COMPARISON AND ASSESSMENT OF SELECTED PARAMETERS OF CHROME-FREE AND CHROME-TANNED LEATHER

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Received: 07.11.2021 Accepted: 21.01.2022 https://doi.org/10.24264/lfj.22.1.1

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ABSTRACT. In the leather tanning industry, decision-makers act resolutely to eliminate chrome as a tanning agent due to its negative effect on human health and the natural environment. Considering this, it makes sense to research opportunities to use chrome-free leather as a substitute for chrome-tanned leather. This paper demonstrates research on the mechanical and hygienic properties of leather tanned with glutaraldehyde as well as chrome-tanned leather, intended for shoe uppers. The results of the tensile strength and percentage extension measurements made by the Instron tensile machine, and the results of water vapour permeability measurements made by a moisture analyser, have been analysed using Statistica. The statistical data analysis has been performed using the following tests: Kolmogorov-Smirnov with Lilliefors correction, Shapiro-Wilk, T, Levene, Brown and Forsythe, Fisher-Snedecor, and Cochran-Cox. Regarding mechanical parameters, no statistically significant difference has been observed between chrome-free and chrome-tanned leather in dry conditions. However, such differences have been observed in wet samples. The tests showed higher stability of mechanical parameters of leather tanned with modified glutaraldehyde compared to chrome-tanned leather. Leather tanned with a chrome tanning agent, tested in both dry and wet conditions, showed significant differences between them, considering their tensile strength and percentage extension. The hygienic properties of both types of leather being researched are more or less similar – the research has not found any statistically significant differences for water vapour permeability.
KEY WORDS: chrome-free leather, chrome-tanned leather, glutaraldehyde, leather quality

COMPARAȚIA ȘI EVALUAREA ANUMITOR PARAMETRI ÎN CAZUL PIEILOR FĂRĂ CROM ȘI TĂBĂCITE ÎN CROM

REZUMAT. În industria de pielărie, factorii decizionali acționează cu hotărâre pentru a elimina cromul ca agent de tăbăcire din cauza efectului său negativ asupra sănătății umane și asupra mediului. Având în vedere acest lucru, este logic să cercetăm oportunități de a înlocui pielea tăbăcită în crom cu piele fără crom. Această lucrare prezintă cercetările privind proprietățile mecanice și igienice ale pielii tăbăcite cu glutaraldehidă precum și ale pielii tăbăcite în crom, destinate fețelor de încălțăminte. S-au analizat cu ajutorul programului Statistica rezultatele măsurătorilor de rezistență la rupere și alungire procentuală efectuate utilizând mașina de tracțiune Instron și rezultatele măsurătorilor de permeabilitate la vapori de apă efectuate cu un analizor de umiditate. Analiza datelor statistice a fost efectuată folosind următoarele teste: Kolmogorov-Smirnov cu corecție Lilliefors, Shapiro-Wilk, test T, Levene, Brown și Forsythe, Fisher-Snedecor și Cochran-Cox. În ceea ce privește parametrii mecanici, nu s-a observat nicio diferență semnificativă din punct de vedere statistic între pielea fără crom și cea tăbăcită în crom în condiții uscate. Cu toate acestea, astfel de diferențe au fost observate în probele umede. Testele au arătat o stabilitate mai mare a parametrilor mecanici ai pielii tăbăcite cu glutaraldehidă modificată comparativ cu pielea tăbăcită în crom. Pieile tăbăcite cu un agent de tăbăcire pe bază de crom, testate atât în condiții uscate, cât și umede, au prezentat diferențe semnificative între ele, în ceea ce privește rezistența la rupere și alungirea procentuală. Proprietățile igienice ale ambelor tipuri de piele cercetate sunt mai mult sau mai puțin similare – nu s-au găsit diferențe semnificative din punct de vedere statistic pentru permeabilitatea la vapori de apă.
CUVINTE CHEIE: piele fără crom, piele tăbăcită în crom, glutaraldehidă, calitatea pielii

COMPARAISON ET ÉVALUATION DE PARAMÈTRES SÉLECTIONNÉS DES CUIRS SANS CHROME ET TANNÉ AU CHROME

RÉSUMÉ. Dans l'industrie du tannage du cuir, les décideurs agissent résolument pour éliminer le chrome comme agent de tannage en raison de son effet négatif sur la santé humaine et l'environnement. Compte tenu de cela, il est logique de rechercher des opportunités d'utiliser du cuir sans chrome comme substitut du cuir tanné au chrome. Cet article présente des recherches sur les propriétés mécaniques et hygiéniques des cuirs tannés au glutaraldéhyde ainsi que des cuirs tannés au chrome, destinés aux tiges pour les chaussures. Les résultats des mesures de résistance à la traction et de pourcentage d'allongement effectuées par la machine de traction Instron, ainsi que les résultats des mesures de perméabilité à la vapeur d'eau effectuées par un analyseur d'humidité, ont été analysés à l'aide du logiciel Statistica. L'analyse statistique des données a été réalisée à l'aide des tests suivants : Kolmogorov-Smirnov avec correction de Lilliefors, Shapiro-Wilk, T, Levene, Brown et Forsythe, Fisher-Snedecor et Cochran-Cox. Concernant les paramètres mécaniques, aucune différence statistiquement significative n'a été observée entre le cuir sans chrome et le cuir tanné au chrome en conditions sèches. Cependant, de telles différences ont été observées dans des échantillons humides. Les tests ont montré une plus grande stabilité des paramètres mécaniques du cuir tanné avec du glutaraldéhyde modifié par rapport au cuir tanné au chrome. Le cuir tanné avec un agent de tannage au chrome, testé dans des conditions sèches et humides, a montré des différences significatives entre eux, compte tenu de leur résistance à la traction et de leur pourcentage d'allongement. Les propriétés hygiéniques des deux types de cuir étudiés sont plus ou moins similaires – la recherche n'a trouvé aucune différence statistiquement significative pour la perméabilité à la vapeur d'eau.
MOTS CLÉS : cuir sans chrome, cuir tanné au chrome, glutaraldéhyde, qualité du cuir

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INTRODUCTION

With the effect of tanning, raw hide is transformed to tanned leather with appropriate mechanical strength and resistance to a number of factors, both biological and physical [1]. The terms which are often present in the literature and presented as opposites, are "*wet-blue leather*", and "*wet-white leather*", which are related to the type of tanning agent used. Both terms refer to leather at an intermediate stage of manufacturing, in a wet condition, yet the former indicates chrome-tanned leather. In contrast, the latter refers to leather tanned by using, for example, zirconium or aluminum salts, modified aldehydes, glutaraldehydes, or syntans [2], i.e., using no chrome. Despite the high popularity of the chrome tanning method, which allows the production of soft and light leather with high thermal resistance and high antimicrobial resistance [1], it is being criticised more frequently. This stems from the fact that chrome has an undesirable effect on the human body as well as the fact that once the tanning process is completed, certain amounts of such element infiltrate into wastewater and therefore into the environment, often at a concentration exceeding permissible limits, which was confirmed, among others, by Asfaw *et al*. [3] or Omm-e-Hany *et al*. [4]. Research is currently underway for the recovery of Cr (VI) from tannery sludge and chrome-tanned leather shavings [5].

Basic chromium sulfate is currently the most popular tanning agent used in leather manufacturing [6, 7]. During chrome tanning, the once trivalent chrome salt - Cr (III), is introduced into the hide, and a cross-linking reaction between collagen and such a tanning agent is induced [1]. Chrome at the sixth oxidation number - Cr (VI), is believed to be highly dangerous; however, it is not used for tanning. However, in some hide processing phases, under favourable conditions (such as elevated pH during neutralisation of wet-blue leather, and the use of fatliquoring agents comprising non-saturated fat acids), it may happen that Cr (III) is oxidated to Cr (VI) [6]. The presence of Cr (VI) in leather has been confirmed in many studies [8-10], as well as the data of the Rapid Alert System for Dangerous Non-Food Products [11].

Employees in the leather tanning industry are professionally exposed to chrome, mostly by skin exposure, due to which they may suffer from chrome eczema. Chrome is also believed to be a strong allergen. Prolonged contact with this element may be a cause septum perforation or even loss of smell or taste. Its harmful effect on the respiratory system can cause bronchitis and an asthma attack [12]. Chrome compounds are also believed to be carcinogenic, mutagenic, embryotoxic, and teratogenic. Chrome (VI) is believed to be a procarcinogen that easily passes through and distributes throughout the organism as it may penetrate biological membranes without much difficulty. The processes related to a reduction of Cr (VI) to Cr (III), occurring in a cell, are connected to the activation of carcinogenic properties of chrome as they increase the probability that Cr (III) will act upon DNA [13]. If such reduction occurs outside a cell (or even outside a cell nucleus), the genetic activity of Cr (VI) is less [12]. Chrome, mostly hexavalent, is very hazardous to pregnant women. It rapidly penetrates the placenta to the fetus, where it accumulates, and in consequence, causes developmental defects (e.g., cleft palate, bone lesions) [13]. The issue of the harmful effect of chrome on the natural environment has also been addressed in many papers. Shanker *et al*. [14], Oliveira [15], Bhalerao, and Sharma [16] indicate, among others, the harmful effects of this element on plant seeds sprouting, their enzymatic activity and photosynthesis, and the presence of chrome is attributed to lower yields.

An example of chrome-free tanning is tanning with glutaraldehyde. It reacts with amine groups of collagens, establishing cross-link bridges. Furthermore, products of the polymerisation of glutaraldehyde, demonstrating high molecular mass, settle in the hide. Such products originate from spontaneous aldehyde polymerisation in solutions. By using this compound for tanning, one can produce leather featuring a higher sweat and alkali resistance. Such leather also feels soft, demonstrates higher fullness, and an evenly distributed shade is possible during the coloring process [17]. Leather tanned without using chrome, treated, among others, with agents such as glutaraldehyde and vegetable tanning agents, is suggested by Plavan and Gaido [18] to be used for prosthetic purposes. The researchers demonstrated that such leather manifests appropriate stability and that using glutaraldehyde has a positive effect on such leather's resistance to ageing. Due to human health protection and restriction of harmful chrome effects on the natural environment, the opportunities to substitute wet-blue leather with wet-white leather are being researched by many other scientists. The research on manufacturing technology and properties of chrome-free leather, defined as ecological substitutes for chrome-tanned leather, was presented in papers: Crudu *et al*. [19], Bacardi *et al*. [20], Raha *et al*. [21], Rosu *et al*. [22], Shi *et al*. [23].

The purpose of this paper is to compare selected mechanical and hygienic properties of chrome-free and chrome-tanned leather intended for shoe uppers. During experiments, tensile strength and percentage extension, as well as the water vapour permeability of bovine hide, which are important parameters to grain leather intended for shoe uppers, were determined.

MATERIALS AND METHODS

Tanned Leathers Used for Research

The research on mechanical and hygienic properties was performed for two types of soft, aniline-finished bovine leather intended for shoe uppers, that is:

- chrome-free ("*wet-white*") leather – tanned with modified glutaraldehyde. The average sample thickness was 1.6 ± 0.03 mm,
- chrome-tanned ("*wet-blue*") leather – tanned with trivalent chrome salt - Cr (III). The average sample thickness was 1.56 ± 0.03 mm.

The research samples were cut out of butt sections of chrome-free leather and chrome-tanned leather, respectively. The assessment of the mechanical properties was performed on both dry and wet leather, while the assessment of hygienic properties was performed only on dry leather. Dry samples included leather conditioned in an atmosphere with a relative ambient humidity of 50% (± 5.0%) and an air temperature of 23ºC (± 2.0ºC). Wet samples were obtained by placing dry samples in water at an ambient temperature (temperature not monitored continuously, approx. 22-25ºC) for 24h. Directly before the test, the samples were put on a paper towel to remove excess water. The reason for performing two research variants, i.e., using dry and wet samples, is that leather moisture content significantly affects its mechanical parameters [24]. Water present in spaces between fibers relaxes the leather structure, therefore decreasing mutual attraction and friction between collagen fibrils [25], consequently affecting leather resistance and stretching.

Research Methods for Mechanical Properties

The basis for the preparation of laboratory samples for tensile strength and percentage extension tests was the ISO 3376:2011 Standard [26]. According to the mentioned standard, it was assumed that the sample size for soft leather, i.e., a length of an oar-shaped sample, was 110 mm, and the width of the tested section (subjected to tensile forces) was 10 mm. Mechanical properties tests were performed on both dry and wet samples. Before testing, dry samples were conditioned in an atmosphere with a relative ambient humidity of 50% (± 5.0%) and an air temperature of 23°C (± 2.0°C), according to the guidelines of the ISO 2419:2012 Standard [27].

For the purpose of statistical analysis, the number of samples was increased, compared to the ISO 3376:2011 Standard [26] recommendation. The following was used for research:

- 12 dry samples acquired from chrome-free leather (6 parallel and 6 perpendicular to the backbone),
- 12 wet samples acquired from chrome-free leather (6 parallel and 6 perpendicular to the backbone),
- 12 dry samples acquired from chrome-tanned leather (6 parallel and 6 perpendicular to the backbone),
- 12 wet samples acquired from chrome-tanned leather (6 parallel and 6 perpendicular to the backbone).

Mechanical properties tests were performed by the Instron 5544 Testing Machine, in accordance with the ISO 3376:2011 Standard [26] guidelines. Once a sample was clamped, it was subject to tensile stress at a velocity of 100 ± 20 mm/min until rupture. Based on measurement data, the tensile strength in megapascals and the percentage extension of the tested section was calculated.

Research Methods for Hygienic Properties

In order to test the hygienic properties of the material being researched, 6 circle-shaped samples with a diameter of 54 ± 2 mm were cut out of both chrome-free and chrome-tanned leather. Water vapour permeability measurements were performed by a testing set shown in Fig. 1, composed of a sampler and the MAC 50 Moisture Analyser. The moisture analyser, being a measurement device, comprises of the following: scales with a 1 mg accuracy, a drying chamber fitted with a halogen system, a temperature sensor, and processing systems with a digital display [28].

Figure 1. Water vapour permeability testing set for tanned leather: 1 – sampler, 2 – moisture analyser

Before testing, samples were conditioned in an atmosphere with a relative ambient humidity of 50% (± 5.0%) and an air temperature of 23ºC (± 2.0ºC). Such parameters were established since, in accordance with the recommendations of the equipment manufacturer, the relative humidity of the space where the test is being performed should be within 40% to 60%, and the temperature should be within 21ºC to 26ºC. After conditioning, a sample was placed in the sampler, with the flesh side facing the water. The measurements were performed at 40ºC for 1h. During a testing cycle, the equipment recorded the water mass that infiltrated through the leather sample tested. Its evaporation was caused by the generation and rise of water vapour pressure, initiated by a rise in water temperature inside the sampler [28].

Statistical Data Analysis

The statistical analysis was performed using *Statistica 13*. As the measurement results were analysed, the following hypotheses were initially verified:

- a hypothesis concerning the conformity of empirical distributions with a normal distribution, checked by the Kolmogorov-Smirnov test with Lilliefors correction, and the Shapiro-Wilk test,
- a hypothesis concerning the homogeneity of variance, checked by the T-test, the Levene test and the Browne and Forsythe test.

At the next stage, there was an attempt to verify a substantive hypothesis concerning the variation of levels of selected parameters, depending on the tanning agent used. Such verification was performed by a one-way analysis of variance using the Fisher-Snedecor test. Statistical inference was drawn at the significance level $\alpha = 0.05$. In the case it was necessary to reject the hypothesis of the homogeneity of variance, a test with independent variance estimation was applied. Individual variance assessments in the groups being researched established a basis for the use of the Cochran-Cox test.

RESULTS AND DISCUSSION

Comparison of the Mechanical Properties of Leather

Mechanical properties are among the essential values that are often verified during the evaluation of the quality and suitability of leathers for various types of use. Moreover, particularly in the case of leather intended for shoe uppers (although not exclusively), the stability of parameters of tanned leather is important, notwithstanding ambient conditions. Excessive stretching, as well as too low susceptibility to tensile force, are not desired in such tanned products. Fig. 2 shows a testing diagram for mechanical properties of both chrome-free and chrome-tanned leather that, aimed to:

I – determine the possible effects of a tanning agent on indicated properties,

II – verify the stability of these properties depending on variances of the water content in the material.

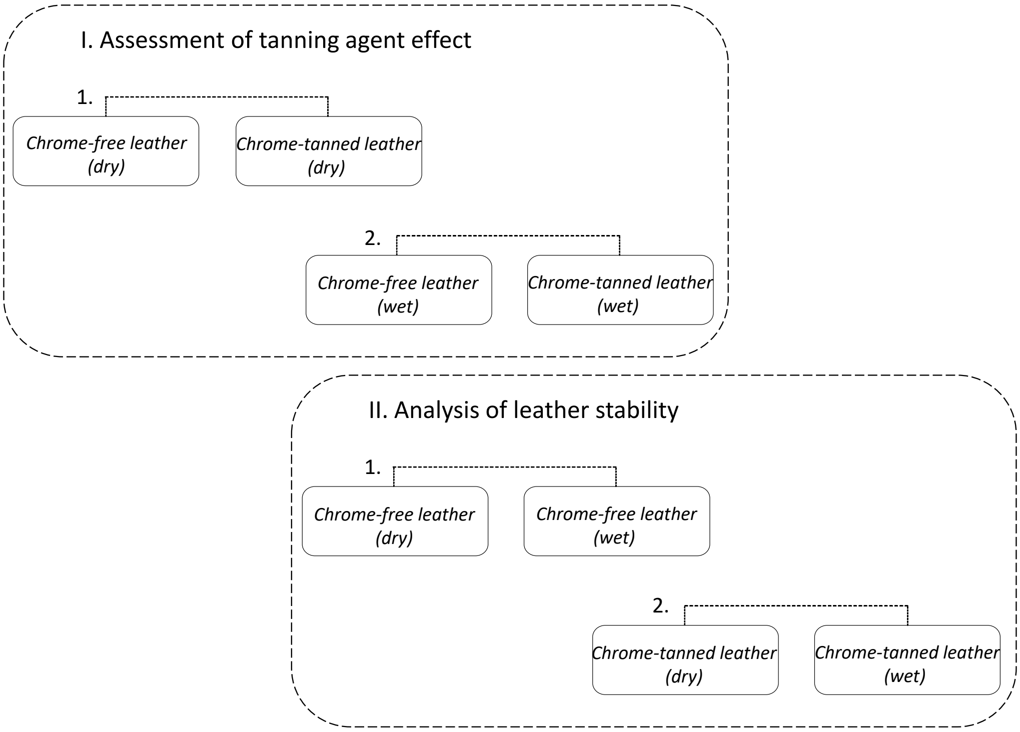

Figure 2. A testing diagram for mechanical parameters for chrome-free and chrome-tanned leather in both wet and dry conditions

Assessment of the Effects of Tanning Agents

1. Preliminary Analysis

The values of mechanical parameters, i.e., tensile strength and percentage extension obtained for samples of dry leather - both chrome-free and chrome-tanned, are shown in Tables 1 and 2, respectively. The results are collated with the appropriate division of samples parallel to the backbone and those which are perpendicular.

As shown in Table 1, the dry chrome-free leather samples cut out in parallel to the backbone have demonstrated a higher mean tensile strength and a lower mean percentage extension compared to the samples cut out perpendicularly to the backbone. In the case of results for dry chrome-tanned leather (Table 2), one can observe varied sample susceptibility to tensile forces, depending on orientation to the backbone. Also, in this case, the samples cut out along the backbone may be attributed with higher mean tensile strength and lower mean percentage extension.

Table 1: Mechanical parameter values for chrome-free leather (dry)

Bovine chrome-free leather (dry)			
Sample	Thickness, mm	Tensile strength, MPa	Extension, %
Parallel to the backbone			
1	1.61	18.59	45.66
2	1.57	18.49	61.66
3	1.58	17.71	66.00
4	1.60	16.89	51.34
5	1.63	15.49	53.00
6	1.69	15.57	40.66
$\bar{x}$ [a/]	1.61	17.12	53.05
s_d [b/]	0.04	1.26	8.69
Perpendicular to the backbone			
1	1.66	17.63	67.00
2	1.70	13.39	63.34
3	1.67	14.15	55.34
4	1.59	13.48	64.66
5	1.60	12.90	57.34
6	1.62	15.67	64.00
$\bar{x}$ [a/]	1.64	14.54	61.95
s_d [b/]	0.04	1.64	4.16

[a/]arithmetic average, [b/]standard deviation

Table 2: Mechanical parameter values for chrome-tanned leather (dry)

Bovine chrome-tanned leather (dry)			
Sample	Thickness, mm	Tensile strength, MPa	Extension, %
Parallel to the backbone			
1	1.58	18.63	47.34
2	1.59	18.09	48.34
3	1.56	16.60	55.34
4	1.58	18.60	48.66
5	1.57	19.00	51.66
6	1.54	15.92	50.34
$\bar{x}$ [a/]	1.57	17.81	50.28
s_d [b/]	0.02	1.14	1.81
Perpendicular to the backbone			
1	1.50	16.26	65.34
2	1.52	13.18	64.34
3	1.53	16.91	63.00
4	1.48	13.13	66.00
5	1.53	13.63	69.00
6	1.51	16.09	61.34
$\bar{x}$ [a/]	1.51	14.87	64.84
s_d [b/]	0.02	1.58	2.41

[a/]arithmetic average, [b/]standard deviation

The results obtained in the tests for chrome-free and chrome-tanned leather, confirm a relationship already described upon in the relevant literature [25, 29]. In the case of both types of leather subjected to testing, there is a variation of mechanical properties in relation to the orientation (to the backbone) of samples, despite the fact that leather is a complicated spatial structure with its mechanical properties affected by many factors [30]. Furthermore, based on the preliminary analysis of the obtained parameter values, it was established that there are relatively few differences between the dry samples of chrome-free and chrome-tanned leather tested in relation to the mean tensile strength and percentage extension.

The values of tensile strength and percentage extension obtained for samples of wet leather, both chrome-free and chrome-tanned, are shown in Tables 3 and 4, respectively. The results are collated with the appropriate division of samples parallel to the backbone and those which are perpendicular.

The results of measurements performed on wet chrome-free leather samples also indicate a variety of tensile strength parameter values depending on the orientation of the samples in relation to the backbone (Table 3). In this case, the observed difference between the mean results for samples cut out along the backbone and across the backbone was less in comparison to dry chrome-free leather, particularly in reference to percentage extension (Tables 1 and 3).

Table 3: Mechanical parameter values for chrome-free leather (wet)

Bovine chrome-free leather (wet)			
Sample	Thickness, mm	Tensile strength, MPa	Extension, %
Parallel to the backbone			
1	1.67	16.39	47.66
2	1.73	15.74	57.34
3	1.75	17.09	60.00
4	1.70	16.92	56.34
5	1.68	15.71	48.34
6	1.78	16.02	58.34
$\bar{x}$ a/	1.72	16.31	54.67
s_d b/	0.04	0.54	4.85
Perpendicular to the backbone			
1	1.62	13.55	58.66
2	1.75	14.30	52.34
3	1.80	14.37	59.34
4	1.70	13.59	63.34
5	1.63	14.28	57.66
6	1.71	13.69	54.00
$\bar{x}$ a/	1.70	13.96	57.56
s_d b/	0.06	0.36	3.60

a/arithmetic average, b/standard deviation

Little variation in the values of mechanical properties can also be observed in wet chrome-tanned leather cut out in two different directions (Table 4). Also, in the case of these leather samples, the differences in tensile strength and percentage extension between the samples cut out in parallel and those cut out perpendicularly to the backbone are less when compared to dry leather (Table 2). Furthermore, test results obtained for wet leather – a higher tensile strength and a lower percentage extension in samples taken along the backbone – comply with previous findings presented in the literature [25, 29]. Based on the preliminary analysis of parameter values, it was established that the results for samples of wet chrome-free and chrome-tanned leather indicate a higher difference in mean tensile strength and mean percentage extension between these samples when compared to dry leather samples.

Table 4: Mechanical parameter values for chrome-tanned leather (wet)

Bovine chrome-tanned leather (wet)			
Sample	Thickness, mm	Tensile strength, MPa	Extension, %
Parallel to the backbone			
1	1.53	16.61	69.34
2	1.53	19.88	54.00
3	1.49	17.43	57.66
4	1.50	19.36	60.66
5	1.64	19.81	90.00
6	1.54	18.90	60.71
$\bar{x}^{a/}$	1.54	18.67	65.38
$s_d^{b/}$	0.05	1.23	11.94
Perpendicular to the backbone			
1	1.68	18.55	61.66
2	1.57	16.52	72.66
3	1.64	17.29	64.00
4	1.54	17.69	69.34
5	1.57	17.37	72.34
6	1.63	16.63	64.66
$\bar{x}^{a/}$	1.61	17.34	67.44
$s_d^{b/}$	0.05	0.68	4.24

$^{a/}$arithmetic average, $^{b/}$standard deviation

According to the Polish Standard P-22225 [31], tensile strength for soft, tanned grain leather intended for shoe uppers should not be less than 13 MPa, and its maximum percentage extension should fall within 30% ÷ 90%. The results obtained for the chrome-free and chrome-tanned leathers tested, both dry and wet samples, demonstrate that these samples comply with the requirements of the indicated Standard [31]. The samples being analysed also conform to qualitative requirements recommended for natural leather for shoe uppers by the Instytut Przemysłu Skórzanego in Łódź. According to this research unit, the tensile strength for leather of such purpose should be no less than 12 MPa, while its maximum percentage extension should be no less than 40% [32].

2. Statistical Analysis

The data provided in Tables 1-4 were a basis for the analysis aiming to confirm or exclude statistically significant differences between the values of mechanical properties for leather tanned with modified glutaraldehyde (i.e., chrome-free) and chrome-tanned leather. The first stage included a comparison of values of tensile strength and percentage extension in dry leather samples. The analysis of data acquired for dry leather tanned with modified glutaraldehyde and dry chrome-tanned leather demonstrated that the empirical distribution of values of mechanical parameters is a distribution close to normal (with $p > \alpha$ where $\alpha = 0.05$). The results are shown in Table 5.

Table 5: Test results for the hypothesis concerning the normal distribution of the values of mechanical parameters for dry chrome-free and chrome-tanned leather

Dry leather	Tensile strength			Extension		
	Test statistic					
	Kolmogorov-Smirnov	Lilliefors	Shapiro-Wilk	Kolmogorov-Smirnov	Lilliefors	Shapiro-Wilk
chrome-free	d = 0.145 p > 0.20	p > 0.20	W = 0.922 p = 0.30	d = 0.188 p > 0.20	p > 0.20	W = 0.913 p = 0.23

Dry leather	Tensile strength			Extension		
	Test statistic					
	Kolmogorov-Smirnov	Lilliefors	Shapiro-Wilk	Kolmogorov-Smirnov	Lilliefors	Shapiro-Wilk
chrome-tanned	d = 0.172 p > 0.20	p > 0.20	W = 0.899 p = 0.16	d = 0.185 p > 0.20	p > 0.20	W = 0.883 p = 0.10

In reference to the dry leather samples tested, the next step included the verification of the homogeneity of variance and the determination of the level of mechanical parameters variation, dependent on the type of tanning agent used. Based on the values and probability levels for the following tests: T, Levene, and Browne and Forsythe (Table 6), it was established that the hypothesis on the homogeneity of variance could not be rejected.

The results of a one-way analysis of variance using the Fisher-Snedecor test (F = 1.067 with p = 0.916 for tensile strength, and F = 1.114 with p = 0.861 for percentage extension) confirm that the tanning method did not significantly affect the mechanical parameters of the dry leathers tested. Tensile strength and percentage extension values for both types of leather tested do not indicate any significant differences between them. Similar conclusions were also provided by Chakraborty *et al*. [33].

Table 6: Test results for the hypothesis concerning the homogeneity of variance for dry chrome-free and chrome-tanned leather (mechanical parameters)

Dry leather	Tensile strength			Extension		
	Test statistic					
	T	Leven (1, df)	Brown and Forsyth (1, df)	T	Leven (1, df)	Brown and Forsyth (1, df)
chrome-free and chrome-tanned	-0,599 p = 0.555	0.016 p = 0.900	0.004 p = 0.947	-0,017 p = 0.986	0.051 p = 0.824	0.043 p = 0.838

In the next stage, the comparison concerned the results obtained for wet leather – both chrome-free and chrome-tanned. It was established whether there are statistically significant differences between the values of mechanical parameters for both types of leather. The analysis showed that the empirical distribution of values of mechanical parameters obtained for wet leather is a distribution close to normal (with $p > \alpha$ where $\alpha = 0.05$). The results are shown in Table 7.

Table 7: Test results for the hypothesis concerning the normal distribution of the values of mechanical parameters for wet chrome-free and chrome-tanned leather

Wet leather	Tensile strength			Extension		
	Test statistic					
	Kolmogorov-Smirnov	Lilliefors	Shapiro-Wilk	Kolmogorov-Smirnov	Lilliefors	Shapiro-Wilk
chrome-free	d = 0.20 p > 0.20	p < 0.15	W = 0.894 p = 0.13	d = 0.186 p > 0.20	p > 0.20	W = 0.928 p = 0.36
chrome-tanned	d = 0.183 p > 0.20	p > 0.20	W = 0.897 p = 0.15	d = 0.170 p > 0.20	p > 0.20	W = 0.894 p = 0.13

In reference to the wet leather tested (both chrome-free and chrome-tanned), the homogeneity of variance was verified as well (using the T-test, the Levene test, and the Browne and Forsythe test). In this case, the results obtained (Table 8) indicated that the homogeneity of variance hypothesis should be rejected.

Table 8: Test results for the hypothesis concerning the homogeneity of variance for wet chrome-free and chrome-tanned leather (mechanical properties)

Wet leather	Tensile strength			Extension		
	Test statistic					
	T	Leven (1, df)	Brown and Forsyth (1, df)	T	Leven (1, df)	Brown and Forsyth (1, df)
chrome-free and chrome-tanned	-5,476 p = 0.000	0,206 p = 0.654	0,299 p = 0.590	-3.391 p = 0.002	2.898 p = 0.103	2.159 p = 0.156

Due to the need to reject the homogeneity of variance hypothesis, analysis with an independent variance estimation was performed using the Cochran-Cox test. The value of this statistic was -5.476, with a probability level of p = 0.00002 for tensile strength and -3.391, with a probability level of p = 0.0026 for percentage extension. Based on the results obtained, it was established that there are statistically significant differences between the values of mechanical parameters for wet chrome-free and chrome-tanned leather, while higher values of the analysed parameters, i.e., tensile strength and percentage extension, were found in chrome-tanned leather (cf. Table 3 and Table 4).

Assessment of Leather Stability

Further analyses were performed with the purpose of assessing the material stability by confirming or excluding the occurrence of statistically significant differences between dry and wet leather samples. First, the leather samples tanned with modified glutaraldehyde were taken into consideration. The results related to testing the hypothesis concerning the homogeneity of variance are shown in Table 9.

Table 9: Test results for the hypothesis concerning the homogeneity of variance for dry and wet chrome-free leather (mechanical properties)

Dry and wet leather	Tensile strength			Extension		
	Test statistic					
	T	Leven (1, df)	Brown and Forsyth (1, df)	T	Leven (1, df)	Brown and Forsyth (1, df)
chrome-free	0.998 p = 0.334	2.579 p = 0.123	2.064 p = 0.165	0.495 p = 0.626	4.728 p = 0.041	4.167 p = 0.053

Based on the obtained values of test statistics and corresponding probability levels, the homogeneity of variance hypothesis cannot be rejected. Furthermore, based on the results of the one-way analysis of variance using the Fisher-Snedecor test (F = 2.396 with p = 0.163 for tensile strength and F = 3.258 with p = 0.062 for percentage extension) it was established that, for leather tanned with modified glutaraldehyde, the values of the tested mechanical parameters do not vary significantly regardless of whether it is dry or wet leather.

Following this, a similar comparative analysis was performed for chrome-tanned leather samples, both dry and wet. As in previous cases, this analysis compared the values of tensile strength and percentage extension. Based on the obtained results of the test statistics provided in Table 10, it was established that the homogeneity of variance hypothesis should be rejected. Due to this, an analysis with independent variance estimation was performed using the Cochran-Cox test. The value of this statistic was -2.360, with a probability level of p=0.03 for tensile strength, and -2.478, with a probability level of p=0.022 for percentage extension. Based on the results obtained, it was established that there are statistically significant differences between the values of mechanical parameters for dry and wet chrome-tanned leather. The higher values of the analysed parameters, i.e., tensile strength and percentage extension, were found in wet leather samples (cf. Table 2 and Table 4).

Table 10: Test results for the hypothesis concerning the homogeneity of variance for dry and wet chrome-tanned leather (mechanical properties)

Dry and wet leather	Tensile strength			Extension		
	Test statistic					
	T	Leven (1, df)	Brown and Forsyth (1, df)	T	Leven (1, df)	Brown and Forsyth (1, df)
chrome-tanned	-2.462 p = 0.023	0.053 p = 0.166	2.063 p = 0.165	-2.478 p = 0.021	0.033 p = 0.856	0.093 p = 0.763

Comparison of Hygienic Properties of Leathers

A comparative analysis for chrome-free and chrome-tanned leather was also performed in relation to hygienic properties, important due to the fact that such leather is intended for shoe uppers. The analysis tested the water vapour permeability of leather samples, and then statistical analysis was conducted to estimate whether such parameter values show any significant differences depending on the tanning agent selection.

Comparing the measurement results, as shown in Table 11, one may observe little difference between the mean water vapour permeability value for chrome-free and chrome-tanned leather. Also, in case of this parameter, both leather types conform to qualitative requirements recommended by the Instytut Przemysłu Skórzanego in Łódź. According to these guidelines [32], water vapour permeability for natural shoe uppers leather should be no less than 1.0 mg/cm^{2}h.

Table 11: Measurement results for the water vapour permeability of chrome-free and chrome-tanned leather

Water vapour permeability, mg/cm^2		
Sample	Chrome-free leather	Chrome-tanned leather
1	15.40	15.40
2	15.30	15.60
3	15.20	15.40
4	15.10	15.35
5	15.40	15.50
6	15.50	15.40
$\bar{x}$ a/	15.32	15.44
s_d b/	0.317	0.084

a/arithmetic average, b/standard deviation

Statistical analysis of data acquired for leather tanned with modified glutaraldehyde and chrome-tanned leather demonstrated that the empirical distribution of values of the tested parameter is close to a normal distribution. The results are shown in Table 12.

In reference to the leather samples tested, the next step included verification of the homogeneity of variance and determination of the level of water vapour permeability value variation depending on the tanning agent selected. Based on the values and probability levels for the following tests: T, Levene, and Browne and Forsythe (Table 13), it was established that the hypothesis on the homogeneity of variance could not be rejected.

The result of a one-way analysis of variance using the Fisher-Snedecor test ($F = 2.574$ with $p = 0.323$), in reference to water vapour permeability, indicates that the values of the tested parameter do not show any significant differences between chrome-free and chrome-tanned leather.

Table 12: Test results for the hypothesis concerning the normal distribution of the values of water vapour permeability for chrome-free and chrome-tanned leather

Leather	Water vapour permeability Test statistic		
	Kolmogorov-Smirnov	Lilliefors	Shapiro-Wilk
chrome-free	d = 0.214 p > 0.20	p > 0.20	W = 0.958 p = 0.80
chrome-tanned	d = 0.341 p > 0.20	p < 0.05	W = 0.847 p = 0.15

Table 13: Test results for the hypothesis concerning the homogeneity of variance for chrome-free and chrome-tanned leather (water vapour permeability)

Leather	Water vapour permeability Test statistic		
	T	Leven (1, df)	Brown and Forsyth (1, df)
chrome-free and chrome-tanned	-1.765 p = 0.108	1.582 p = 0.237	1.561 p = 0.240

SUMMARY AND CONCLUSIONS

While the leather manufacturing technology using chrome tanning is fully developed, and the properties of such leather are well known and researched, the research on products tanned with alternative and more environment-friendly tannins is underway. One may point to examples in the literature – Chakraborty *et al*. [33] or Rachmawati and Anggriyani [34], which indicate satisfactory effects in reference to the values of mechanical parameters, i.e., tensile strength and percentage extension, that may be achieved by using modified glutaraldehyde as a tanning agent. Conducting works aiming to obtain leather with parameters close to chrome-tanned leather seems to be necessary and well justified, considering the harmfulness of chrome with respect to its negative influence on human health and the natural environment, thus having life quality improvement in mind.

The research concerning the basic mechanical and hygienic parameters, significant due to the material being fit for use in shoe uppers as well as the final product quality, conducted for chrome-free and chrome-tanned leather as well as their statistical analysis allowed to formulate the following conclusions:

1) Leathers tanned with modified glutaraldehyde and chrome-based tanning agent, tested in a dry condition, do not show significant differences between them, considering their tensile strength and percentage extension.
2) Leathers tanned with modified glutaraldehyde and chrome-based tanning agent, tested in a wet condition, show significant differences between them, considering their tensile strength and percentage extension. Higher values of the mentioned parameters are present in leather tanned with a chrome-based tanning agent.
3) Leathers tanned with modified glutaraldehyde, tested in both dry and wet conditions, do not show significant differences between them, considering their tensile strength and percentage extension. This confirms that such leather is stable under the conditions provided during the experiment.
4) Leathers tanned with a chrome-based tanning agent, tested in both dry and wet conditions, showed significant differences between them, considering their tensile strength and percentage extension. Higher values of the mentioned parameters are present in wet leather. This confirms chrome-tanned leather is less stable in comparison to chrome-free leather.
5) Leathers tanned with modified glutaraldehyde and chrome-based tanning agents do not show significant

differences between them, considering their water vapour permeability, a parameter that demonstrates its hygienic properties.

Funding

This publication was financed from the subsidy granted to the Cracow University of Economics.

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