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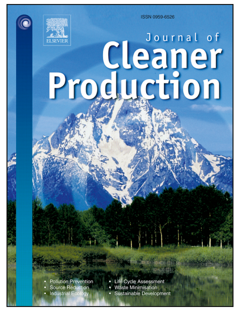

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Study of several variables in the penetration stage of a vegetable tannage using ultrasound

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Abstract

This study concerns the implementation and improvement of a 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 investigated the influence of several variables on the tannins absorption by the hides. The results show significant differences in the tanning degree of the leathers tested in relation to the work system tested, the ultrasonic power used and the resting time of the leather after tanning. The leathers we obtained showed no scratches, which is 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 kind of tannages.

Keywords: *Vegetable tanning; Leather; Ultrasonic disintegration; Vegetable extracts; Tanning using ultrasounds.*

1. 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 (Krishnamoorthy et al., 2013).

Vegetable tanning is considered an eco-friendly tanning process (Kanth et al., 2009). 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 tans 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 size (Morera, 2000). These molecules tend to be joined, 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 (Soler, 2000), 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 (Heidemann, 1993), which facilitates its penetration on 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 significally.

However, this process has 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 (Fig 1). 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 extracts solutions. The problem with 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 from 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 (Ernst and Gutmann, 1950). In the following decades, several researchers studied the application of ultrasound in different processes related to tanning process (Alexa et al., 1964). 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 (Brown et al., 2006) and on several operations that make up the tanning process has been studied: soaking (Morera et al., 2013), unhairing (Jian et al., 2010), degreasing (Sivakumar et al., 2009a), chrome tanning (Mantysalo et al., 1997), titanium salts tanning (Peng et al., 2007), retanning (Sivakumar et al., 2013), dyeing (Gong et al., 2011) and fatliquoring (Xie et al., 2000). The effectiveness of ultrasound use in the manufacture of different vegetable extracts (Killicarislan and Ozguna, 2013), dyes (Sivakumar et al., 2009b) and oils (Sivakumar et al., 2007) for tanning, in the enzymatic hydrolysis of leather waste (Jian et al., 2008) and in the treatment of residual floats

(Lakshmi and Sivashanmugam, 2013) and solid wastes (Sun et al., 2003) from tanning process has been tested.

In a previous paper (Morera et al., 2010) our team studied the implementation and improvement of a system that applies ultrasound technology to vegetable tanning floats. The results demonstrate that the use of ultrasound in vegetable tanning is technically feasible in industrial practice.

This work represents a step forward in the same direction. In our study, we focused on the use of a portable source of ultrasound for the penetration of tannins into the hide. Depending on the chosen work system, ultrasound can act on the hide and the tanning float or just above the tanning float. These systems do not require modifications in the tannery and do not involve substantial investment. Properties studied include the tanning degree of the hides, their tensile strength and their elongation in relation to the work system used, the applied ultrasonic power and the hide resting time after tanning.

2. Materials and methods

2.1. Materials

2.1.1. 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 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.

2.1.2. Equipment

The tests were carried out using two 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 tanning pit. Capacitance: $1m^3$.

A submersible water pump (approximate flow: 40L/min) and an electric stirrer were also used.

2.2. Methodology

2.2.1. 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: Working system (Direct and External), power applied to ultrasound (100% and 50%), and resting time of hides after tanning operation (0, 24 and 48 hours).

2.2.2. 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 pit 24 hours before each tanning to get the correct solution of vegetable extracts in water. 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 (19ºBé approx.) was controlled.

2.2.3. Tannage

To perform the tests, two different work systems were tried out.

In the Direct system, the transmitters were submerged in the tanning float that was inside the HDPE pit. In this work system, ultrasound is acting throughout the process evenly over the whole float, as Fig. 2 shows.

In the External system, 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 for a specified period of time. In this system, 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. Fig. 3 shows a diagram of this work system.

A 2×2×3 experimental design was chosen in order to carry out the experimentation.

Table 1 shows the variables and levels tested.

Table 1

Variables and levels tested

Variables	Levels		
	-1	0	1
Work system	Direct		External
Ultrasound power (%)	50		100
Resting time (h)	0	24	48

Table 2 shows the tests conducted.

Table 2
Tests conducted

Test	Work system	Ultrasound power	Resting time
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	0
6	1	-1	0
7	-1	1	0
8	1	1	0
9	-1	-1	1
10	1	-1	1
11	-1	1	1
12	1	1	1

The tests were carried out hanging 10 bovine hides vertically inside the pit. The hides were fully immersed in the tanning float. Ultrasound equipment were placed depending on the work system chosen (Figs. 2 and 3) and were started up. Ultrasound worked for 7 hours and remained standing for 17 hours. This operation was repeated the next two days. Therefore, the common step in all tests lasted for 3 days. The hides remained inside the pit, immersed in the tanning float and without ultrasound, during the resting time after the tanning stipulated in the experimental design.

2.2.4. Final Operations

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

2.2.5. 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 (IUC 4, 2008). Determination of matter soluble in dichloromethane and free fatty acid content.
- IUC 5 (IUC 5, 2005). Determination of volatile matter.
- IUC 6 (IUC 6, 2006). Determination of water soluble matter, water soluble inorganic matter and water soluble organic matter.
- IUC 7 (IUC 7, 1977). Determination of sulphated total ash and sulphated water insoluble ash.
- IUC 10 (IUC 10, 1984). Determination of nitrogen and hide substance.
- IUP 4 (IUP 4, 2002). Measurement of thickness.
- IUP 6 (IUP 6, 2011). Measurement of tensile strength and percentage extention.

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 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.

Measurement of tensile strength and percentage elongation were performed to verify that the leathers obtained had the mínimum structural strength recommended by the United Nations Industrial Development Organization (UNIDO, 1994) for this type of leather.

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

3. Results and discussion

Table 3 shows the Tannin Degree values obtained.

Table III
Results of the chemical analyses and physical tests

Test	Tanning Degree (%)	Tensile Strength (N/cm^2)	Elongation (%)
1	49.6	2727	34.0
2	51.1	2973	48.0
3	50.1	2653	36.7

4	54.0	3223	28.9
5	51.0	2202	54.3
6	52.9	2874	39.3
7	55.0	3195	28.4
8	54.5	2301	48.6
9	51.3	2107	54.6
10	53.6	2873	28.2
11	52.9	2593	33.6
12	57.0	2777	32.7

The values obtained range from 49.6 to 57. Taking into account that the working conditions are in a penetration stage, these values can be considered very high, more typical of leather soles than leather goods.

Table 4 shows the analysis of variance (ANOVA) based on the results of the variables and levels tested.

Table 4
Analysis of Variance for Tanning Degree - Type III Sums of Squares

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
Ultrasound power	16.3333	1	16.3333	14.59	0.0065
Work system	14.52	1	14.52	12.97	0.0087
Resting time	14.66	2	7.33	6.55	0.0249
RESIDUAL	7.83667	7	1.11952		
TOTAL (CORRECTED)	53.35	11			

The ultrasonic power and work system variables show a significance level over 99% (P-Value < 0.01). The resting time variable shows a significance level over 97% (P-Value < 0.03). That is, for all variables, it is valid to say that the results depends on the level at which you work.

Table 5 shows the Table of Least Squares Means for the tanning degree.

Table 5
Table of Least Squares Means for Tanning Degree with 95,0 Percent Confidence Intervals

Level	Count	Mean	Stnd. Error	Lower limit	Upper limit
GRAND MEAN	12	52.75			
Ultrasound power					
-1	6	51,5833	0,431958	50,5619	52,6048
1	6	53,9167	0,431958	52,8952	54,9381
Work system					
-1	6	51,65	0,431958	50,6286	52,6714
1	6	53,85	0,431958	52,8286	54,8714
Resting time					
-1	4	51,2	0,529038	49,949	52,451
0	4	53,35	0,529038	52,099	54,601
-1	4	53,7	0,529038	52,449	54,951

Figures 4, 5 and 6 show the results for each variable of Table V in a graphic way.

From Figure 4 it follows that by increasing the ultrasonic power, the tanning degree will also be increased. It is a logical result since by increasing the energy provided to the system, the aggregation of tannin molecules is harder and its penetration into the hide is easier. As penetration increases, fixation and consequently the tanning degree also increase.

From Figure 5 it follows that the External work system allows obtaining leathers with the highest tanning degree. Thus, the disintegrating effect is more effective when the ultrasound transmission is focussed in small volumes of the tanning float. Considering the same volume of float, in order to prevent the tannin molecules aggregation it is better to supply a lot of energy in a period of short time than less amount of energy in a long time.

Figure 6 shows that leathers without resting time after the tannage have lower tanning degrees. No significant changes between leathers with 24 or 48 hours resting time were observed. This result is consistent with what is observed in a typical vegetable tanning using a drum. It takes 24 hours to complete the kinetics of chemical reactions between tannins and collagen.

Table 3 also shows the measurement of tensile strength and percentage elongation results.

The analysis of variance revealed that the results do not depend on the levels tested for any of the variables studied.

According to the quality recommendations of UNIDO for sole leathers, the values of tensile strength must exceed 2000N/cm^2 and the values of tensile elongation should be less than 70%. All tests exceeded quality recommendations of UNIDO. Therefore it can be concluded that the use of ultrasound in the conditions applied in the tests did not lead to a damage to the physical structure of the leather and that the quality of the final leather do not decrease.

After evaluating the organoleptic properties of the final leathers the panel of experts confirmed that the leathers showed no scratches and were suitable for commercialization as high-end leather goods.

The displayed results confirm and expand the findings of other studies (Sivakumar et al., 2014, 2013, 2010, 2008) on the effect of ultrasound on the diffusion of vegetable extracts (or similar chemicals such as syntans), through the hide matrix. Regarding previous studies, four new facts have been established:

a. A reasonable electric power consumption (approx. 2W/L of tanning float) is required to obtain leather with a high tanning degree in semi-industrial working conditions.

b. The ultrasound effect is more effective when the ultrasound transmission is focused on small volumes of the tanning float.

c. Like in traditional tanning, once the application of ultrasound has been finalized it is necessary to leave the leathers to stand for 24 hours in order to increase their tanning degree.

d. The working system is versatile and requires no major modifications or expenses for tanneries.

From the economic point of view it should be noted that the absence of scratches can mean a significant economic benefit to the tanner because the price of the final leather is increased by approximately 5%.

Because of the large amount of pollution generated, several authors have studied the toxic hazards of the leather industry and the need for sustainable cleaner technologies (Dixit, 2015) as well as eco-friendly waste management strategies for a greener environment (Kanagaraj, 2015).

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 items, 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 whole process.

4. Conclusions

The results indicate that the working system, the ultrasonic power and the resting time after the tannage influence the penetration of tannins in the ultrasound vegetable leather tanning. The more concentrated energy the vegetable extract solution receives, the more tannins are absorbed by the leather. A minimum resting time of 24 hours after the tannage also contributes to increase the tanning degree. Therefore our research shows that the parameters may be regulated to obtain an adequate penetration of the tannins into the leather depending on the desired final item being pursued. The use of ultrasound thus emerge as a solution to an endemic problem in vegetable tanning, since it enables us to obtain high quality leathers without the usual scratches, which is extremely difficult when a drum is employed. Besides, the tanning is performed in an acceptable time frame, which is virtually impossible when a pit or paddle are being used. These gains in time effectiveness result, in turn, in cost savings for tanneries.

This study provides new insights to suggest a realistic and feasible scale-up of the process under study. Furthemore, the implementation of ultrasound would lead to increase the use of vegetable extracts, which are considered to be and eco-friendly tanning agent compared to other more polluting agents such as chromium salts.

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CAPTIONS

Fig. 1. Damaged hide.

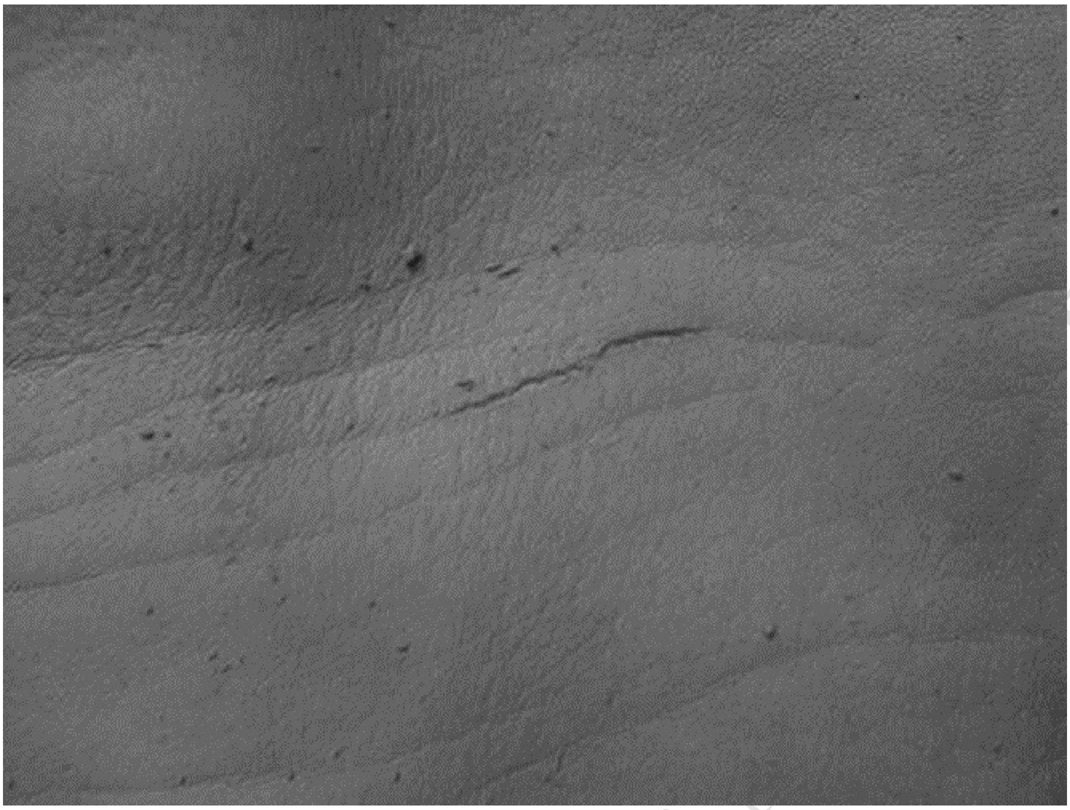
Fig. 2. Direct system: 1. Transmitter; 2. Generator; 3. Coaxial cable; 4. Pit; 5. Float; 6. Hide; 7. Stirrer; 8. Temperature sensor.

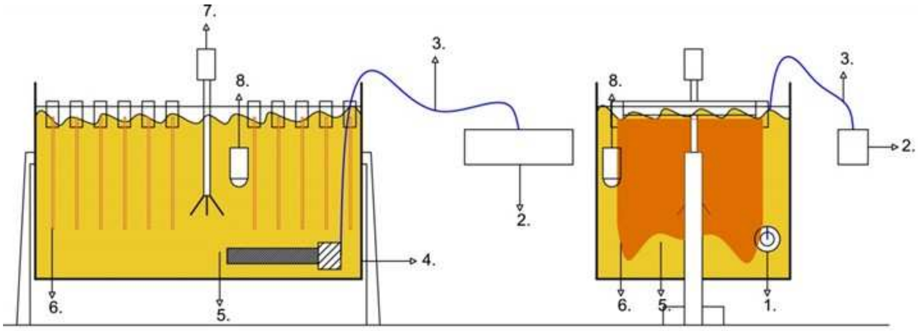
Fig. 3. External system: 1. Transmitter; 2. Generator; 3. Coaxial cable; 4. Pit; 5. Float; 6. Hide; 7. Steel casing; 8. Pump; 9. Stirrer; 10. Temperature sensor.

Fig. 4. Influence of power applied to ultrasound on the tanning degree.

Fig. 5. Influence of work system on the tanning degree.

Fig. 6. Influence of resting time on the tanning.degree

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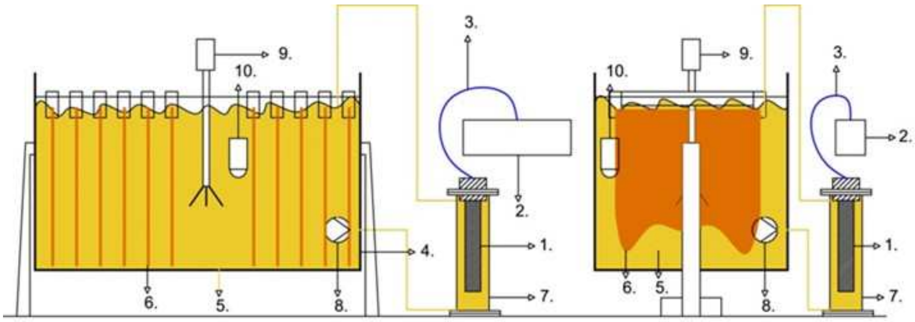
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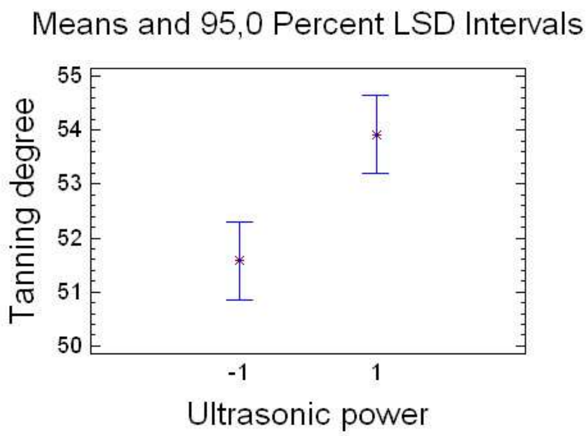
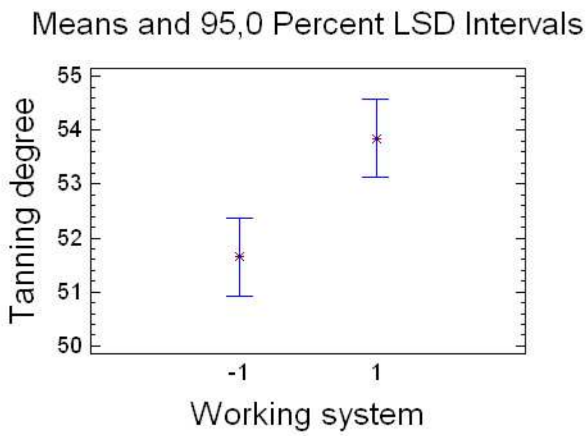
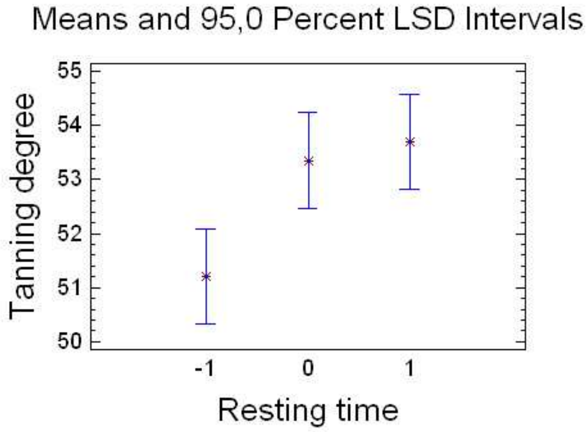

Means and 95,0 Percent LSD Intervals
Tanning degree
55
54
53
52
51
50
-1
1
Ultrasonic power


Means and 95,0 Percent LSD Intervals
Tanning degree
55
54
53
52
51
50
-1
1
Working system



Means and 95,0 Percent LSD Intervals
Tanning degree
55
54
53
52
51
50
-1
0
1
Resting time

Ultrasound is applied to vegetable tanning floats.

The influence of work system, ultrasound power applied and resting time was studied.

The tanning degree depends on the level of each variable studied.

The penetration of tannins can be regulated.

Leather without scratches was obtained in less time.