Study of a Chrome Tanning Process without Float and with Low-Salt Content Compared to a Traditional Process. Part I*

by

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Abstract

The traditional chrome-tanning process poses several disadvantages from the environmental point of view including effluent volume as well as chromium and chloride content. We have thus modified the process in order to minimize these disadvantages. The tanning process has been carried out with almost no float by simply utilizing the float already contained in the hide. As there is very little water, the quantity of sodium chloride required to avoid the swelling of the skin decreases sharply, due to the acidic conditions. In a corresponding manner, the mechanical work on the skin increases and the fixation of chrome salt is greater.

Water consumption and chrome discharge are dramatically lower using the new system instead of the traditional system. A comparison of results shows that by using the new system water consumption decreases by 78 percent, chrome oxide content by 86 percent and chlorides present in the effluents by 94 percent.

Abstracto

El proceso tradicional de curtido al cromo posee varias desventajas desde el punto de vista ambiental incluyendo el voluminoso efluente como también por su contenido de cromo y cloruro. Por tal motivo hemos modificado el proceso para minimizar estas desventajas. El proceso de curtición fue efectuado casi sin baño simplemente utilizando el baño residual ya contenido en la piel. Como el contenido de agua es tan mínimo, la cantidad de cloruro de sodio requerido para evitar el hinchamiento, debido a las condiciones ácidas, disminuye fuertemente. Correspondientemente el efecto mecánico aumenta y la fijación de la sal de cromo se incrementa.

El consumo de agua y la descarga de cromo dramáticamente disminuyen utilizando este nuevo sistema en vez del sistema tradicional. Comparando resultados demuestra que el uso del nuevo sistema reduce el consumo de agua en 78%, y reduce en los efluentes el contenido de óxido de cromo en 86% y cloruros en 94%.

Introduction

The traditional chrome-tanning process poses some disadvantages from the environmental point of view. The most significant of these are effluent volume as well as chromium and chloride content[1-6]. The traditional system consists of carrying out the tanning by submerging the hides in a water float within the drum. Then the drum rotates round its axle producing the required movement so that the tanning chemical (chromium salt) can spread throughout the hide [7-11].

To obtain a suitable pH we must add acid. However, added acid will swell the hides, which hampers the spreading of chromium salt within the hide and prevents tanning. In order to avoid this counterproductive effect, sodium chloride is added to the float. By osmotic pressure the salt reduces swelling of the hides and dehydrates the fibers.

This traditional tanning process generates significant amounts of effluents with high concentrations of both chlorides and chromium salt that have not been fixed in the hide. Different systems have been proposed in order to minimize the negative effect of such pollution, but without rejecting on the use of chrome as a tanning material. These systems are, for instance, recirculation and/or recycling of tanning floats[12-17] and processes with high-exhaustion of chrome[18-22].

* The contents of this paper are part of the "Savewatertan" CRAFT Project funded by the EU. Partners involved include Curtits Aqualata, S. A., EUETII and LGR.
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Manuscript received August 8, 2005, accepted for publication November 7, 2005

TABLE I
Low-salt Content Tanning Formulation

(on split weight):		
Delime-Bate	**200%** H_2O a 30-35ºC	rotate- 15', Drain
	150% H_2O a 35ºC	
	1.5% Dicarboxilic acids	rotate-30', pH = 8.5
	0.7% Bate 1200 u.	rotate - 1 h, pH = 8.5
		Drain and wash
Pickle-Tanning	**x%** NaCl	rotate - 15'
	0.5% HCOOH (1:10)	rotate - 30'
	y% H_2SO_4 (1:10)	rotate - 90'
	2% chrome salt 33ºSch.	
	5.5% chrome salt 66ºSch.	
	0.15% MgO	rotate – 6 hours

Rest (24 hours), drain, shave and weigh, neutralize (pH= 5) and fatliquor
x and **y** quantities were added depending on the variables to be studied.

In order to overcome these problems, the solution considered was the undertaking of a process with almost no water, i.e. simply using the water already contained in the hide. Without added water, the amount of sodium chloride required to avoid swelling would be less. At the same time, the mechanical work on the hide would increase and the fixation of chrome salt would be greater.

In order to validate this new method, it is necessary both to analyse the dependence of the leather properties in relation to the main process variables and to quantify the minimisation of the generated waste waters. This includes quantifying their chloride content and chromium content in comparison with the traditional tanning system.

Experimental

Materials

The tests were carried out using 1m. diameter and 0.4m-wide stainless steel drums. The temperature was controlled by using controllable electrical resistances, which were attached between the wall of the drum, and a temperature sensor. Bovine salted hides were used in order to perform the tests. The chemicals employed in the operations are those normally used in the leather industry. The chemical products used in the delime-bate and pickle-tanning processes are:

-Dicarboxilic acids provided by Cromogenia Units, S.A.
-Bate 1200 u. Kubelka (Oropon ORE) provided by Curtex, S.A.
-Sodium Chloride (NaCl)
-Formic Acid (85%) (HCOOH)
-Sulphuric Acid (96%) (H_2SO_4)
-Chrome salt 33ºSch. provided by Curtex, S.A.
-Chrome salt 66ºSch. provided by Stoppani
-Magnesium Oxide (MgO)

Methodology

1. A study of the influence of the main process variables on the quality of the final leather obtained

The hides were first soaked, then unhaired using 2 percent sodium sulfide and 3 percent lime, defleshed and split at 3mm.

A type formulation was designed so that two of the chemical additions (i.e. salt and sulphuric acid) were the variables to be studied. The difference with a classical formulation lies in the absence of water in the Pickle-Tanning process. This formulation was as follows in Table 1.

A second-order centralized, orthogonal and rotatable experimental design was chosen in order to carry out the experimentation. Table II shows the thirteen 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 13 are replicates and give a measure of experimental error, which is important of measuring the significance of the variable effects[23-24].

The levels of the experimental design were chosen and are detailed in Table III.

The tests were carried out and the following physical and chemical leather properties were analysed:

- Tensile strength (TS) in accordance with the IUP 6 Standard

- Elongation (E) in accordance with the IUP 6 Standard
- Tear load (TL) in accordance with the IUP 8 Standard
- Grain crack load (GCL) in accordance with the IUP 9 Standard
- Grain crack distension (GCD) in accordance with the IUP 9 -Standard
- Leather burst load (LBL) in accordance with the IUP 9 Standard
- Leather burst distension (LBD) in accordance with the IUP 9 Standard
- Chromium oxide content (%Cr_2O_3) in accordance with the IUC 8 Standard
- Shrinkage temperature (Tg) in accordance with the IUP 16 Standard (Modified)

2. A Comparison of the results obtained through the tanning process under study with those obtained following the classical tanning process

From the results obtained in the last section, the salt (1.5 percent) and sulphuric acid (0.5 percent) additions were chosen in order to begin the experimentation stage.

Five processes with the same formulation as the one described earlier were carried out although the final tanning temperature was increased to 50ºC.

The float volumes and the residual chrome and chlorides resulting from tanning and draining were quantified in each of the processes. Also, the same physical and chemical tests on leather as the ones described earlier were performed.

A hide batch was processed following a traditional formulation. This formulation is Table IV.

The same analysis as those performed on the leather subjected to the pickle-tanning under study were performed with the aim of comparing the results obtained.

A panel of five experts compared the organoleptic properties of the leather obtained following the tanning process under review.

RESULTS AND DISCUSSION

A study of the influence of the main process variables on the quality of the final leather.

The results obtained are detailed below in Tables V and VI.

The statistical analysis of the results obtained in the experimental plan was carried out by means of the Statgraphics Plus Program. All the possible linear, quadratic effects and interactions were included in the mathematical model. The non significant variables were excluded from the model so as to obtain the optimum regression equations. The regression equation coefficients were estimated by means of the least squares procedure, whereas the significance levels of each variable as well as the determination coefficient (R^2) of the model were calculated by the variance analysis (ANOVA).

TABLE II
Experimental Design

Test	NaCl Offer	H_2SO_4 Offer
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
13	0	0

TABLE III
Levels of the Experimental Design

	-1.414	-1	0	1	1.414
NaCL Offer (%)	0	0.44	1.5	2.56	3
H_2SO_4 Offer (%)	0	0.15	0.5	0.85	1

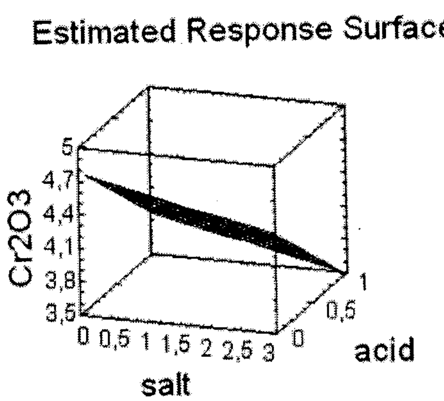

Figure 1. Variation of the chrome oxide content

For each of the analyzed properties we established the following relations:

$$\%Cr_2O_3 = 4.7 - 0.1\,[NaCl] - 0.9\,[H_2SO_4] \quad (1)$$

The higher the salt and sulphuric acid additions, the lower the chrome content of the final leather. (Fig. 1).

$$Tg = 118 - 2\,[NaCl] \quad (2)$$

TABLE IV
Classical Formulation

(on split weight):		
Delime-Bate	200% H_2O a 30-35ºC	rotate- 15' Drain
	150% H_2O a 35ºC	
	1.5% Dicarboxilic acids	rotate-30'
	0.7% Bate 1200 u.	rotate - 1 h pH = 8.5 Drain and wash
Pickle-Tanning	100% H_2O	
	7% NaCl	rotate - 15'
	0.5% HCOOH (1:10)	rotate - 30'
	0.7% H_2SO_4 (1:10)	rotate - 90'
	2% chrome salt 33ºSch.	
	5.5% chrome salt 66ºSch.	
	0.15% MgO	rotate – 6 hours
Rest (24 hours), drain, shave and weigh, neutralize (pH= 5) and fatliquor		

The higher the salt addition, the lower the shrinkage temperature of the final leather.

$$TS = 19.6 + 5.2\,[H_2SO_4] + 0.3\,[NaCl]^2 \quad (3)$$

The higher the sulphuric acid addition, the higher the tensile strength of the final leather.

$$E = 70.69 - 33.46\,[H_2SO_4] + 44.13\,[H_2SO_4]^2 \quad (4)$$

The higher the sulphuric acid addition, the higher the elongation of the final leather. Lower sulphuric acid additions cause a stabilisation in elongation.

$$TL = 97.0 - 32.5\,[NaCl] - 53.0\,[H_2SO_4] + 8.3\,[NaCl]^2 + 98.1\,[H_2SO_4]^2 \quad (5)$$

The higher the sulphuric acid addition, the higher the tearing load in the leather obtained. The higher the salt addition, the lower the tearing load of the final leather.

No relation was found between the additions and the grain crack load.

$$GCD = 10.64 + 1.50\,[H_2SO_4] \quad (6)$$

The higher the sulphuric acid addition, the higher the distension of the grain crack.

$$LBL = 521 + 63\,[NaCl] + 162\,[H_2SO_4]^2 \quad (7)$$

The higher the salt addition, the higher the leather burst load of the final leather.

$$LBD = 15.19 - 5.25\,[H_2SO_4] + 8.64\,[H_2SO_4]^2 \quad (8)$$

The higher the sulphuric acid addition, the higher the leather burst distension. Low acid sulphuric additions cause a stabilisation in the values.

Comparing the results obtained through the tanning process under study with those obtained following the classical tanning process

The appropriate calculations were carried out and the results were as follows in Table VII.

The hides that underwent the new pickle-tanning process showed significant differences regarding physical and chemical properties as compared to those that underwent a classical pickle-tanning. In particular we must stress the higher chrome uptake of leather.

This difference has a negative impact on some of the physical properties that have been analyzed, specially in relation to tearing load and leather burst load.

Experience indicates that in the working ranges the higher the chrome content in a piece of leather the lower the physical properties. This fact and the experimental results lead us to think that a correct and appropriate implementation of the system studied will enable us to obtain same-quality

TABLE V
Physical and Chemical Properties

Test	Grain Crack Load (N)	Shrinkage Temperature (C°)	Tensile Strength (N/mm²)	Elongation (%)	Tear load (N/mm)
1	4.6±0.1	116±1	20.4±0.3	70.9±2.3	85.7±6.0
2	4.0±0.1	118±1	29.6±0.5	77.3±3.3	112.7±5.1
3	4.0±0.1	105±1	22.3±0.4	61.6±2.3	55.4±3.4
4	3.6±0.1	114±1	24.1±0.4	69.5±2.5	97.5±7.8
5	4.7±0.1	115±1	21.8±0.4	71.1±3.9	67.9±4.1
6	3.7±0.1	114±1	24.9±0.6	82.2±3.0	108.7±7.8
7	4.2±0.1	117±1	25.9±0.5	65.7±2.6	88.7±6.8
8	4.2±0.1	115±1	29.4±0.5	72.1±3.6	76.3±3.8
9	4.2±0.1	117±1	18.9±0.2	60.4±2.7	56.3±2.8
10	4.1±0.1	116±1	22.7±0.3	58.5±2.2	58.7±4.3
11	4.0±0.1	115±1	21.4±0.3	64.5±1.9	60.1±4.1
12	4.2±0.1	116±1	17.5±0.2	71.9±3.0	63.0±3.9
13	4.2±0.1	115±1	23.0±0.3	63.1±2.1	87.3±4.5

TABLE VI
Physical Properties

Test	Grain Crack Load(N)	Leather Burst Distension (mm)	Load (N)	Distension(mm)
1	304±16	10.13±0.29	582±30	14.05±0.42
2	296±14	11.45±0.30	621±30	16.15±0.44
3	308±12	11.65±0.33	588±23	14.12±0.41
4	339±17	11.17±0.27	832±40	15.62±0.34
5	321±13	10.39±0.25	761±30	15.57±0.36
6	420±29	12.78±0.31	813±55	19.76±0.57
7	361±21	11.44±0.34	642±37	15.02±0.44
8	545±34	12.89±0.34	866±52	15.75±0.38
9	334±20	11.86±0.30	583±36	15.47±0.42
10	361±21	11.45±0.31	515±30	13.81±0.39
11	277±15	10.79±0.23	544±29	14.63±0.29
12	284±20	11.63±0.27	706±49	15.06±0.33
13	360±23	10.48±0.24	635±42	14.95±0.36

TABLE VII
Analysed Properties

Properties	Low-salt Process	Classical Process
Tensile strength (N/mm²)	29.2±0.5	20.4±0.4
Elongation (%)	64.5±1.9	70.5±2.3
Tear load (N/mm)	65.6±3.0	78.7±3.1
Grain crack load (N)	394±28	317±22
Grain crack distension (mm)	13.24±0.53	11.74±0.65
Leather burst load (N)	497±30	622±44
Leather burst distension (mm)	14.64±0.56	14.80±0.74
Cr_2O_3 in leather (%)	4.6±0.1	3.2±0.1
Shrinkage temperature. (°C)	116±1	109±1
Float volume (L/t hide)	241±1	1000±1
Chlorides in float (kg/t hide)	1.90±0.01	30.70±0.01
Cr_2O_3 in float (kg/t hide)	0.88±0.01	6.13±0.01

leather with savings in chrome salt addition and subsequent discharge.

Water consumption and chrome discharge are lower using the new system than with the traditional system. The reduction may be quantified in approximately 76 percent in the case of water (float volume) and in 86 percent in the case of chrome oxide content (chrome in float) and in 94 percent in the case of chlorides content present in the effluent (i.e. chlorides in float) when using the new proposed system as opposed to the traditional system. These percentages refer directly to the pickle and tannage operations. If we consider the whole tanning process, from soaking to finishing, the percentages would obviously be lower.

As for the organoleptic properties of the resulting leather obtained, they were checked by a panel of five experts. It was agreed that the properties were acceptable. The leathers did not show grain abrasion and were therefore considered commercially viable.

CONCLUSIONS

A tanning process without a float has been developed. The absence of float prevents acid swelling and allows for minimal salt additons. These salt additions as well as the sulphuric acid additions influence both chrome uptake and several physical properties of the final leather.

The final leather obtained through the developed process has a higher chrome uptake than those leathers obtained through the classical process, that is the process with float.

The process developed shows considerable environmental advantages since it contributes significantly a decrease in water consumption, wastewater volume and the presence of chrome and chlorides in effluents.

ACKNOWLEDGEMENT

The authors are indebted to the EU for the financial support given through the project CRAFT-1999-71560.

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