

EFFECT OF ULTRASOUND ON SEVERAL CHROMIUM TANNING PARAMETERS

by

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ABSTRACT

This work studies the effect of several variables on a series of properties of the final leather obtained from chrome tanning, using ultrasounds as the sole mechanical effect during the tanning operation. The variables studied (at two levels by means of a 2^3 factorial design) are tanning temperature, condition of chrome offered (solid or dissolved) and salt basicity. Our studies indicate that the results obtained measuring parameters such as struck-through time of tanning agent, chromium uptake and its distribution, shrinkage temperature, tensile strength, tear load, grain distension and leather burst distention significantly depend on the previously selected level of one or more of the variables being studied. The study of the evolution of the concentration and basicity of the chromium salts has led us to conclude that reutilization is possible. Results show that ultrasound use in chrome tanning is a possibility to consider in the case of leather goods in which the use of drum may not be advisable.

RESUMEN

En este trabajo se estudia el efecto de un conjunto de variables sobre una serie de propiedades del cuero obtenido al curtir al cromo una piel mediante el uso de los ultrasonidos como único efecto mecánico durante la curtición. Mediante un diseño experimental del tipo 2^3 se han estudiado, a dos niveles, las variables temperatura de curtición, estado de la sal de cromo empleada (sólida o en disolución) y la basicidad de esta sal de cromo. Se demuestra que los resultados obtenidos al medir el tiempo de atravesado del curtiente, cromo absorbido y su distribución, temperatura de contracción, resistencia a la tracción, resistencia al desgarrar, distensión de la rotura de flor y distensión de la rotura total, dependen significativamente del nivel escogido de una o más de las variables estudiadas. El estudio de la evolución de las concentraciones y las basicidades de las sales de cromo utilizadas llevan a la conclusión de que su reutilización es posible. Los resultados obtenidos permiten concluir que el uso de los ultrasonidos en la curtición al cromo es una posibilidad a considerar en el caso de artículos donde el uso del bombo es desaconsejable.

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Manuscript received September 30, 2009, accepted for publication January 19, 2010

INTRODUCTION

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 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 1950's. Results from these studies have generally been satisfactory. However, it is necessary to carry out more research to make an industrial application feasible.

The use of ultrasound could be beneficial in the chrome-tanning operation. Certain types of leather are not to be tanned in drums due to their damaging mechanical effect. A clear example of this is sheepskin in which wool is to be preserved (double-face). If these skins were tanned using the drum, a felting effect on the wool would appear and thus the desired outcome would not be reached. Nowadays, to obtain the desired leather goods, vessels with little mechanical effect on the skins are being used, thus avoiding wool felting. Paddles are an example of this type of vessels. However, this working system presents several serious drawbacks. The first is tanning time, since the process takes longer to be completed and consequently productivity drops as manufacturing costs rise. Another inconvenient is the great amount of water and chemicals required.

Several researchers have provided evidence to support the fact that ultrasounds accelerate the penetration of chromium salts into the skin or hide. Nevertheless, more advanced research is needed to examine the influence of the various variables involved (or that may be involved in chrome tanning) on both the leather and wastewater generated.

Therefore, our objective has been to further study the matter to be able to later develop a feasible industrial system for chrome tanning in a static system with ultrasounds. To this aim we have changed three of the variables of this type of tanning in different tests. Then, we have examined the differences observed in some of the properties of tanned leather, using only ultrasounds as mechanical effect in the tanning. An experimental design and statistical calculus were used.

EXPERIMENTAL

Hide and chemicals

The tests were carried out using pieces (200mm X 150mm approx.) of split pickled bovine hide (pH = 2.8).

The chemical products used in the processes were: Chromium (III) salts (33 and 42% basicity), sodium bicarbonate (99.5-100%) P.A., sodium formate (99%) P.A., formic acid (85%) P.A., sulphated oil (75% active matter), sulphited oil (70% active matter), and phosphoric ester oil, (60% active matter).

Equipment

The following instruments were used:

- Tank with a built-in ultrasounds generator, P. Selecta brand. Working frequency: 40 kHz. Capacity: 6L. Power of ultrasounds: 150W. A system allowing the addition of cold water was built in so as to control the working temperature (Figure 1).
- Laboratory drums, Inoxvic brand. Measurements: 150mm in width X 300mm in diameter.
- Pilot plant splitting machine, Gines brand.

Variables studied and experimental design

The three variables studied were tanning temperature, chromium salt state (solid or liquid) at the beginning of the tanning, and the basicity of the chromium salt used. Each variable was studied on two levels using a type 2³ experimental design. The variables and the levels selected are shown in Table I. Table II shows the eight experiments required by the experimental design.

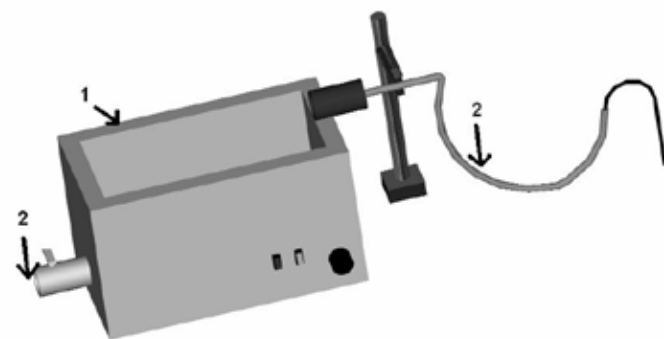


Fig. 1. Ultrasound tank (1) fitted with a system of water circulation (2) in order to control the temperature.

Methodology

1. Sample Preparation

Each piece of pickled hide was introduced in an airtight, sealed plastic bag together with the corresponding salt. In the tests in which the chromium salt was in the liquid form, a solution was prepared at 50 percent (weight/vol.) with water of which 300mL was introduced in the plastic bag. In the tests in which solid salt was required, the amount to be used was such as to be able to cover the whole surface of the hide. Overall, in all cases the amount of salt offered was more than enough to be able to tan the piece of hide involved.

TABLE I
Variables and levels
of the experimental design 2³

Variables	Level 0	Level 1
A = Tanning temperature (°C)	20-25	30-35
B = Chrome salt state	50% solution	Solid
C = Basicity (%)	33	42

TABLE II
Experimental design 2³

Test	Temperature	Chrome salt state	Basicity
1	0	0	0
2	0	0	1
3	0	1	0
4	0	1	1
5	1	0	0
6	1	0	1
7	1	1	0
8	1	1	1

2. Tannage

Three replicas of one of the eight experiments in the experimental design were carried out. In each experiment the plastic bag containing the piece of hide and the corresponding chromium salt were put in the ultrasound tank full of water. After turning on the ultrasound generator, the degree of penetration of the chromium was periodically checked by cutting the hide. When the piece of hide was completely crossed by the chromium, the struck-through time was recorded. Later on, the bag was removed from the ultrasound tank and was gently washed.

3. Basification

Once washed, each piece of hide was basified in an individual basis in a lab drum. Once the piece of hide was put in the drum, 500mL of an aqueous solution adjusted at pH 2.9 with formic acid was added. The drum was set to run and several takes of a 5 percent (weight/weight) aqueous solution of sodium bicarbonate was added, as the aim was to keep the pH of the float at 4 for two hours and also that at the end of the operation the cut in the hide would also show a pH value of 4. The operation finished by removing the leather from the drum and letting it rest for 24 hours.

4. Neutralization and Fatliquoring

These two operations were carried out independently for each of the leather pieces in a laboratory drum with the following formulation (Table III).

5. Chemical analyses and physical tests

The thickness of the dry pieces was approximately 5mm. The samples needed to analyze the chromium contained in each piece were taken. Later on the pieces were introduced in the splitting machine achieving thus three layers, namely grain layer with 2mm thickness approximately, 2mm-intermediate split, and a last layer corresponding to the flesh layer, with

TABLE III
Formulation

(On Split Weight):		
Neutralization	100% H ₂ O	r – 10 min.
	1% NaHCOO (1:10) slowly	r – 10 min
	X% NaHCO ₃ (5%) slowly since pH 5.5	r – 2 h. Check through tannage
		Overnight rest
Fatliquoring	100% H ₂ O	
	6% Sulphated oil	
	2% Phosphoric ester oil	
	2% Sulphited oil	T = 40°C r – 2h. 30 min.
	1% HCOOH (1:10)	r – 30 min.
		1 day rest
Toggling		

1mm thickness approximately. Physical tests were carried out on the grain layer. The chromium content of the intermediate split in experiments 1, 2, 7 and 8 was also analyzed.

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

- IUP 6. Measurement of tensile strength (TS) and percentage elongation (E).
- IUP 8. Measurement of tear load (TL).
- IUP 9. Measurement of distension of grain by the ball burst test (GD).
- Leather burst distension (LBD). Value obtained with the lastometer, following almost the same steps as with IUP

9 in the previous case but finishing with the total crack of the leather.

- IUP 16. Measurement of shrinkage temperature up to 100°C (Ts).
- IUC 8. Determination of chromium oxide content.

The chrome content, the basicity of the floats and the initial and final chrome contents of tests 2, 5, 7 and 8 were also analyzed³³ to assess any variations that would compromise reutilization of floats.

6. Mathematical analysis of the results

A computer program named Statgraphics Plus (Statpoint Technologies, Inc. (USA)), allowed us to carry out the variance analyses and linear regressions to be able to reach pertinent conclusions.

TABLE IV

Results of physical tests and chemical analysis performed on the leather

Test	A	B	C	Cr ₂ O ₃ (%)	Ts (°C)	TS (N)	E (%)
1	0	0	0	3.49±0.01	108±1	2009±40	34.8±1.4
1	0	0	0	3.19±0.01	106±1	1839±37	33.7±1.3
1"	0	0	0	3.10±0.01	107±1	1982±40	34.2±1.4
2	0	0	1	2.22±0.01	99±1	2311±46	42.8±1.7
2'	0	0	1	2.87±0.01	102±1	2377±48	39.7±1.6
2"	0	0	1	2.79±0.01	103±1	2344±47	38.2±1.5
3	0	1	0	4.56±0.01	116±1	1407±28	33.2±1.3
3'	0	1	0	3.51±0.01	108±1	1774±35	34.2±1.4
3"	0	1	0	3.89±0.01	113±1	1577±32	33.8±1.4
4	0	1	1	4.30±0.01	116±1	2140±43	37.9±1.5
4'	0	1	1	3.37±0.01	106±1	2117±42	36.0±1.4
4"	0	1	1	3.61±0.01	109±1	21.35±43	36.8±1.5
5	1	0	0	3.30±0.01	106±1	21.04±42	34.4±1.4
5'	1	0	0	2.89±0.01	104±1	1830±37	33.3±1.3
5"	1	0	0	2.73±0.01	104±1	2024±40	38.5±1.5
6	1	0	1	2.56±0.01	102±1	2198±44	41.1±1.6
6'	1	0	1	2.39±0.01	104±1	2370±47	46.9±1.9
6"	1	0	1	2.43±0.01	102±1	2284±45	35.0±1.4
7	1	1	0	3.99±0.01	115±1	1989±40	40.4±1.6
7'	1	1	0	3.38±0.01	107±1	2065±41	34.4±1.4
7"	1	1	0	3.71±0.01	107±1	2304±46	44.6±1.8
8	1	1	1	3.60±0.01	108±1	2285±45	35.8±1.4
8'	1	1	1	3.43±0.01	107±1	2313±46	33.3±1.3
8"	1	1	1	3.83±0.01	110±1	2242±45	41.9±1.7

RESULTS AND DISCUSSION

1. Final properties of the leather

Results of the tests performed are shown in Table IV and Table V. These results indicate that the pieces of leather obtained comply with the necessary requirements to manufacture a wide range of leather goods.

Variance analysis was performed to determine whether the time of fully penetration (struck-through time) depended on any of the tested variables. Results shown on Table VI show that the fully penetration time depended significantly (confidence interval equal or over 95%) on the three variables essayed: working temperature, state (solid or liquid) of the chromium salt offered, and salt basicity. Confidence interval (expressed in percentage) is obtained by subtracting the value

of the P-value column to 1 and then multiplying the result by 100. The fact that a variable is significant means that the result of the property studied is clearly different depending on the level (0 or 1) at which that variable is applied in the experiment.

The data reflected on Table VII allow us to draw a comparison between the means obtained working on each of the levels.

Finally Figure 2 shows the significant differences for the temperature variable when working with one or the other level.

The results of the variance analysis indicate that the penetration was faster when working at higher temperatures (30-35°C), with the chromium salt offered in liquid form and with greater basicity (42%). The first result may be explained

TABLE V

Results of physical tests and chemical analysis performed on the leather

Test	A	B	C	TL (N/mm)	Struck-through time (h)	GD (mm)	LBD (mm)
1	0	0	0	81±5	3.42±0.01	14.7±0.4	15.2±0.4
1'	0	0	0	82±5	3.00±0.01	14.7±0.4	15.6±0.4
1"	0	0	0	90±5	3.92±0.01	15.9±0.4	17.6±0.4
2	0	0	1	100±6	2.42±0.01	15.8±0.4	17.1±0.4
2'	0	0	1	93±6	2.25±0.01	14.2±0.4	17.1±0.4
2"	0	0	1	83±5	3.83±0.01	15.4±0.4	16.7±0.4
3	0	1	0	70±4	5.00±0.01	13.0±0.3	15.2±0.4
3'	0	1	0	68±4	5.00±0.01	14.6±0.4	15.0±0.4
3"	0	1	0	73±4	5.00±0.01	13.8±0.3	15.1±0.4
4	0	1	1	82±5	5.33±0.01	15.3±0.4	15.9±0.4
4'	0	1	1	88±5	3.58±0.01	14.2±0.4	15.1±0.4
4"	0	1	1	78±5	4.80±0.01	14.8±0.4	15.4±0.4
5	1	0	0	81±5	2.75±0.01	16.1±0.4	18.0±0.5
5'	1	0	0	69±4	3.50±0.01	15.9±0.4	16.8±0.4
5"	1	0	0	93±6	2.33±0.01	14.2±0.4	15.7±0.4
6	1	0	1	87±5	2.00±0.01	16.1±0.4	17.8±0.4
6'	1	0	1	119±7	1.67±0.01	14.5±0.4	18.1±0.5
6"	1	0	1	103±6	3.00±0.01	16.5±0.4	18.0±0.5
7	1	1	0	98±6	4.75±0.01	15.1±0.4	16.0±0.4
7'	1	1	0	95±6	3.33±0.01	15.6±0.4	16.3±0.4
7"	1	1	0	93±6	4.58±0.01	15.9±0.4	16.2±0.4
8	1	1	1	98±6	3.45±0.01	15.0±0.4	16.9±0.4
8'	1	1	1	87±5	4.17±0.01	14.3±0.4	17.6±0.4
8"	1	1	1	112±7	3.17±0.01	15.4±0.4	16.1±0.4

TABLE VI

Analysis of Variance for time

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:Temperature	3.26344	1	3.26344	9.20	0.0066
B:State	13.6052	1	13.5062	38.35	0.0000
C:Basicity	1.9895	1	1.9895	5.61	0.0281
RESIDUAL	7.09522	20	0.354761		
TOTAL	25.9534	23			

All F-ratios are based on the residual mean square error

TABLE VII

Table of Least Squares Means for time with 95 Percent Confidence Intervals

Level	Count	Mean	Std. Error	Lower Limit	Upper Limit
GRAND MEAN	24	3.59375			
Temperature					
0	12	3.9625	0.17194	3.60384	4.32116
1	12	3.225	0.17194	2.86634	3.58366
State					
0	12	2.84083	0.17194		
1	12	4.34667	0.17194		
Basicity					
0	12	3.88167	0.17194	3.52301	4.24033
1	12	3.30583	0.17194	2.94717	3.66449

as follows: the higher the temperature, the higher the diffusion speed of the chrome towards the inner part of the hide. The fact that the chromium in liquid state penetrates faster than in the solid state may be because solid salt needs to dissolve prior to penetration and this of course entails additional time. Finally, the fact that salt with greater basicity shows faster penetration may be because it is less cationic and thus reacts

less with the reactive anionic points in the hide, spreading more quickly towards the center of the hide.

The next step was to check which of the properties analyzed through the physical tests and chemical analyses of the hide depended directly on struck-through time, that is to say, the time in which the pickled hide had been in contact with the

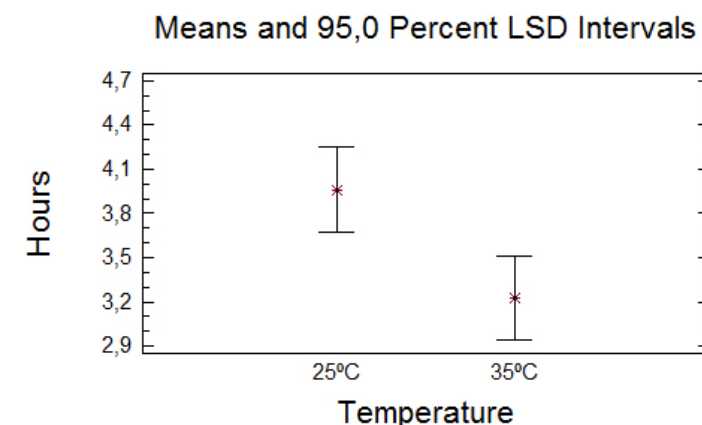


Fig. 2. Influence of the temperature on the struck-through time of the chromium.

chromium salt. To do this, analysis linear regressions were calculated with the penetration time as an independent variable and the different properties analyzed as dependent variables. These linear regressions were carried out with the means of the results obtained in the three repetitions of each experiment. The analyses of the results demonstrated that three of the properties analyzed (chrome content, shrinkage temperature and total distension) were intimately related with struck-through time. The equations obtained and their determination coefficients were as follows:

$$\%Cr_2O_3 = 0.56t + 1.27 \quad R^2 = 0.913686 \quad (1)$$

$$Ts = 3.68t + 93.77 \quad R^2 = 0.861239 \quad (2)$$

$$DT = -0.90t + 19.69 \quad R^2 = 0.871805 \quad (3)$$

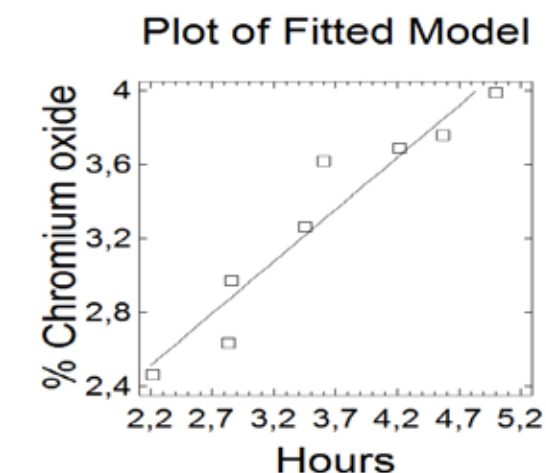


Fig. 3. Example of the graphic obtained in a Regression Analysis.

R² represents parts per unit of the experimental results that are explained with the equation provided. When working with hides, that is to say, an uneven initial substratum, R² obtained show a great dependence of each of the depending variables considered towards the tanning time of each piece of pickled hide.

Table VIII is an example of the results obtained. Figure 3 shows a graphic representation of the results.

Therefore we can state that the longer the struck-through time, the greater the chrome content in the hide and the higher the shrinkage temperature, but the lower the burst distension.

If we calculate the equation of the regression line, considering the grain distension as depending variable and the struck-through time as independent variable, we obtain:
 $DF = -0.46t + 16.69 \quad R^2 = 0.558072 \quad (4)$

TABLE VIII

Regression Analysis – Linear model: Y = a + b*X
Dependent variable: % Cr₂O₃
Independent Variable: time

Parameter	Estimate	Std. Error	T Statistic	P-Value
Intercept	1.27265	0.261768	4.86173	0.0028
Slope	0.563438	0.0706988	7.96955	0.0002

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	2.01664	1	2.01664	63.51	0.0002
Residual	0.190508	6	0.0317513		
Total	2.20715	7			

Although R² is rather low, the equation explains 56% of the experimental results. Taking into account the afore-mentioned variability due to the uneven appearance of hides, it is very probable that the longer the tanning time, the lower the grain distention values. If we bear in mind that the amount of chrome being fixated on the grain is increasing and that the tendency is the same than that obtained for total distention values, the consideration seems to be quite reasonable.

Finally, the variance analysis was carried out to determine whether the analyzed properties that were not directly related with struck-through time (tensile strength, elongation and tear load) depended somehow on the variables selected when designing the experimental design (working temperature, state and basicity of the chromium salt being used). Results indicated that when salt basicity is 42°Sch the values obtained for tensile strength and tear load are higher. The same results are obtained when the working temperature is 30-35°C. Finally, when the 50% salt chrome solution is used the values obtained for tearing strength are higher. These results show that the levels of the variables that enable a shortening of struck-through times involve higher values for the physical properties of the final leather. The variance analysis allowed us to detect that the interaction between the variables of working temperature and state of chromium had an influence on the results obtained when measuring both tensile strength and tear load. In both cases we observed that tanning at 20-25°C the values obtained are higher if the 50% chromium salt solution was used. However, when tanning at 30-35°C similar values were obtained regardless of the state of the chromium salt being used. The variance analysis also allowed us to detect that the interaction between the variables of working temperature and basicity of the chromium salt had an influence on the results obtained when measuring tensile

strength. If the basicity of the chromium salt is 33% the values obtained are lower than those obtained if the chrome salt basicity is 42%. However, the difference between values is significantly greater when working at 20-25°C than when working at 30-35°C. Figure 4 shows one of these interactions.

Table IX outlines a summary of the relations established between the different parameters studied. “*” sign indicates that a significant relation may be established between the variable and the property. The number in parentheses indicates the level of the variable in which best results have been found for each of the properties.

2. Distribution of chrome in the hide

Table X shows results obtained in the analyses of total chrome content in the hides and chrome content of the intermediate splits carried out on four pieces of hide from different tests performed.

Results show that when using 33% chrome salt, more chrome gets fixated on the leather. On the other hand, the greater the basicity of the chrome salt, the more evenly distributed throughout the thickness of the hide the chrome will be. Our conclusions are consistent with the fact that struck-through tanned times in less basic chrome salt are longer. This is probably due to the fact that the less basic the chrome salt, the more cationic it will be and then the more chrome will be linked in the anionic reactive points of the pickled hides. Consequently, the more basicity the salt has, the more evenly and rapidly the salt will spread through the cut in the hide.

3. Study of tanning floats

Table XI below shows the results obtained in the analysis of chrome content and basicity of initial and final tanning floats

TABLE IX

Relations between variables and analyzed properties

Properties	A	B	C	AB	AC	BC
Time	*(1)	*(0)	*(1)			
TS	*(1)	*(0)	*(1)	*	*	
E						
TL	*(1)		*(1)	*		
% Cr ₂ O ₃	Values increase with struck-through time				R ² = 0.913686	
Ts					R ² = 0.861239	
GD	Values decrease with struck-through time				R ² = 0.871805	
LBD					R ² = 0.558072	

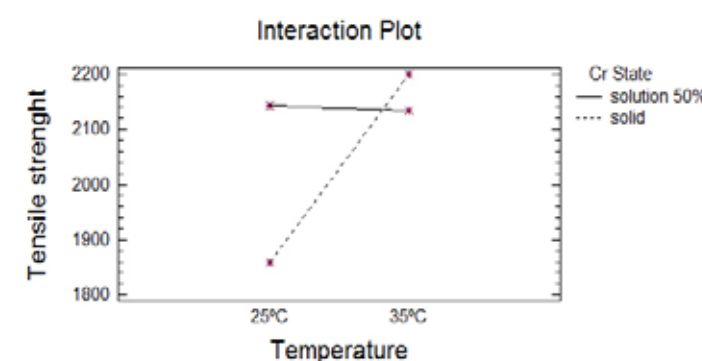


Fig. 4. Interaction affecting TS results

corresponding to four different tests of the experimental design.

Results obtained indicate that, in all cases analyzed, both the chrome concentration and the basicity of the offered salts decrease, which is logical, since the pickled hides uptake chrome and acidify chromium salts. However, such decrease

is rather small and consequently the residual chrome salt may be reutilized. In the case of solid residual chrome salt the results are deceiving since the decrease in chrome is explained because it has been partially dissolved with the pickle float, not simply because it has been taken up by the hide.

CONCLUSIONS

Our study shows that the use of ultrasound as a source of mechanical effect should be considered when chrome tanning poses health hazards or threatens the quality of the outcome.

Results also indicate that variables such as struck-through time by tanning agent, uptake of chrome and its distribution, shrinkage temperature, tensile strength, tear load, grain distention and leather burst distention, are significantly related to the tanning temperature, the state of the chromium salt, and /or the basicity of such chromium salts. Also, the analyses of the residual floats indicate that these may be reutilized.

TABLE X

Contents of chrome in hide and splits

Test	A	B	C	Cr ₂ O ₃ hide (%)	Cr ₂ O ₃ splits (%)	Δ Cr ₂ O ₃ hide/splits (%)
1	0	0	0	3.49±0.01	3.13±0.01	10.30
2	0	0	1	2.22±0.01	2.08±0.01	6.31
7	1	1	0	3.99±0.01	3.81±0.01	4.51
8	1	1	1	3.60±0.01	3.48±0.01	3.33

TABLE XI

Evolution of chrome and basicity of salt in tanning processes

Test	A	B	C	Basicity (°Schor.)		Cr ₂ O ₃ (dis.) (g/L)		Cr ₂ O ₃ (sol.) (%)
				Initial	Final	Initial	Final	
2	0	0	1	42.0±0.1	40.8±0.1	175.0±0.1	142.0±0.1	
5	1	0	0	33.3±0.1	30.2±0.1	177.4±0.1	143.3±0.1	
7	1	1	0	33.3±0.1	32.3±0.1			16.9±0.1
8	1	1	1	42.0±0.1	39.8±0.1			16.5±0.1