

OPTIMIZATION OF VARIOUS PARAMETERS IN VEGETABLE TANNING USING ULTRASOUND*

by

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ABSTRACT

The influence of different variables has been determined in vegetable tanning when using ultrasound (US). US is used in a traditional tanning process in order to replace the mechanical effect of the drums. This prevents the damaging of the grain which results from the hitting of the hides against the pivots in the drum. However, it is necessary to optimize certain variables so that the use of US can be economically viable.

The variables in this study were (a) the power applied (from 16.7 to 4.2 W/L), (b) the time devoted to the effect of US, and (c) the concentration of tanning liquor. These variables are of fundamental importance when attempting to determine the economic viability of the tanning system proposed here. The parameters that have been controlled during the tests were (a) the density of the float, (b) the absorption of the vegetable extract in the hide, and (c) the time devoted to tan-through.

The tests provided positive results when using US with a power of 8.35 W/L and processing only for 5 hours. The quality of the grain in the pieces of leather obtained using US is higher than that of similar pieces of leather made using the drums.

RESUMEN

La influencia de diferentes variables ha sido determinada en el curtido vegetal cuando se ha utilizado ultrasonido (US). US se utilizó en el proceso de curtición tradicional para así reemplazar los efectos mecánicos de los fulones. Esto evitaría estropear la flor debido a los golpes de la piel sobre los tacos del fulón. Sin embargo, es requerido optimizar ciertas variables operacionales tal que el empleo de US pueda ser económicamente factible. Las variables en este

estudio fueron (a) la potencia aplicada (desde 16.7 a 4.2 W/L), (b) el tiempo destinado al efecto del US, y (c) la concentración del licor curtiente. Estas variables son de fundamental importancia cuando se trata de determinar la factibilidad económica del sistema de curtición aquí propuesto. Los parámetros que han sido controlados durante las pruebas fueron (a) la densidad del baño, (b) la absorción del extracto vegetal en la piel, y el tiempo requerido para curtir atravesado. Las pruebas rindieron resultados positivos cuando se utilizó US con potencia de 8.35 W/L y procesamientos de sólo 5 horas. La calidad de la flor obtenida en los pedazos de cuero utilizando US es más alta que la de pedazos análogos de cuero producidos empleando los fulones.

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 1950s¹⁻²⁸. Results from these studies have generally been satisfactory. However, such results have only been obtained at a laboratory scale as the ultrasonic power employed would have been too high for replication in industrial practice.

The use of ultrasound may be important in the operation of vegetable tannage. Nowadays, 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 in turn their commercial value decreases. In fact, up to a 50%

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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 (hence forth US) accelerate the penetration of vegetable extracts into the skin or hide. These researchers concluded that the depolymerising action of ultrasound on the structure of tannins facilitates the penetration of the tanning agent into the pelt. Hence, the use of US may reduce the time of tannage while avoiding damage to the grain.

Several variables have been optimized in our study in an attempt to allow for the application of vegetable tannage using US in industrial practice.

EXPERIMENTAL SECTION

The experiment consisted of two stages:

Stage One

A laboratory ultrasonic cleaner (32 kH and 550 W) with a capacity of 8 L was employed to carry out the first series of experiments.

Three different types of commercial extracts were used: mimosa, quebracho and chestnut. Several aqueous solutions of different vegetable extracts were prepared in duplicate. The concentrations of the solutions were 30% and 60% and the testing temperatures were 27°C and 40°C. Only one of the duplicates was subject to the effect of US. Particle size for each of the dissolutions was periodically measured using a Coulter Counter Particle Size Analyser.

Stage Two

During the second stage, several pieces of hide were tanned in a larger ultrasonic tank using quebracho extract. Different tannages were carried out modifying both the power of US and the concentrations of the tanning solution.

A 60 L capacity ultrasonic tank with a built-in ultrasounds generator (27 kH and 1000 W) was employed to carry out the second series of experiments. The power can be controlled at 100%, 75%, 50% or 25% in relation to maximum power. During the second stage, the Power/Volume ratio of the float was much lower than the one used during the first stage (68.75 W/L), which can not be obtained in industrial practice. The ratio in the 60 L tank at maximum power is 16.67 W/L and 4.17 W/L at minimum power.

The tests at this stage were conducted using pretanned pieces of hide. The pieces of hide were immersed in an aqueous solution of quebracho and were subject to the effect of US at a constant temperature (40°C). The variables were (a) concentration of tanning solution (30% and 60%), (b) amount of power applied and (c) elapsed time under the effect of US. The time necessary to obtain a through tannage, the variation of density of the tanning solution and the absorption of extract by the skin were controlled throughout the tests. Finally, a comparison of the

appearance of the grain was made between two pieces of hide, one of which tanned with the aid of US and the other of which tanned in a drum.

Three different tests were carried out.

Test One

The concentrations of the tanning liquor were at 30% and at 60%. The percentages of power tested were at 100%, 75%, 50% and 25%. The pieces of hide were immersed in the tanning solution and US were applied for two hours. Next, the pieces of hide were left to stand in the tanning float at room temperature, and the degree of penetration of the liquor through the cross-section of the piece of hide was controlled periodically.

Test Two

This test was carried out considering those variables which rendered shorter times of through-tannage in the previous test, that is to say, the ones at 60% concentration of liquor and at 100% power. Different times of application of US and different means of application were tested.

Test Three

The previous experiment was replicated, the difference being that the times and systems which rendered the best results were used. The power was reduced to 50% in an attempt to minimise the amount of energy expended.

RESULTS AND DISCUSSION

Stage One

The results obtained indicated that particle sizes of those dissolutions subject to the effect of US were smaller than those of the other dissolutions. It was also demonstrated that working with a temperature of 40°C when using US causes a further reduction of particle sizes (Fig 1).

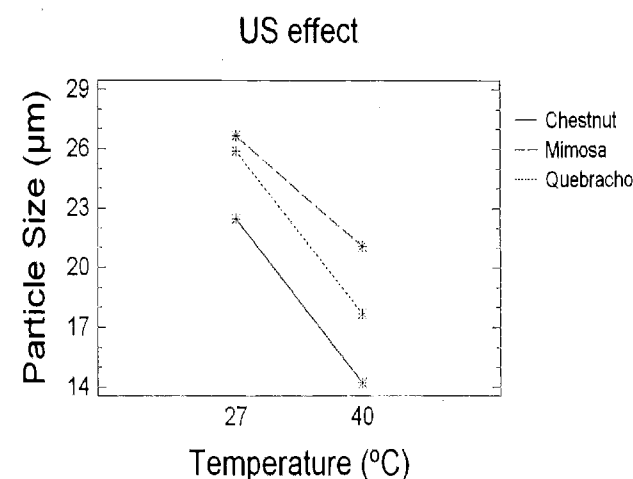


Figure 1. Graph representing one of the analyses conducted

TABLE I
Results of Test One

Power (%)	Concentration (%)	Δ Weight (%)	Δ Baumé (%)	Time of through-tannage (h)
100	30	36.98	7.97	24
100	60	29.38	5.60	12
75	30	38.47	6.06	24
75	60	34.53	2.38	14
50	30	40.50	3.79	24
50	60	35.91	3.80	24
25	30	38.44	2.25	24
25	60	34.6	3.34	24

TABLE II
Results of Test Two. hUS = amount of hours of application of US; hR = amount of hours on stand without application of US

Time and System of application of US (h)	Δ Weight (%)	Δ Baumé (%)	Stand time until through-tannage is achieved
3 hUS + 3 hR + 3 hUS	32.92	5.2	0
2 hUS + 2 hR + 2 hUS	36.20	2.35	24h
3 hUS	25.59	3.30	24h
6 hUS	28.67	2.42	1h 45min
5 hUS	23.07	3.27	1h 45min
4 hUS	28.16	1.85	24h
2 hUS + 2 hR + 2 hUS + 2 hR + 2 hUS	26.21	2.80	0
2 hUS	29.04	2.29	24h

TABLE III
Results of Test Three. hUS = amount of hours of application of US; hR = amount of hours on stand without application of US

Time and System of application of US (h)	Δ Weight (%)	Δ Baumé (%)	Stand time until through-tannage is achieved
3 hUS + 3 hR + 3 hUS	25.62	5.30	2h
6 hUS	25.85	2.71	1h 50min
5 hUS	24.61	3.30	1h 40min
2 hUS + 2 hR + 2 hUS + 2 hR + 2 hUS	26.86	5.11	1h

Stage Two

Test One

Both the tests conducted and the results obtained are shown in Table I.

The results obtained indicate that:

- A US application time of 2 hours is insufficient.
- The more concentrated the tanning liquor and the higher the power of US, the more rapid the through-tannage.

Test Two

The tests conducted and the results are shown in Table II.

It may be concluded that a minimum amount of time of US action is required in order to obtain quick through tannages. In this case, the minimum time was 5 hours.

Test Three

Both the tests and the results are shown in Table III.

The results obtained are very similar to those from the previous test. Hence, what can be concluded from these results is that the effect of the US remains almost unaltered when the power has been reduced in half.

Finally, the grain of the skins from the tests with US was compared to that of skins tanned in a drum. The former have a finer grain of higher quality.

CONCLUSIONS

The results obtained demonstrate that the use of US in vegetable tannage is technically feasible in industrial practice. Therefore, it may be an interesting choice when it is desirable to obtain high quality leathers while largely avoiding the grain defects caused by the mechanical effect of the drum.

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BIBLIOGRAPHY

1. Fridman, V. M.; Zaider, A. L.; Dolgoplov, V.; Mikhailov, A. M. *Legk. Promst.* **14**, 43, 1954
2. Herfeld, H. *Gerbereiniss. Pranis* **30**, 144, 1978
3. Akseband, A. M.; Grif, M. G.; Nozhenko, A. N. *Kozh. Obuvn. Promst.* **3**, 24, 1961
4. Timochin, N. A.; Barinov, I. G.; Kraminora, K. G. *Kozh. Obuvn. Promst.* **3**, 15, 1961
5. Ernst, R. L.; Gutmann, F. J. *Soc. Leather Technol. Soc.* **34**, 454, 1950
6. Simoncini, E.; Criscuolo, I. *Cuio Pelli Mater Concianti* **29**, 82, 1953
7. Fridmann, V. M.; Zaider, A. L.; Dogoplov, V.; Mikhailov, A. M. *Legk. Promst.* **18**, 13, 1958
8. Karpman, M. J. *Kozh. Obuvn. Promst.* **4**, 34, 1962
9. Witke, F. *Ost. Leder. Ztg.* **7**, 165, 1952
10. Cujan, Z.; Kolomaznik, K.; Mladek, M. *Leder. Waren.* **19**, 180, 1984
11. Sivakumar, V., Swaminathan, G., Rao, P. G., *JALCA* **88**, 249, 2004
12. Sivakumar, V., Rao, P. G., *Environ. Sci. Technol* **38**, 1616, 2004
13. Sivakumar, V., Rao, P. G., *Ultrasonic Sonochemistry* **10**, 85, 2003
14. Sivakumar, V., Rao, P. G., *JALCA.* **98**, 230, 2003
15. Hauber, R., Germann, H., *World Leather* **14**, 49, 2001
16. Die, J. P., Ding, J. F., Attenburrow, G. E., *JALCA* **95**, 85, 2000
17. Sivakumar, V., Rao, P. G., Proc. Of the XXV IULTCS Congress, Chennai, 1999, 146.
18. Sivakumar, V., Rao, P. G., Proc. of the XXV IULTCS Congress, Chennai, 1999, 216.
19. Ding, J. F., Xie, J. P., Mason, T. J., Proc. of the XXV IULTCS Congress, Chennai, 1999, 185.
20. Ding, J. F., Xie, J. P., Mason, T. J., *JALCA* **83**, 149, 1999
21. Ding, J. F., Xie, J. P., Mason, T. J., *JALCA* **83**, 275, 1999
22. Xie, J. P., Ding, J. F., Attenburrow, G. E., Mason, T. J., Proc of the XXIV IULTCS Congress, London, 1997, 584
23. Xie, J. P., Ding, J. F., Attenburrow, G. E., Mason, T. J., *World Leather* **10**, 57, 1997
24. Xie, J. P., Ding, J. F., Attenburrow, G. E., Mason, T. J., *J. Soc. Leather Technol. Soc.* **81**, 217, 1997
25. Mantysalo, E., Marjoniemi, M., Kilpeläinen, M., *Ultrasonic Sonochemistry* **4**, 141, 1997
26. Xie, J.P., Ding, J. F., Mason, T.J., Attenburrow, G. E., Proc. of the ALCA Annual Meeting, Michigan, 1996, 584.
27. Xie, J.P., Ding, J. F., Mason, T.J., Attenburrow, G. E., Proc. of the XXIII IULTCS Congress, Friedrichshafen, 1995, 60.
28. ALPA SpA, *World Leather* **8**, 54, 1995