Effective pressure acts in the soil skeleton. The change in the ratio of phases per unit volume is determined by the law of water filtration through the fibrous layer and the conditions for the continuity of the solid and liquid phases. Thus, the filtration theory of consolidation satisfies all three requirements for a two-phase system model.

The filtration of liquid from the skin product into the porous cermet roll depends on the following factors.

The dependences of the quality indicators of chrome-plated leather on the properties of the extracted fluid and the parameters of the porous permeable metal-ceramic roll used are:

a) on the porosity of the skin product;

b) on the thickness of the skin product and its deformability;

c) on the radius of the capillaries of the skin product;

d) on the viscosity of the liquid;

e) on the coefficient of surface tension of the liquid over the skin;

f) on the contact angle of wetting over the skin;

g) on the specific gravity of the removed liquid;

h) on the radius of skin capillaries;

i) on the tortuosity of capillaries in the skin;

j) on the amount of skin deformation in the zone of contact with the roll;

k) on the skin fluid filtration coefficient;

l) on changes in the diameter of the capillaries in the zone of contact with the squeezing roll;
m) on the porosity of the ceramic-metal roll;
n) on the filtration coefficient of the porous metal-ceramic roll;
n) on the radius of the ceramic-metal roll;
o) on the nip angle of the roll during the skin squeezing;
p) on the rate of deformation of the skin product.

The filtration of liquid from the skin product into a moisture-wicking capillary porous fibrous material depends on:
a) the filtration coefficient of the wicking material;
m) the porosity of the moisture-wicking material;
b) the thickness of the moisture-wicking material and its deformability.

Today, environmentally friendly "green leather, fur" has begun to develop in line with environmental concerns, using chromium since the use of heavy metals should be limited and emission standards should be met. Every country has different wastewater regulations. According to the standards adopted in developing countries, emissions of chromium III valence are from 1.5 to 5 mg/l and emissions of chromium VI valence are from 0.1 to 0.5 mg/l on leather. Chrome-plated leather and fur contain a valence III tanning agent that is slightly toxic, so its use is still permitted. However, liquid runoff and solid waste should be handled in accordance with existing laws and regulations [10]. The treatment, storage, and disposal of wastewater and sludge is a major challenge. There are different approaches, such as the improvement of tanning parameters, modification of tanning agents or collagen, and the use of auxiliary agents or combined tanning agents to prevent these technical and environmental problems caused by traditional tanning. Today, the extraction of chromium oxides from the waste of leather production is very relevant. Therefore, it is necessary to switch to waste-free technologies in leather production.

Let us consider some studies devoted to solving the above problems and issues. For example, tanning leads to significant contamination of wastewater with chromium and chlorides. A new method of tanning leather without flotation and with a minimum salt content was developed. Besides, during tanning, the amount of chromium salts is significantly reduced [11].

This leather tanning technology is relevant in terms of reducing wastewater pollution, and protecting the environment.

Further, new promising technologies and methods of leather tanning are considered, which are gradually being introduced into the production standards in the leather industry [12–14].

The authors of [15] synthesized a pre-tanning agent for leather. The agent for initial tanning reacts with collagens and improves the hydrothermal properties of leather.

The authors of [16] synthesized and developed a new material based on collagen fibers with high adsorption of chromium salts as a modifying agent. The resulting material has a high hydrothermal property compared to traditional tanning methods.

In [17], the problems of tanning skins, and the issues related to the disposal of various wastes are considered. A detailed review and analysis of the state of these problems, especially in large enterprises, are presented. Some solutions were proposed to mitigate environmental impact and reduce leather waste.

The study in [18] is devoted to the development of environmentally friendly tannin salt. The results of the study showed high technical and economic efficiency of this development. Thus, the chrome tanning process was developed.

In [19], based on known rheological and mechanical models, an improved rheological model of skin was developed. For the first time, the use of the property of the inert resistance of the skin during its deformation, for example, during mechanical squeezing, was proposed in the model.

However, this rheological model could be applied to finished leather only. Since the physical and mechanical properties of raw hides and finished leathers differ significantly, this model is not suitable for application to raw hides. Therefore, it needs to be improved taking into account the physical and mechanical properties and characteristics of the skin product.

2. MATERIAL AND METHOD OF RESEARCH

The technology of pickling process and chrome tanning of skin samples is used in the leather procurement enterprise “Premium Leather” LLC (Kokand, Uzbekistan). The bovine hides of medium weight harvested in the regions of the Fergana Valley of Uzbekistan were used as raw materials. Pickling is performed in a tanning drum with a float ratio of 0.7–0.8 at a temperature of 18–20°C, the duration of processing is from 4 to 5 hours in the presence of common salt 6–7%, sulfuric acid 1–1.1%. The rawhide is processed for 5–10 minutes in a salt solution, and then sulfuric acid is added. The ratio of sulfuric acid diluted in water is 1:10.

At the end of the process, the acid content is no more than 0.6 g/l, and the salt content is no less than 50 g/l. The pickling of the rawhide in dense sections of the skin should be total (Figure 1).
The advantage of the proposed installation (Figure 1) is the relative ease of operation at relatively low fluid pressure. During the operation of the installation, the characteristics of the tested samples do not change.
The disadvantage of this device is that there is some difficulty in operating the installation at high liquid pressures, due to the significant height of the installation.
The pickling bath is drained and the tanning drum is filled with clean water. At the end of the pickling process, a solution of chromium tanning compounds is poured into the tanning drum, counting as chromium oxide 2.0–2.3% with a basicity grade of 38–42%. 20–30 minutes after adding a solution of chromium tanning compounds or dry tanning agent to the tanning drum, a dichromate solution (1:10) is added.
After 4–6 hours from the start of tanning, the rawhide dyeing is checked. After total dyeing, hyposulfite 2% or sodium sulfate 1.7–2% is added to the tanning drum. At the end of tanning, the “KMI (control and measuring instrument)” test is conducted; shrinkage is not allowed [20].

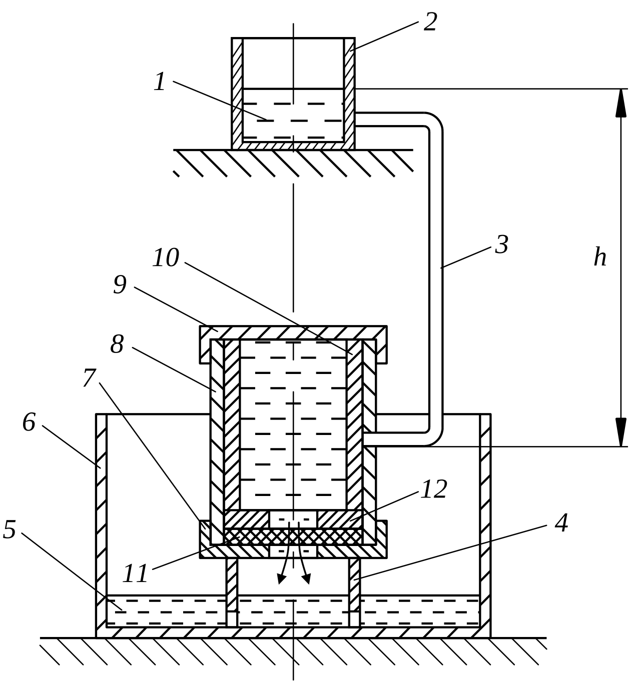

Fig. 1. Scheme of an installation for determining the permeability property of tannin liquid: 1-liquid, 2-vessel, 3-tube, 4-stand, 5-liquid, 6-vessel, 7, 9-lids, 8-cylinder, 10-cup, 11-sample of skin product, 12-washer

After that, samples were taken from the skin products (“shoulder”, “butt”, and “belly” topographic sections) to be used in experiments.
In the experimental study, we used the thickness gauge TR 25-11, with an absolute error of up to 0.01 mm (Russia), laboratory scales XES-1000, with a resolution of 0.01 g (China), liquid pressure gauge ZTP MP-160, 1/2", 0-6 bar (Belarus), stopwatch Integral S-01 with the discreteness of measured time intervals, 0.01 s (Russia) and other special devices.

3. RESULTS

Samples of skin product after chrome tanning were taken for the experiment according to the International Standard ISO 2588-85 (Leather. Sampling, the number of specimens for the total sampling, 2003, Updated on 2019) by formula $n = 0.2\sqrt{x}$, where *x* is the number of samples of the skin product in a batch. 100 pieces were selected, so, *n* =3 [21–25]. The results of the experiment are given in Tables 1, 2, and 3.
In the process of research, we considered the filtration of a liquid of a porous material with a working body. The flow rate of the fluid flowing through the porous material is, equation (1):

$$g = \frac{K_f J}{\Delta h} \Delta P \tag{1}$$

where g is the amount of fluid outflowing per unit area of the porous material, [sm^3]; K_f is the coefficient of fluid filtration in the porous material [m/s], ΔP is the hydraulic pressure of the fluid, [Pa]; J is the initial porosity of the porous material, [sm^3]; Δh is the amount of deformation of the porous material in the contact zone, [sm].

Table 1. Determination of the filtration coefficient of skin samples and cloth at a pressure of tanning liquid of $0.5 \cdot 10^4$ Pa

Type of material	Thickness n, cm	Time t, s	Area S, cm^2	Average consumption of tanning liquid Q, m$^3 \cdot 10^{-6}$	Filtration rate V_f, m/s	Filtration coefficient K_f, m/s $\cdot 10^{-6}$
1. Shoulder	0.2	300	3.14	32.3	3.3	0.22
2. Shoulder	0.2	300	3.14	31.8	3.3	0.22
3. Shoulder	0.2	300	3.14	32.0	3.3	0.22
4. Butt	0.2	300	3.14	39.8	4.2	0.28
5. Butt	0.2	300	3.14	39.0	4.2	0.28
6. Butt	0.2	300	3.14	41.2	4.3	0.29
7. Belly	0.2	300	3.14	50.7	5.2	0.35
8. Belly	0.2	300	3.14	51.0	5.2	0.35
9. Belly	0.2	300	3.14	51.2	5.2	0.35
10. LASCH cloth	0.32	30	3.14	81.2	8.6	9.2
11. BM cloth	0.8	30	3.14	272	28	7.3

Table 2. Determination of the filtration coefficient of skin samples and cloth at a pressure of tanning liquid $1 \cdot 10^4$ Pa

Type of material	Thickness n, cm	Time t, s	Area S, cm^2	Average consumption of tanning liquid Q, m$^3 \cdot 10^{-6}$	Filtration rate V_f, m/s	Filtration coefficient K_f, m/s $\cdot 10^{-6}$
1. Shoulder	0.2	300	3.14	85	9	0.18
2. Shoulder	0.2	300	3.14	85	9	0.18
3. Shoulder	0.2	300	3.14	85	9	0.18
4. Butt	0.2	300	3.14	113	12	0.24
5. Butt	0.2	300	3.14	113	12	0.24
6. Butt	0.2	300	3.14	113	12	0.24
7. Belly	0.2	300	3.14	146	15	0.31
8. Belly	0.2	300	3.14	146	15	0.31
9. Belly	0.2	300	3.14	146	15	0.31
10. LASCH cloth	0.32	30	3.14	395	35	7.71
11. BM cloth	0.8	30	3.14	321	34	6.02

Table 3. Determination of the filtration coefficient of skin samples and cloth at a pressure of tanning liquid $1.5 \cdot 10^4$ Pa

Type of material	Thickness n, cm	Time t, s	Area S, cm^2	Average consumption of tanning liquid Q, m$^3 \cdot 10^{-6}$	Filtration rate V_f, m/s	Filtration coefficient K_f, m/s $\cdot 10^{-6}$
1. Shoulder	0.2	300	3.14	99.1	10.56	0.14
2. Shoulder	0.2	300	3.14	99.0	10,50	0.14
3. Shoulder	0.2	300	3.14	99.0	10.50	0.14
4. Butt	0.2	300	3.14	135.5	14.31	0.19
5. Butt	0.2	300	3.14	135.5	14.31	0.19
6. Butt	0.2	300	3.14	191.5	15.1	0.20
7. Belly	0.2	300	3.14	191.5	20.25	0.27
8. Belly	0.2	300	3.14	191.5	20.25	0.27
9. Belly	0.2	300	3.14	191.5	20.25	0.27
10. LASCH cloth	0.32	30	3.14	424	45.01	6.05
11. BM cloth	0.80	30	3.14	397	42.0	5.04

From the selected samples, according to the main topographical sections, namely, the “shoulder”, “butt” and “belly”, samples 10×10 cm in size were cut out.

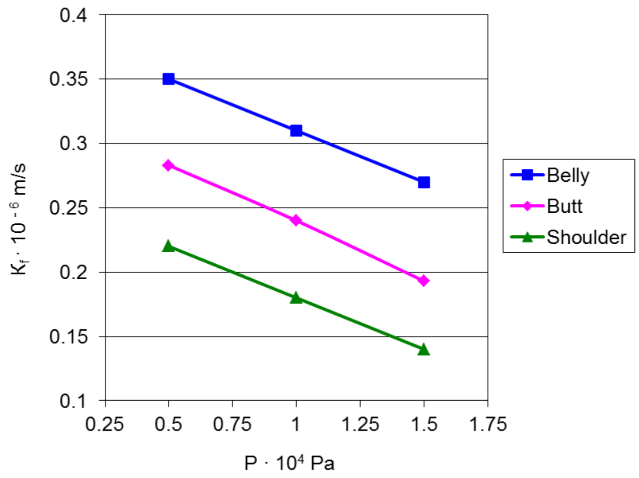

Fig. 2. Dependence of the filtration coefficient (K_f) on the pressure of the tanning liquid *(P)* in the topographic sections of the skin product

The thickness of the skin samples was measured with a TR 25-11 thickness gauge at five points. The tested sample of the skin product was placed in a special installation to determine the permeability property of the tannin liquid.

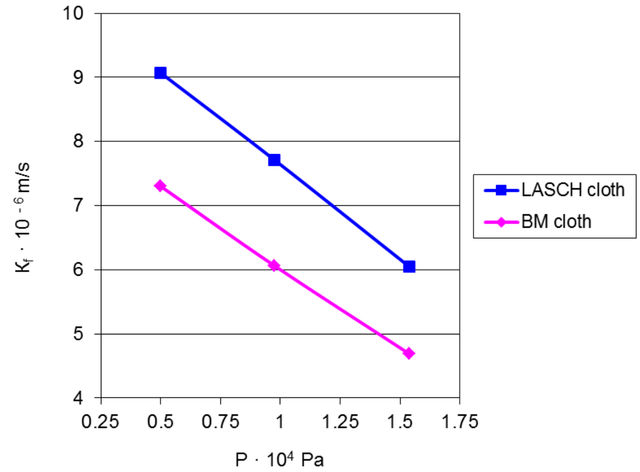

Fig. 3. Dependence of the filtration coefficient (K_f) on the pressure of the tanning liquid (P) through the LASCH cloth and BM cloth (moisture-removing coatings for rollers and conveyor belts)

During the experiment, the tannin liquid was filtered through a sample of semi-finished leather or cloth (moisture-removing material) placed on the cover of the installation [26–29].
From the graph in Figure 2, it can be seen that the filtration capacity of the semi-finished leather product decreases with an increase in the pressure of the tanning liquid. The highest value of the filtration coefficient is observed in the "belly" section, the lowest – in the "shoulder", and the average – in the "butt" section, which is explained by the density of the structure of collagen fibers and pores, which in the "belly" has a looser structure, on the "shoulder" –the densest structure, and in the "butt" in between them.
Thus, based on the results obtained (Tables 1, 2, 3), we recommend the following technological parameters of the squeezing process on a roller machine: working roll of a diameter of 0.2 m, working roll pressure of 0.2 MPa, and porous material feed rate to the processing zone 0.17 m/s. For working shaft coating, BM brand cloth is recommended.

4. CONCLUSION

From the graph in Figure 3, it can be seen that the filtration capacity of the LASCH and BM cloths decreases with an increase in the pressure of the tanning liquid, similar to Fig. 2. The highest value of the filtration coefficient is observed with the LASCH cloth, and the lowest value with the BM cloth, which depends on the density of the structure of the considered cloths and the size of the pores. The LASCH cloth is made of polymer threads, the BM cloth consists of 94% of natural wool fibers and 6% of synthetic yarns.
The results of the research will be used in the design and calculation of the multi-operation technological roller machine the authors are developing now, which will meet the modern requirements put forward by the leather

industry.
Thus, we experimentally determined that, with an increase in fluid pressure, the filtration coefficient of skin samples, namely, in the shoulder section decreases from 0.22 to 0.14 m/s, in the butt section -from 0.28 to 0.20 m/s, in the belly srction – from 0.45 to 0.27 m/s.
The filtration coefficient of cloth samples of the LASCH brand reduces from 9.2 to 6.05 m/s, and of the BM brand - from 7.3 to 5.04 m/s.
The results obtained show (Tables 1, 2, 3, Figures 2, 3) that by increasing the pressure of the liquid, the filtration property of the samples of porous materials under study, decreases.
This means that the filtration properties of leather samples and cloth coatings make it possible to optimize and select the parameters of the technological process and the roller machine for squeezing excess fluid from wet hides [30].

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