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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Received: 29.01.2021 Accepted: 16.07.2021 https://doi.org/10.24264/lfj.21.3.2

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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.

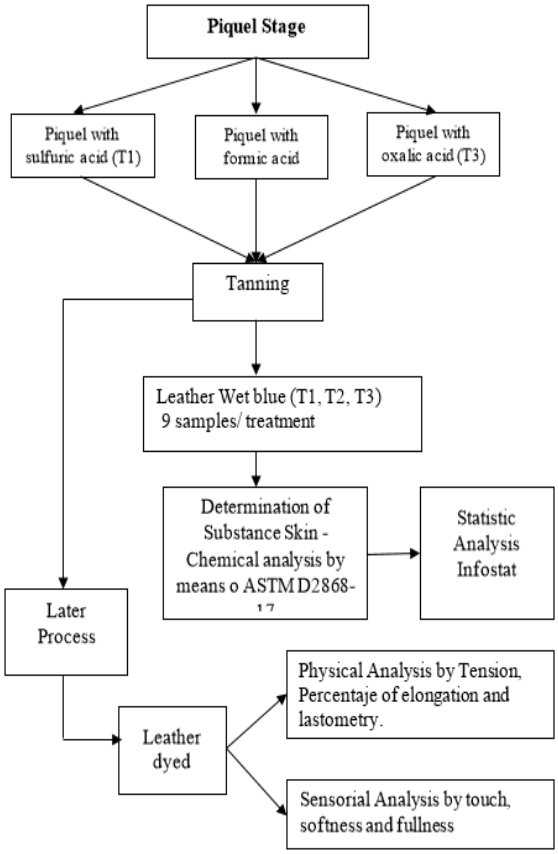

Figure 1. Experimental Design

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.

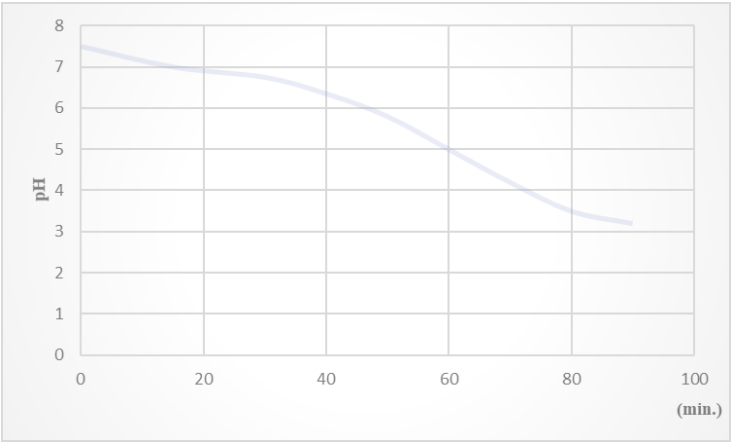

Figure 2. Pickling – Sulfuric Acid Curve (T1)

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.

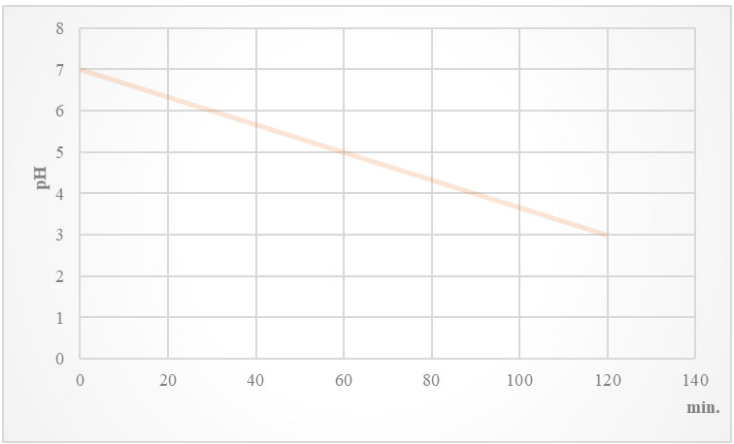

Figure 3. Formic acid pickling curve (T2)

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.

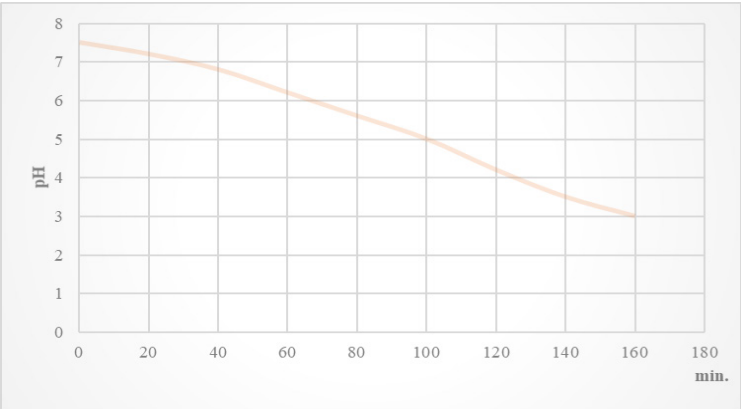

Figure 4. Pickling curve with oxalic acid (T3)

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.

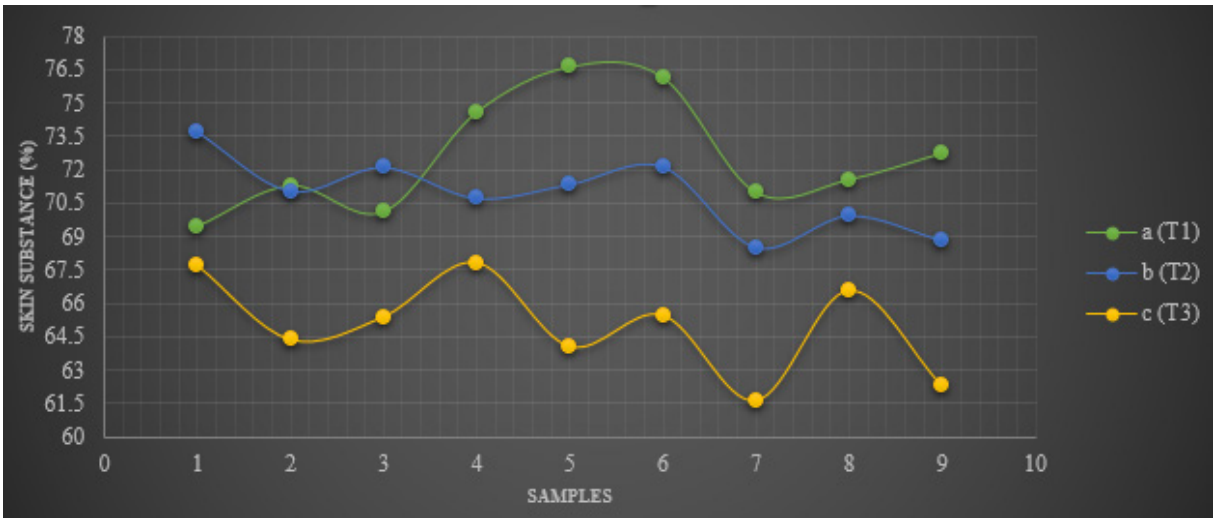

Figure 5. Curves of skin substance for (a) Pickling with sulfuric acid, (b) Pickling with formic acid, and (c) Pickling with oxalic acid

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.

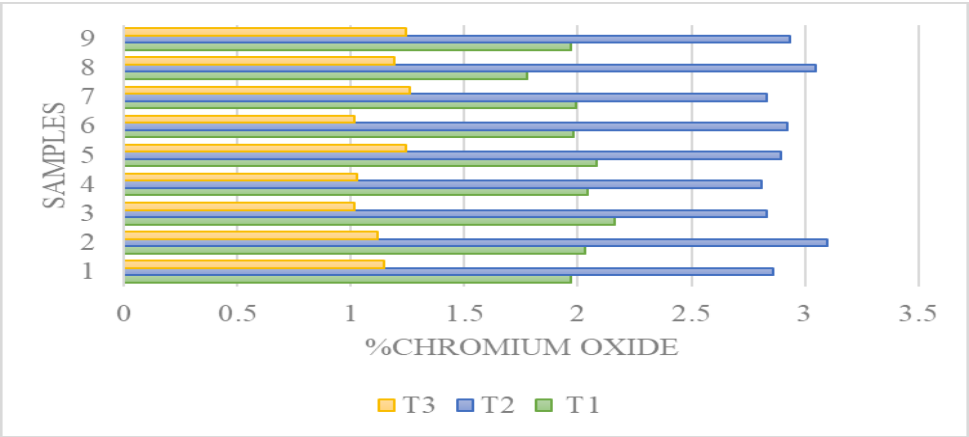

Figure 6. Percentage of Chromium results for each treatment T1, T2 and T3

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

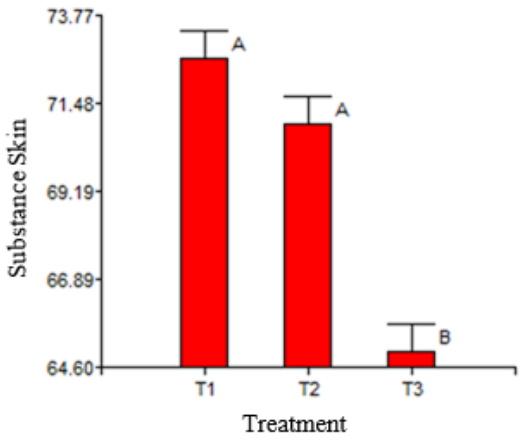

Figure 7. Statistical analysis

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.

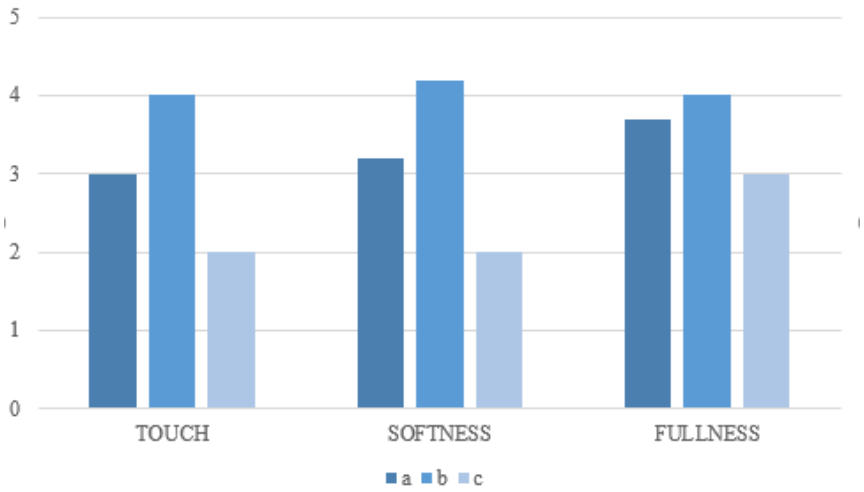

Figure 7. Sensorial analyses of: (a) Sulfuric acid pickling, (b) Formic acid pickling, (c) Oxalic acid pickling

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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