Study of Several Variables in the Fixation Stage of a Vegetable Tannage after Penetration under Ultrasound

by
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Abstract

This study concerns the implementation and improvement of a new system that applies ultrasound technology in vegetable tanning, which is an eco-friendly tanning process. The system is versatile and requires no major modifications or expenses for tanneries. In particular, the study investigates the influence of several variables in the fixation stage of a vegetable tannage after penetration under ultrasound. The results show significant differences in the tanning degree of the leathers tested in relation to the pH of the fixation float and the amount of time that the hides remain in it. It has been demonstrated that this tanning system allows to obtain leathers with a high degree of tannin fixation. The leathers we obtained showed no scratches, which are the main cause for their devaluation when applying the traditional tanning system and were suitable for commercialization as high-end leather goods. Ultrasound technology can increase the use of vegetable tannage versus other less eco-friendly types of tannage.

Introduction

The main goals of leather tanning are (1) to achieve the stabilization of collagen regarding the hydrolytic phenomena caused by water and/or enzymes, and (2) to provide the hide with higher resistance to extreme temperatures.

Different chemicals can be used to tan. The most common one is chromium salt, but due to pressures related to the environment, every day more free-chrome leather articles are increasingly demanded.[1]

Vegetable tanning is considered an eco-friendly tanning process.[2] It is carried out using plant materials. The vegetable extracts are used in the making of leather for shoe soles, saddles, handbags, belts and many other goods with multiple uses. Vegetable extracts contain tannins. These polyphenolic compounds are responsible for the tanning effects. Tannins become fixed on collagen by means of hydrogen bonds within the pH interval of 2 to 8. The -OH groups of tannic molecules form cross-links through hydrogen bonds with the collagens' peptidic groups, the main protein of the hide.

Tannin stabilizes collagen because it contains various reactive groups and a sufficient size to be able to bind several fibers at once. Thus, the amount of cross-links depends on the size of the polyphenolic molecule and the number of -OH groups present. Additionally, both excessively small molecules ($M < 500$) and excessively big molecules ($M > 3000$) will not tan.

In order to tan using vegetable extracts, it is necessary for the hides to be in contact with the extracts for a considerable time. The reason for this is that the vegetable extracts are not simple products; they are composed of organic molecules of different molecular sizes.[3] These molecules tend to be associated, thus the size of the tanning agent (i.e. vegetable extracts) increases and its penetration and fixation in the hide becomes more difficult. The tanning can be done through a static process and thus high quality leathers may be obtained. Traditionally, a long period of time (greater than a month) was necessary for the process to be finished,[4] which was an inconvenience. Nevertheless, later, with the introduction of the drums, most tanners chose to tan dynamically, which increased the speed of penetration of the vegetable extracts in the hides. This was done through the mechanical effect produced by the turning of the drum. To a certain extent, such an effect prevents the joining of the molecules that constitute the vegetable extract,[5] which facilitates its penetration into the hide. Nowadays, tanning using vegetable extracts can be accomplished in less than 24 hours. During the process of drum tanning, the hides are dragged by stakes called pegs, which are attached to the inner walls of the drum. This results in a movement that speeds up the process significantly.

However, this process presents a shortcoming. Sometimes, the hides are damaged when they hit against the pegs. When this occurs, the leathers show scratches and their commercial value decreases (Figure 1).

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Figure 1. Damaged hide.

In fact, flaws resulting from the damaging of the surface of the leather during the process of manufacturing are the cause of an 80% devaluation of the final product. In order to prevent this, part of the tanning can be carried out immersing the hides in tanks called pits, which are filled with vegetable extract solutions. The inconvenient of this method, as already mentioned, is that the process takes too long, which in turn increases the price of the final product.

Sound waves with a frequency above the human audible range of 16 kHz are called ultrasound. Ultrasound may be broadly classified as power ultrasound and diagnostic ultrasound. Power ultrasound, with a frequency range of 20-100 kHz, is commonly used to enhance physical processes and to accelerate chemical reactions.

The application of ultrasound in the tanning operations has been investigated for many years. The first documented experiments were published in 1950.[6] In the following decades, several researchers studied the application of ultrasound in different processes related to tanning process.[7] Technological problems prevented their application in industrial practice. However, the materials and technology used in the manufacture of ultrasound equipment have significantly improved over time. For this reason, in recent years, several research groups have become interested in the possibilities offered by this technology and the feasibility of its application in the leather field. The effect of ultrasound on the skin structure[8] and on several operations that make up the tanning process has been studied: soaking,[9] unhairing,[10] degreasing,[11] chrome tanning,[12] titanium salts tanning,[13] retanning,[14] dyeing,[15] fatliquoring[16] and mink fur processing.[17] The effectiveness of ultrasound use in the manufacture of different vegetable extracts,[18] dyes[19] and oils[20] for tanning, in the detection of looseness in bovine hides,[21] in the prediction of leather mechanical properties,[22] in Cr and Pb determination in leather,[23] in the enzymatic hydrolysis of leather waste[24] and in the treatment of residual floats[25] and solid wastes[26] from tanning process has been tested.

In a previous paper[27] our team studied the influence of several variables in the penetration stage of a vegetable tannage using ultrasound. The results obtained demonstrated that the parameters studied could be regulated in order to obtain the adequate penetration of tannins into the leather according to the desired features for the final product. Furthermore, the tannage was achieved in a shorter time and high-quality leathers were obtained. This reinforced the idea that the use of ultrasound in vegetable tanning was technically feasible in industrial practice.

The products of the aforementioned testing system satisfied almost all market demands. However, it did not permit the production of those leather goods that required the absorption and fixation of high amounts of tannins, such as leather soles. This was logically due to the fact that vegetable extract tanning consists of two equally important stages. In addition to optimizing penetration, which was the focus of the previous research, the tannins have to be fixated as much as possible to the hide.[28,29] This is generally achieved by warming up the tannic float and decreasing its pH. Thus, the quantity of vegetable extract required is optimized from both the environmental point of view (less tannins in the residual float) and the economical (the greater the fixation, the less vegetable is needed). The present study focuses on the analysis of the influence on fixation of the two most important variables in this stage: the pH of the float and the amount of time for the hide to remain in the float. Such findings would allow to obtain leather with a high level of tannin fixation and thus to satisfy the whole market demand. Properties studied include the tanning degree of the hides and their resistance to grain cracking. The organoleptic properties of the leathers obtained have also been analyzed.

Experimental

Materials and Chemicals

Tests were performed with split (5.5 mm) and pre-tanned bovine hide.

The following vegetable extracts were used for tanning:

Quebracho extract: Ato Unitan. Richness: 72% of tannins. pH (6.9 ºBé) = 4.3-4.8

Mimosa extract: Clarotan. Richness: 68% of tannins. pH (6.9 ºBé) = 4.0-4.5

Other chemicals used in the operations before and after tanning were chemicals of common use in the tanning industry.

Equipment

The tests were carried out using two pieces of ultrasound tubular equipment composed of a generator, a transmitter and a stainless steel cylindrical casing. The generator can deliver a maximum power up to 1500w that can be regulated. It can emit four different power levels corresponding to 100%, 85%, 75% and 60% of maximum power, and is Telsonic brand.

A modified high-density polyethylene (HDPE) was used as a tanning pit, capacity: $1m^3$.

A submersible water pump (approximate flow: 40L/min), an electric stirrer, an electrical resistance, a pH sensor and a temperature sensor were also used.

Methods

Studied Parameters

Experiments were performed to find out the influence of certain parameters in different properties of the obtained leather. The parameters and the different intervals of each parameter tested were as follows: pH of the fixation float (3 to 5) and amount of time of hides in the float (12 to 72 hours).

Sample Preparation

We started off with salted bovine hides. The following operations were carried out: soaking, unhairing, liming, fleshing, splitting, deliming, bating, and pickling. Finally, a pre-tanning was performed with 0.7% glutaric dialdehyde and 6% synthetic phenol, added after two hours in the same float.

The tanning floats were prepared in the pit 24 hours before each tanning to get the correct solution of vegetable extracts in water. It is necessary to control the concentration of tannin so that it reacts uniformly through the cross section of the hide.[30] To prepare each float 140kg of mimosa and 140kg of quebracho were added to 420L of water. The electric stirrer rotated until a complete dissolution was reached (6 hours). Finally, the density of the resulting tanning float (19°Bé approx.) was controlled.

Penetration Stage

To perform the penetration stage of the tanning process, the pumps were submerged in the tanning float that was inside the HDPE pit. The pumps sucked up the float through two hoses to the cylindrical casings containing the ultrasound transmitters. The float would then return to the pit after being subjected to the action of ultrasound. Ultrasound worked for 7 hours and remained standing for 17 hours. This operation was repeated the next two days. The two generators worked at a power of 1500w each. Ultrasound is acting throughout the process only on a part of the float. The ultrasonic power applied to this part of the float is higher, but it is applied discontinuously. Figure 2 shows a diagram of this work system. The leathers obtained presented a tanning degree of 54.

Fixation Stage

Once the penetration stage had finished, the ultrasound equipment was removed and an electric resistance was introduced in the tanning float (Figure 3), together with a pH sensor and a temperature sensor.

A temperature of 38°C was maintained throughout the fixation stage. Such temperature is widely used in the industry to obtain a good degree of fixation without damaging the leather. In vegetable tanning, temperatures under 40°C are always used to prevent the hides from suffering hydrothermal damage.

A second-order centralized, orthogonal and rotatable experimental design was chosen in order to carry out the experimentation. Table I shows the twelve experiments required by this experimental design. The first four experiments investigate the linear and interactive effects of the variables. Experiments 5 to 8 study the quadratic effects and experiments 9 to 12 are replicates and give a measure of experimental error, which is important of measuring the significance of the variable effects.[31]

The correspondence of the design levels with the real additions is shown in Table II.

For each of the tests the temperature of the tanning float was adjusted to 38°C and the pH was adjusted with formic acid according to the experimental design. The hides were fully immersed in a vertical position in the tanning float. The hides remained inside the pit during the time stipulated in each test of the experimental design.

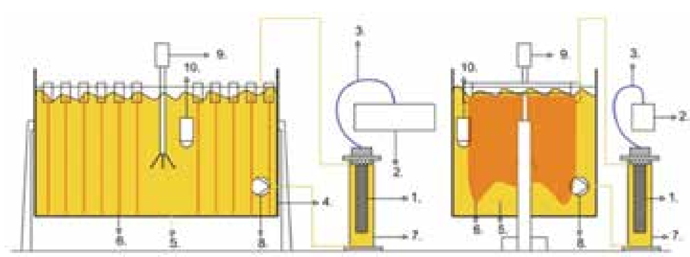

Figure 2. Penetration stage: 1. Transmitter; 2. Generator; 3. Coaxial cable; 4. Pit; 5. Float; 6. Hide; 7. Steel casing; 8. Pump; 9. Stirrer; 10. Temperature sensor.

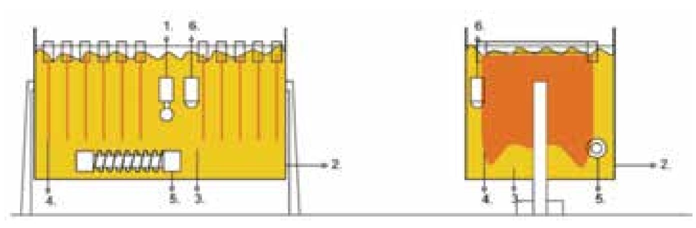

Figure 3. Fixation stage: 1. pH sensor; 2. Pit; 3. Float; 4. Hide; 5. Electric resistance; 6. Temperature sensor

Final Operations

Once the tannage was completed the leathers were removed from the pit, washed, fatliquored and air dried.

Chemical Analyses and Physical Tests

The chemical analyses and physical tests carried out in the leathers, together with the methods followed are detailed below:

- IUC 4.[32] Determination of matter soluble in dichloromethane and free fatty acid content.

- IUC 5.[33] Determination of volatile matter.

- IUC 6.[34] Determination of water soluble matter, water soluble inorganic matter and water soluble organic matter.

- IUC 7.[35] Determination of sulphated total ash and sulphated water insoluble ash.

- IUC 10.[36] Determination of nitrogen and hide substance.

- IUP 4.[37] Measurement of thickness.

- IUP 12.[38] Measurement of resistance to grain cracking and the grain crack index.

From the results of these analyses the values of the combined tannins were calculated. This amount is expressed in percentage in relation to dried and degreased leather weight.

The equation used is as follows:

Combined tannins (%) = 100 – Water soluble matter – Sulphated total ash – Hide substance (1)

Finally, the tanning degree was calculated according to the following equation:

*Tanning degree = (Combined tannins / Hide substance) * 100 (2)*

As this is a vegetable tannage, the resulting tanning degree is comparable to the percentage of chromium absorbed in a chrome tannage, as it indicates the amount of tanning agent remaining in the leather. This amount is usually expressed in percentage in relation to dried and degreased leather weight.

Measurements of resistance to grain cracking were performed to verify that the grain of the leathers obtained had enough elasticity. Otherwise, the leather would easily crack.

A panel of five experts examined the organoleptic properties of the leathers and passed judgement on the suitability of leathers for commercialization.

Table I

Experimental design.

Test	Time	pH
1	-1	-1
2	-1	1
3	1	-1
4	1	1
5	0	-1.414
6	0	1.414
7	-1.414	0
8	1.414	0
9	0	0
10	0	0
11	0	0
12	0	0

Table II

Levels of the experimental design.

	-1.414	-1	0	1	1.414
Time	12h	20h 47min	42h	63h 13min	72h
pH	3	3.3	4	4.7	5

Results and Discussion

Table III shows the tanning degree and the resistance to grain cracking values obtained.

The values of tanning degree obtained range goes from 54.7 to 73. These values can be considered very high, more typical of leather soles than leather goods.

Table IV shows the analysis of variance (ANOVA) based on the results of the variables and levels tested.

The Time and pH variables show a significance level over 95% (P-Value < 0.05). That is, for all variables, it is valid to say that the result depends on the level at which you work. The quadratic variables also show a significance level over 95%, which implies that the relationship between the tanning degree and the variables is non-linear.

The coefficients of the equation that defines the response surface were later analyzed. The resulting equation is as follows:

Tanning degree (%) = 72.7 + 1.4 × Time - 5,4 × pH- 4.6 × Time² + 2.4 (Time × pH) - 4.0 × pH² (3)

$$\text{Tanning degree }(\%) = 72.7 + 1.4 \times Time - 5{,}4 \times pH - 4.6 \times Time^2 + 2.4\,(Time \times pH) - 4.0 \times pH^2 \quad (3)$$

Figure 4 shows the calculated response surface.

The response surface obtained indicates that as the pH of the float is decreased, the tannin fixation increases up to a maximum. This is because as the pH decreases, the leathers swell and tannins insolubilize. Both effects increase the tannin fixation and therefore the tanning degree. The same occurs when the process time increases. In this case, the main reason for the fixation level decrease -once the maximum has been reached- is that under 38°C for a long time, a part of syntans and vegetable extract being not firmly fixed were de-tanned and moved into the float.

Table III
Tanning degree and resistance to grain cracking results.

Test	Time	pH	Tanning Degree	Mandrel
1	20h 47min	3.3	72.3	6
2	20h 47min	4.7	54.7	7
3	63h 13min	3.3	70.2	6
4	63h 13min	4.7	62.1	7
5	42h	3	70.2	5
6	42h	5	58.0	7
7	12h	4	61.0	7
8	72h	4	64.9	7
9	42h	4	73.0	7
10	42h	4	72.9	7
11	42h	4	72.8	7
12	42h	4	72.2	7

The maximum tanning degree value can be calculated. The maximum tanning degree would be of 74.5, which could be obtained in a pH of the float of 3.5 and a process time of 41 hours and 22 minutes, around two days approximately. This would imply an increase of the 27.5% in the tanning degree due to the fixation stage.

Table III shows the results of the measurement of resistance to grain cracking.

In summary, the test consists in the bending of the leather around a mandrel of known diameter and observation whether the leather cracks. According to the quality guideline for heavy leather[39] leather must resist mandrel number 6.

Results indicate that, except in test 5, the leathers obtained adjust to the guideline. The materials exceed it in most of the cases, as the majority of the leathers pass the 7 mandrel test.

Regarding the evaluation of the organoleptic properties, the five experts valued the touch, fineness of the grain and absence of scratches on the surface and determined that the leathers were suitable for commercialization as high-end goods.

In a previous paper,[40] the possibility of obtaining high-quality vegetable tanned leathers employing moderate energy consumption and within a reasonable space of time was demonstrated. However, the tanning degree of the leathers seemed to have a limit. That is, products with tanning degree over 60, such as leather soles, could not be obtained. The present research has surpassed this limit thanks to the inclusion of a tannin fixation stage in the tanning process. In fact, this stage is usually performed in traditional tanning processes, both in drums and in pits, which are the two common reactors used in tanning. Furthermore, the features that allowed classifying the use of ultrasounds in tanning as a sustainable alternative have been maintained. From an economic perspective, the introduction of the fixation stage lengthens the process in some days and increases energy consumption (because of the use of

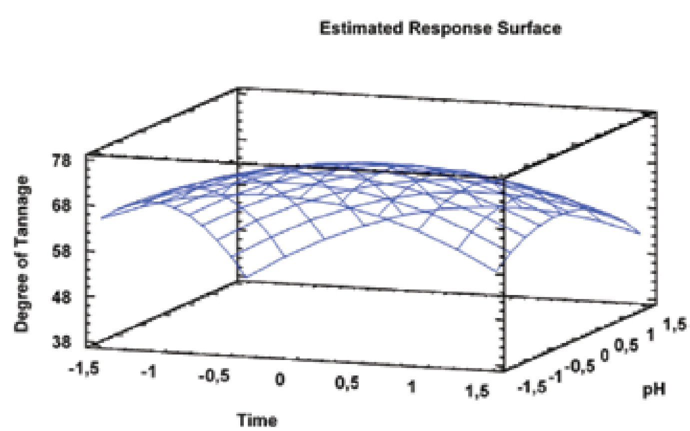

Figure 4. Degree of Tannage: Response Surface.

Table IV
Analysis of Variance for Tanning degree - Type III Sums of Squares.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Time	14.6217	1	14.6217	6.91	0.0391
B: pH	230.631	1	230.631	108.98	0.0000
AA	133.203	1	133.203	62.94	0.0002
AB	22.5625	1	22.5625	10.66	0.0171
BB	101.739	1	101.739	48.07	0.0004
Total error	12.6981	6	2.11634		
Total (corr.)	476.673	11			
R-squared = 97,3366 percent					
R-squared (adjusted for d.f.) = 95,1171 percent					
Standard Error of Est. = 1,45477					
Mean absolute error = 0,796661					
Durbin-Watson statistic = 2,24484 (P=0,3065)					
Lag 1 residual autocorrelation = -0,251598					

electric resistance to maintain the temperature of the tanning float at 38°C). However, the process is still economically feasible at an industrial level, as it allows adding value and obtaining excellent quality leathers that can be used in high-end goods. It is also important to acknowledge that the working system is versatile and requires no major modifications or expenses for tanneries.

On the other hand, it is commonly known that because of the large amount of pollution generated, several authors have studied the toxic hazards of leather industry and the need for sustainable cleaner technologies[41] as well as eco-friendly waste management strategies for a greener environment.[39]

Our work is closely related to such environmental concerns. Thus, our results show that the technology under study allows us to obtain a wider range of products, since the tanning degree of the leather can be controlled. Furthermore, the tannage is achieved in a shorter time and high quality leathers are obtained. These positive results will probably involve an increase in the use of vegetable extracts, which are considered to be an eco-friendly tanning agent, versus other more pollutant agents such as chromium salts. In addition, the technology we are proposing enables the reuse of tanning floats, which also contributes to the sustainability of the process.

Conclusions

The results obtained in this paper indicate that the tanning fixation in vegetable tanning using ultrasound increases considerably when, after its use, the pH is adjusted and the temperature of the tanning float is raised for a certain period of time. The study of the response surface allows observing a clear dependence of the value of the tanning degree regarding the two parameters aforementioned. In order to obtain the maximum tanning degree, tannins must be fixed in a hot tannic float (38°C) with a pH of around 3.5 for approximately 40 hours. The fixation stage allows us to increase the tanning degree in a 27.5% in relation to that of the leathers when solely subject to a single penetration stage.

This implies that high-quality leathers presenting a very high tannin fixation, like sole leathers, can be obtained. The use of ultrasound may be the solution to an endemic problem in vegetable tanning because it enables us to obtain high quality leathers without the usual scratches (always produced when a drum is used), in an acceptable time for the tanneries from an economic perspective (which is also virtually impossible when a pit or a paddle are used). This study provides new insights to suggest a realistic and feasible scale-up of the process studied. This could increase the use of vegetable extracts, which are considered and eco-friendly tanning agent, versus others more pollutant agents such as chromium salts.

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