Study of the Application of Ultrasound in a Vegetable Tannage*

by

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Abstract

This study concerns the implementation and improvement of a system that applies ultrasound technology to vegetable tanning floats. The system is versatile and requires no major modifications or investment expense for tanneries. In particular, the study investigated grain fineness and fixation of tannins in relation to several mechanical approaches, which included: no mechanical effect (pits), drum, ultrasound, and ultrasound plus drum. A comparative study of energy expenses on the basis of the mechanical effect being used was also carried out.

Resumen

Se estudia y pone a punto un sistema externo de aplicación de los ultrasonidos en los baños de curtición vegetal. Este sistema es muy versátil y su uso no requiere realizar modificaciones en la tenería ni supone grandes gastos de inversión. Se estudia, entre otras propiedades, la finura de flor obtenida y la fijación de los taninos en la piel en función del efecto mecánico empleado para curtir: sin efecto mecánico (tina), bombo, ultrasonidos y combinación de ultrasonidos más bombo. También se realiza un estudio comparativo del gasto energético en función del efecto mecánico empleado.

Introduction

Sound waves with 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 having a frequency range of 20–100 kHz is commonly employed for enhancing physical processes and for accelerating chemical reactions.

The application of ultrasound to different operations of the tanning process has been the aim of research since the 1950s.[1-19] Results from these studies have generally been satisfactory. However, such results have only been obtained in the laboratory as the ultrasonic power employed would have been too costly for replication in industrial practice.

The use of ultrasound has potential to be important in the operation of vegetable tannage. Currently tannage with vegetable extracts can be accomplished in less than 24 hours. The use of the drum makes this possible as it provides the necessary mechanical effect. However, this process has a shortcoming. Sometimes, the hides are damaged when they hit against the pivots of the drum. When this occurs, the leathers show scratches and therefore their commercial value decreases. In fact, up to a 50% devaluation of the final product may result from such a flaw. Damage to the grain of the leather can be prevented by using pits instead of drums, although the process is excessively long. Several researchers have provided evidence to support the fact that ultrasound accelerates the penetration of vegetable extracts into the skin or hide. These researchers concluded that the depolymerizing action of ultrasound on the structure of tannins facilitates the penetration of the tanning agent into the pelt. Hence, the use of ultrasound may reduce the time of tannage while damage to the grain is avoided.

In two previous papers[20-21] our team studied the influence of parameters such as applied ultrasound power, application time, and float concentration on vegetable tanning floats and also

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the speed of penetration in the hides during tannage. The results obtained demonstrate that the use of ultrasound in vegetable tannage is technically feasible in industrial practice. This work represents a step forward in the same direction. In our study, we focused on an external source of ultrasound into the tanning floats. The system tested is much more versatile as it is not necessary to apply ultrasound in the container where the hides are. Therefore, this system does not require modifications in the tannery and does not involve substantial investment. Properties studied include grain fineness and the fixation of tannins in the hide in relation to the mechanical effect employed, namely no mechanical effect (pits), drum, ultrasound, and ultrasound plus drum combination. An economic study of energy expenses on the basis of the mechanical effect being used has also been carried out.

EXPERIMENTAL

Hide and chemicals

Tests were performed with pre-tanned bovine hide. The following vegetable extracts were used for tanning:

Quebracho extract: ATO UNITAN. Richness:
72% of tannins. pH (6.9°Bé) = 4.3-4.8

Mimosa extract: CLAROTAN. Richness:
68% of tannins. pH (6.9°Bé) = 4.0-4.5

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

Equipment

The tests were carried out using an ultrasound tubular equipment composed of a generator, a transmitter and a stainless steel cylindrical casing. The generator can deliver a maximum power of 1500w and it can be regulated. It can emit at four different powers levels corresponding to 100%, 85%, 75% and 60% of maximum power, and is Telsonic brand. We also used a 1m-high (i.e. diameter) and 0.4m-wide polypropylene drum, Italoprogetti brand and a submersible water pump (approximate flow: 40L/min), Leader brand. To perform tests, the pump was submerged in the tanning float that was inside the drum. The pump sucked up the float through a hose to the cylindrical casing containing the ultrasound emitter. The float would then return to the drum after being subjected to the action of ultrasound for a specified period of time. Figure 1 represents a diagram of the system described and Figure 2 is a photo of the system.

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 levels of each parameter tested were as follows: Power applied to ultrasound (85%, 75% and 60%), time of action of ultrasound (3, 4 and 6 hours), time of action of drum (3, 4, 6 and 7 hours) and rest times of hides after the tanning operation (3 and 7 days).

We also obtained and analyzed samples of vegetable tanned leather (morocco and sole) at an industrial scale with the same mixture of plant extracts as those used in our experiments.

Methodology

1. 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 glutaric dialdehyde, synthetic naphthalenesulfonic and synthetic phenol.

The tanning floats were prepared in the drum 24 hours before each tanning to get the correct solution of vegetable extracts in

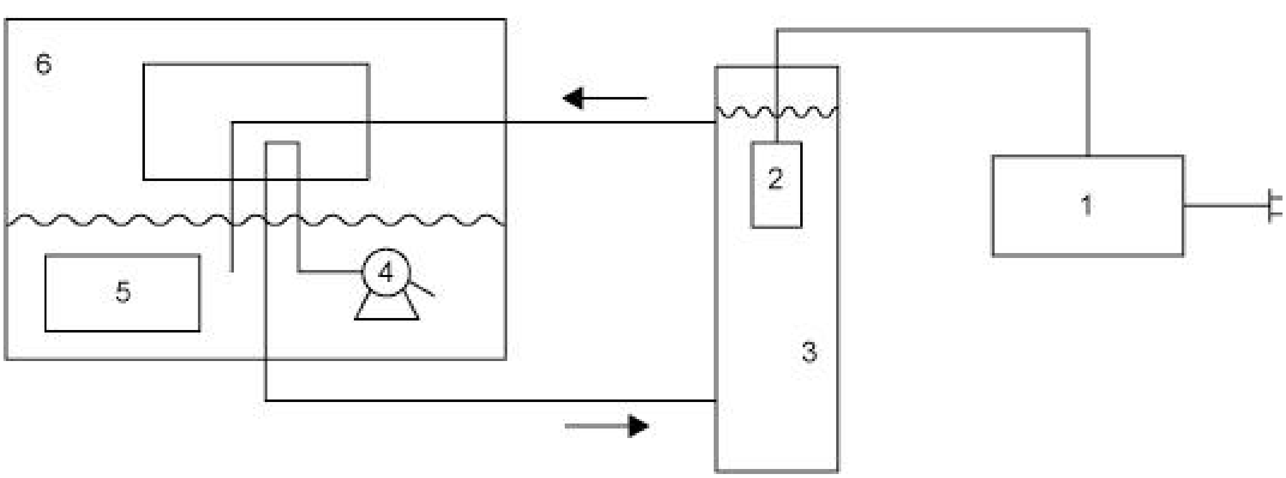

Figure 1. Setup diagram. 1: US Generator; 2: US Transmitter; 3: Steel casing; 4: Pump; 5: Hide; 6: Drum.

water. To prepare each float 27 kg of mimosa and 27 kg of quebracho were added to 90 L of water. The drum rotated intermittently until a complete dissolution was reached. Finally, we controlled the density of the resulting tanning float (19°Bé approx.).

2. Tannage
Four types of tests were performed: With totally static floats (no mechanical effect), floats subjected to ultrasound action (mechanical effect on the float), rotating drums (mechanical effect on both hides and float), and finally combined action of ultrasound and drums.

To carry out tannages in static floats or in drums the pre-tanned skins were introduced in the tanning float and were either left to rest or drummed at a 10 rpm speed.

To carry out the tannings with ultrasound, the pre-tanned skins were inserted in the tanning floats in the drum. Next the pump was introduced in the float and recirculation was started. Finally the ultrasound generator was started.

To combine the action of ultrasound with the drums, the pump in the tanning float was introduced in the drum and removed from it, as it seemed fit. The drum was thus conveniently started or stopped.

3. Final Operations
Once the tannage was completed the leathers were washed, fatliquored and air dried.

Figure 2. Photo of experimental setup

4. Chemical analyses and physical tests
The chemical analyses and physical tests carried out, together with the methods followed[22], are detailed below:

- IUC 4. Determination of matter soluble in dichloromethane and free fatty acid content
- IUC 5. Determination of volatile matter
- IUC 6. Determination of water-soluble matter, water soluble inorganic matter and water soluble organic matter
- IUC 7. Determination of sulphated total ash and sulphated water insoluble ash
- IUC 10. Determination of nitrogen and hide substance
- IUC 11. Determination of pH and difference figure
- IUP 4. Measurement of thickness
- IUP 5. Measurement of apparent density
- IUP 6. Measurement of tensile strength and percentage elongation
- IUP 7. Measurement of static absorption of water
- IUP 8. Measurement of tear load
- IUP 12. Measurement of resistance to grain cracking and the grain crack index
- IUP 15. Measurement of water vapor permeability
- IUP 16. Measurement of shrinkage temperature up to 100°C

From the results of these analyses we calculated the values of the combined tannins.

This amount is expressed in percentage in relation to dried and degreased leather weight. The formulation 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 formula:

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

As this is a vegetable tannage, the resulting 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.

Results and Discussion

As explained in the Methodology section, several physical tests on the final leathers were carried out. Likewise, chemical analyses were performed on the wastewater tanning floats. The results indicated that all leathers obtained met the quality requirements for vegetable tanned leathers (fancy leathers type). However, except for the tanning degree, the results of the chemical analyses and physical tests showed no correlation with the parameters under study (power applied to ultrasound, time of action of ultrasound, time of action of drum and rest times of hides after the tanning operation) and therefore will not be included in this section.

1. Industrial Samples
Table I shows the results obtained by analyzing samples from industrial goods in a tannery.

The hides were submersed in the float and left to rest for a week. The experiment was performed in duplicate and tanning degrees obtained were 43.3 and 46.8. These degrees are well below those of commercial samples. However, the quality of the grain produced was much higher, since it did not present any scratch or blemish. Figure 3 is a photograph of the grain of one of the hides from view with a 50× loupe.

2. Tanning using the drum as the only mechanical effect
These tanning were performed to compare the results with those obtained in subsequent tests in which the type of mechanical effect was changed. The hides were tanned in a pilot-plant drum rotating at 10 rpm. They were then left to rest

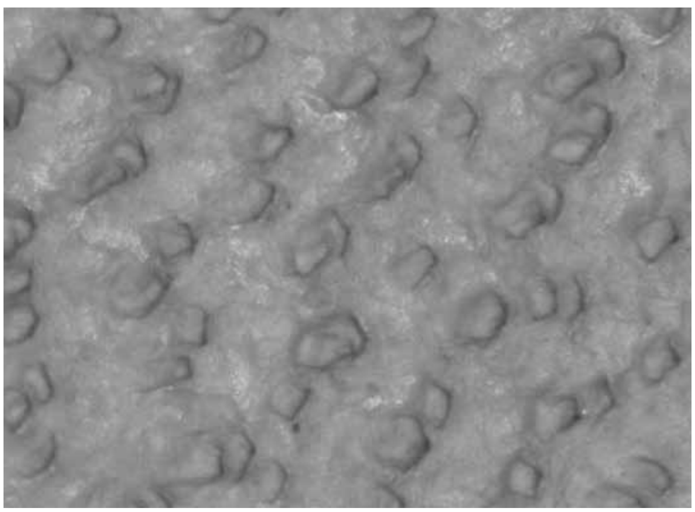

Figure 3. Grain appearance after a tanning without mechanical effect. (50×)

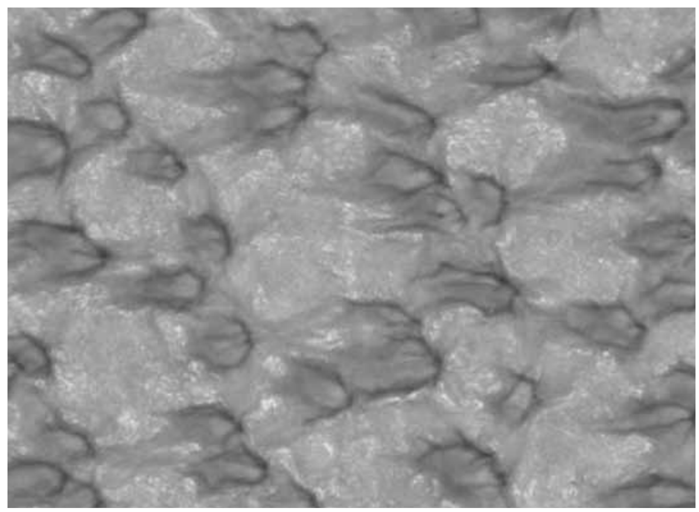

Figure 4. Grain appearance after leather has been tanned in drum (50×)

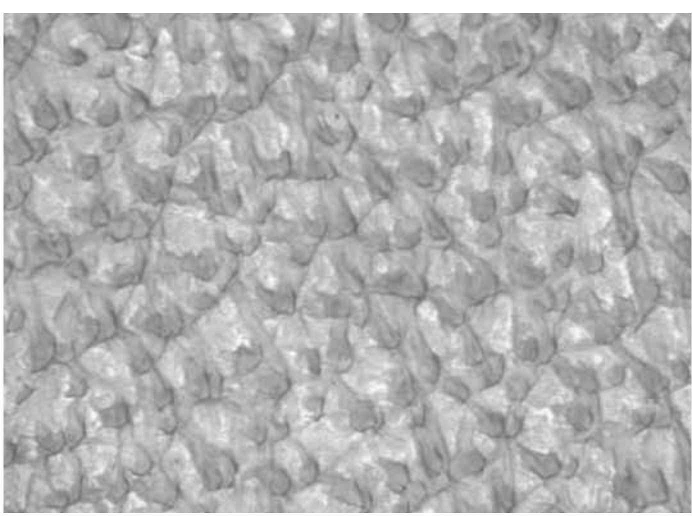

Figure 5. Grain appearance after ultrasound tanning (50×)

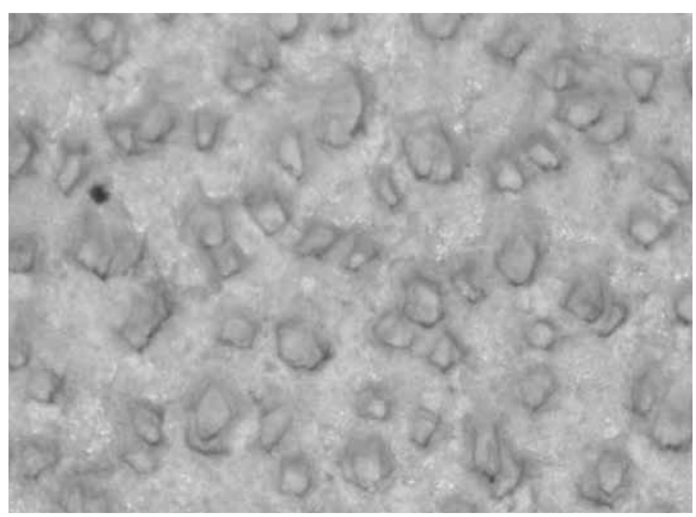

Figure 6. Grain appearance after a tannange combining drum and ultrasound (50×)

for some time in the tanning float before proceeding with the process. Table II shows tests and results.

Comparing these results with those of industrial samples we can observe that final leathers obtained a tanning degree similar to fancy leathers. Figure 4 is a photograph of the grain of one of the hides from a 50× loupe.

3. Tanning using ultrasound as the only mechanical effect

In some of the tanning with the aid of ultrasound, the ultrasound was applied intermittently in the tanning bath, whereas in other tests the application was non-stop. Table III shows the tests and results.

Observing the results we can infer that the power applied is important in terms of time of application. In tests in which the exposure time of the float to ultrasound was only 3 hours (Tests 3 and 4), the outcome was that the higher the ultrasonic power, the higher the tanning degree. In contrast, for exposure times of 4 hours or more, there was not a relationship between applied power and tanning degree (Tests 6 and 7). Differences in tanning degrees were found on the basis of the time the hides remained resting in the float once the exposure to ultrasound was finished (Tests 5 and 9). Likewise, the fact that exposure to ultrasound was either non-stop or in different stages (Tests 8, 9 and10) did not show significant differences in the tanning degrees of the final leather.

Tanning degrees obtained were generally lower, though not too much, than those obtained in tests in which the drum was used as the only mechanical effect on tanning (comparing tests with same resting times after the mechanical effect). These tanning degrees were also lower than tanning degrees from both fancy leather samples tanned at an industrial scale. However, the tanning degrees of tests 9 and 10 are of the same order. On the other hand, none of the resulting tanning degrees are comparable to the sole samples tanned at an industrial scale.

We obtained leather of tanning rates similar to leather tanned with no movement whatsoever, and in less than half the time (Test 5).

TABLE I

Analysis of industrial-scale samples

Sample	Tanning Procedure	Tanning Index (%)
Fancy leather	12 h drum + 12 h static	54.4
Sole leather	30 h drum + 42 h static	62.4

TABLE II

Analysis of the samples tanned with drum

Test	Tanning Procedure	Tanning Degree (%)
1	7 h drum + 72 static	47.7
2	7 h drum + 168 static	55.8

TABLE III

Analysis of the samples tanned with ultrasound

Test	Tanning Procedure	Tanning Degree (%)
3	3h (60%) US + 168 h S	39.4
4	3h (75%) US + 168 h S	42.3
5	3h (75%) US + 3h S + 3h (75%) US + 72 h S	46.1
6	2h (60%) US + 2h S + 2h (60%) US + 168h S	47.4
7	2h (85%) US + 2h S + 2h (85%) US + 168 h S	46.9
8	24h S + 6h (75%) US + 168 h S	49.7
9	3h (75%) US + 3h S + 3h (75%) US + 168 h S	51.5
10	[2h (75%) US + 2h S] x 3 + 168 h S	52.5

US = Ultrasound; S = static; Between parenthesis ⟶ Power applied to ultrasound

TABLE IV
Analysis of tanned samples combining ultrasound and drum

Test	Tanning Procedure	Tanning Degree(%)
11	2h (75%) US + 2h D + 2h (75%) US + 2h D + 72h S	47.7
12	3h (75%) US + 3h D + 3h (75%) US + 72 h S	48.1
13	3h (60%) US + 3h D + 3h (60%) US + 168 h S	49.2
14	[10 min. D + 50 min S] x 24 + 4h (75%) US + 168 S	51.2
15	3h (75%) US + 3h D + 3h (75%) US + 168 h S	55.3
16	2h (75%) US + 2h D + 2h (75%) US + 2h D + 168h S	55.5

US = Ultrasound; D = Drum; S = Static; Between parentheses ⟶ Power applied to ultrasound

TABLE V

POWER

	Drum	Ultrasound	Pump
Power (w)	2000	600 (75%)	380

ENERGY CONSUMPTION

Test	Energy (kwh)
2: 7 h D +168 S	14
10: [2h (75%) US + 2h S] x 3 + 168 h S	5.88
15: [2h (75%) US + 2h D] x 2 + 168 h S	11.92

US = Ultrasound; D = Drum; S = Static; Between parentheses ⟶ Power applied to ultrasound

Final grain quality was definitely superior to that of leather obtained by tanning in the drum and of the same quality level as leathers obtained by tanning in pits. Figure 5 is a photograph of the grain of one of the hides from a 50× loupe.

4. Tanning combining ultrasound and drum

To improve tanning rates, a series of tests in which we combined both the mechanical effects of ultrasound and of the drum were performed. Table IV below shows the tests and the results.

When comparing the different tests we concluded that the longer the time in static tanning (Tests 12 and 15) the higher the tanning degree.

Similar results were achieved by applying the ultrasound for 6 hours (75% power) and the drum for 3 as were obtained from only 4 hours of ultrasound (75% power) and 4 hours of drum treatment (Tests 15 and 16). This confirms that operation time being equal; the mechanical effect of the drum is superior to ultrasound. In our case, for each hour of drum it took about two ultrasound hours to achieve the same tanning degree.

Tanning degrees obtained are now comparable to those obtained in tests at a pilot plant scale in which the tanning was performed only with the drum and are also comparable to the tanning rate of the fancy leather sample tanned at an industrial scale.

As to the assessment of organoleptic qualities such as tact and flexibility, experts unanimously reached the conclusion that the samples showed the same characteristics as those of fancy leather.

By comparing the appearance of the grain of the final leather, the experts reached the conclusion that the samples presented an intermediate quality between the samples tanned either in completely static mode or with the assistance of ultrasound and the samples tanned simply in the drum. Figure 6 is a photograph of the grain of one of the leathers from a 50× loupe.

5. Energy study

In this section we have made a brief comparative study of the energy consumed at the pilot plant during tanning: (1) with the drum, (2) with ultrasound, (3) combining drum, in order to obtain three leathers with similar tanning degrees. To carry out the comparison tests 1, 8 and 15 have been chosen. The powers of each of the machines used and the calculation of the energy consumed can be found in Table V.

Our calculations indicate that tanning with only the assistance of ultrasound we get a 58% savings in energy consumption versus tanning with drum alone. The combined system drum plus ultrasound process also saves energy, but only a modest 15%.

Therefore, observing the overall results of the tests performed it can be said that the application of ultrasound to vegetable tanning floats has the advantage of significantly accelerating the tanning versus static tanning, while maintaining excellent grain quality in the final leathers. Tanning in the drum accelerate the process even further, but then grain quality decreases significantly. Combining the two mechanical effects we get intermediate results in terms of processing time and grain quality.

It also follows from the results that it would be interesting to perform more tests increasing the processing time when tanning with the help of ultrasound only. As a result we may then get tanning degrees close to those of footwear soles. New tests are being prepared to ratify this. It is important to bear in mind, however, that in order to quantify the feasibility of the method as a whole, further studies should be carried out. Factors like the possible reutilization of tanning floats should be taken into account. And utilization at an industrial scale may furnish even better results with less energy consumption, thanks to the use of ultrasound.

CONCLUSIONS

The results obtained in this work indicate that the use of ultrasound in vegetable tanning extracts is an alternative worth considering if the objective is to perform the process without using a drum. Grain quality is significantly improved and the drawback of the excessive length of the process, typical of tanning in pits, is avoided.

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