

OPTIMIZATION OF TWO LOW-SALT CHROME TANNING PROCESSES WITHOUT FLOAT

by

J.M. MORERA^{1*}, A. BACARDIT¹, L. OLLÉ¹, J. COSTA², S. BANASZAK³

¹*Igualada Technical Engineering School. (EUETII)
Technical University of Catalonia (UPC)
PLAÇA DEL REI, 15. 08700-IGUALADA, SPAIN*

²*Chemical and Metallurgical Engineering Department. Chemistry Faculty
University of Barcelona (UB)
MARTÍ FRANQUESA, 1. 08028-BARCELONA, SPAIN*

³*Lederinstitut Geberschule Reutlingen
ERWIN-SEIZ-STRASSE, 9. D-72764 REUTLINGEN, GERMANY*

ABSTRACT

The aim of this study was to develop at pilot plant level two systems of pickle-tanning that would reduce both the amount of waste water and its content in chrome and chlorides while obtaining leathers that are commercially acceptable. In the first one, the effect of the variation of the final tanning temperature as well as the system of adding the basificant in the formulation of a chrome tanning without float were studied. A 87 percent reduction of the residual float was obtained with this system. The amount of chrome in wastewater was reduced by 96 percent in this study as compared to that of a traditional tanning process. The reduction of chlorides in all the tanning tests without float was maintained at around 94 percent. In the second one, the pickle process was carried out without float and with low salt addition, and the inorganic acids were replaced by a sulphoaromatic acid. The effect of the variation of the final temperature was studied in the tanning, as well as the type of basification used for the chrome exhaustion in the residual float. A 88 percent reduction of the residual float was obtained with this system, as well as a 99 percent reduction in chrome content in wastewater and a 93 percent reduction in chlorides content in wastewater.

ABSTRACTO

El objetivo de este estudio fue el desarrollo, a nivel de planta piloto, de dos sistemas de piqué-curción que permitan reducir tanto la cantidad de agua residual como su contenido en cromo y cloruros, obteniendo al mismo tiempo cueros comercialmente aceptables. En el

primer sistema se ha estudiado, en una curción al cromo sin adición de baño, tanto el efecto de la variación de la temperatura final de curción como el sistema de adición del basificante. Con este sistema se obtuvo una reducción del 87 por ciento del baño residual. Al comparar el sistema estudiado con un proceso de curción al cromo tradicional se observó una reducción del 96 por ciento de la cantidad de cromo contenido en el baño residual. En todas las pruebas de curción sin baño realizadas la reducción de los cloruros se mantuvo alrededor del 94 por ciento. En el segundo sistema desarrollado, el piqué se realizó sin baño y con baja adición de sal, y los ácidos fueron reemplazados por un ácido sulfoaromático. Se estudió el efecto en el agotamiento del cromo en el baño residual en función de la variación de la temperatura final en la curción y del sistema de adición del basificante. Con este sistema se obtuvo una reducción del 88 por ciento del baño residual, una reducción del 99 por ciento en el contenido de cromo en las aguas residuales y la reducción de un 93 por ciento de los cloruros contenidos en las aguas residuales.

INTRODUCTION

Quite a few studies have been carried out in order to solve the environmental problem caused by the pickle-tanning process¹⁻⁷. These studies focus mainly on the recovery and treatment of the residual chrome⁸⁻¹³ and on high exhaustion tanning processes¹⁴⁻¹⁸. But the floats resulting from pickle tanning are also high in chlorides content and these should be reduced. Because of this, two earlier studies¹⁹⁻²⁰ had developed two pickle-tanning processes at pilot plant level without float, with very low salt content and with high chrome exhaustion. In the second study, the inorganic acids were also replaced by a sulphoaromatic acid.

* Corresponding author - Tel.: +34-93-803-5300; Fax: +34-93-803-1589; E-mail: jmmorera@euetii.upc.edu
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The sulphoaromatic acid is fixed on the external structure of the leather and the remaining section is maintained by the pH of the bating process. In doing so, both grain and shrinking problems when in contact with the chrome salt can be avoided. At the same time, this leaves the leather with a high affinity for the chrome salt which in turn results in a tanning with very high exhaustion²¹⁻²².

If no water is added to the hides at the start of the pickle-tanning, the swelling capacity will decrease and thus much less salt will be needed than in a traditional process. Water floats are used in a traditional process and these oscillate between 60-100 percent of the fleshed weight of the hides. Also, the almost complete absence of float produces a better absorption of the chrome by the hides, both physically (mechanical effect) and chemically (chemical balance).

It has also been shown that the working temperature affects the chrome tanning when a float is used²³⁻²⁸. An increase in temperature results in an increase in the absorption of chrome by the hide. This is very important from an environmental point of view since it causes a decrease in the concentration of chrome in the residual float.

The present study follows on the two aforementioned earlier studies¹⁹⁻²⁰. However, some modifications have been introduced in order to make improvements in the process from the environmental point of view. The present study has investigated both variations in the final temperature and the type of basification used in tanning. An increase in the final temperature of tanning (i) helps the formation of chrome complexes, (ii) increases the diffusion speed of such complexes, and (iii) increases their reaction speed, which results in a higher exhaustion of floats.

At the same time, the fixation of chrome is higher when the basicity of the chrome complex increases. However, the increase of pH has to be slow and as gradual as possible. That is the reason why this study has analyzed the effect of the system of adding the basificant both on the physical properties of the leather and on the resulting residual floats.

Considering the aforementioned, the present study aims to investigate the dependence of the final properties of the manufactured leather as well as the residual floats obtained according to the increase of the final temperature and to the system of adding the basificant. Also, it aims to compare these properties with those of the manufactured leather using the traditional system, as well as to check whether the tested systems results in significant improvements in the sustainability of the traditional process.

EXPERIMENTAL

Material

The tests were carried out using 1m-high (i.e. 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:

- Dicarboxylic 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%) (H₂SO₄)

TABLE I
Low-salt content tanning (Formulation I)

(on split weight):		
Delime-Bate	200% H ₂ O at 30-35°C	rotate- 15' Drain
	150% H ₂ O at 35°C	
	1.5% Dicarboxylic acids	rotate - 30'
	0.7% Bate 1200 u.	rotate - 1 h pH = 8.5 Drain and wash
Pickle-Tanning	1.5% NaCl	rotate - 15'
	0.5% HCOOH (1:10)	rotate - 30'
	0.5% H ₂ SO ₄ (1:10)	rotate - 90'
	2% chrome salt 33°Sch.	
	5.5% chrome salt 66°Sch.	
	0.15% MgO	rotate - 6 h pH = 3.8
Rest (24 hours), drain, shave and weigh, neutralize (pH= 5) and fatliquor		

TABLE II
Low-salt content tanning (Formulation II)

(on split weight):		
Delime-Bate	200% H ₂ O at 30-35°C	rotate- 15' Drain
	150% H ₂ O at 35°C	
	1.5% Dicarboxilic acids	rotate - 30'
	0.7% Bate 1200 u.	rotate - 1 h pH = 8.5 Drain and wash
Pickle-Tanning	1.5% NaCl	rotate - 15'
	2% Sulphoaromatic Acid (1:10)	rotate - 90'
	2% chrome salt 33°Sch.	
	4% chrome salt 66°Sch.	
	0.15% MgO	rotate - 6 hours pH = 3.8
Rest (24 hours), drain, shave and weigh, neutralize (pH= 5) and fatliquor		

- Sulphoaromatic Acid (Sellatan P) provided by TFL Holding GmbH.
- Chrome salt 33°Sch. provided by BASF Curtex, S.A.
- Chrome salt 66°Sch. provided by Stoppani Mediterranea S.L.
- Magnesium Oxide (MgO)

Methodology

Each test was conducted in triplicate. 50 kg of hides were processed in each test.

1. Study of the influence of the temperature on the final leather and on the float obtained

Two systems of pickle-tanning were developed. In both, the hides were first soaked, then unhaired using 2 percent sodium sulphide and 3.5 percent lime, and finally defleshed and split at 3 mm.

The tests were carried out in accordance with the same formulation throughout the tanning process, but changing the final temperature in each case. In order to obtain the final temperature, the float was heated up with the drum heater immediately after the addition of the chrome salts and basificant. Once the appropriate temperature was reached, it was maintained throughout the whole of the process. The final temperatures measured were 30°C, 35°C, 40°C, 45°C and 50°C. The formulations are shown in Table I and Table II.

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

- 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). 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.
- Leather burst distension (LBD). The same methodology followed in previous case is used here.
- Chromium oxide content (%Cr₂O₃) in accordance with the IUC 8 Standard.
- Shrinkage temperature (Tg) in accordance with the IUP 16 Standard (Modified).

Both the tanning float and the float resulting from sammying the leathers were mixed. The parameters of the resulting residual float were analyzed:

- Float volume (L/t hide)
- Chlorides in float (kg/t hide)
- Cr₂O₃ in float (kg/t hide)

A hide batch was processed following a traditional formulation. This formulation is detailed in Table III:

The same analysis as those performed on the leather subjected to the pickle-tanning processes 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 processes under review.

2. Experimentation with increases in temperature in the study

An increase in the range of temperature was considered once the results of the study were analyzed. Three tests with final

TABLE III
Traditional formulation

(on split weight):		
Delime-Bate	200% H ₂ O at 30-35°C	rotate- 15' Drain
	150% H ₂ O at 35°C	
	1.5% Dicarboxilic acids	rotate - 30'
	0.7% Bate 1200 u.	rotate - 1 h pH = 8.5 Drain and wash
Pickle-Tanning	100% H ₂ O	
	7% NaCl	rotate - 15'
	0.5% HCOOH (1:10)	rotate - 30'
	0.7% H ₂ SO ₄ (1:10)	rotate - 90'
	2% chrome salt 33°Sch.	
	5.5% chrome salt 66°Sch.	
	0.15% MgO	rotate - 6 h Final Temperature 30°C
Rest (24 hours), drain, shave and weigh, neutralize (pH= 5) and fatliquor		

temperatures of 50°C, 55°C and 60°C were conducted in both systems. The same methodology as in the previous tests was used; a traditional tanning process was included in order to compare the results obtained with those in the tanning without float. The hides used in these tests originally came from a batch different to those used in the previous tests. This fact may influence the results obtained from the physical tests. Repeating the same traditional process with leathers from the new batch helps to draw comparisons between the results from all the tests, since the differences in the results from the leathers obtained in the traditional processes will depend on the origin of the hides. These differences can be extrapolated to the all the remaining tests. This favours the comparison between the results from the different tests of the new processes without float.

3. Study of the effect of the change of the basification system

Finally, the tests at 50°C, 55°C and 60°C were repeated and this time a variable was introduced in the process. This variable meant that the basificant (MgO) was added once the chrome salts had been left rotating for two hours. After two more hours of rotation, the temperature was increased until the six-hour rotation was completed. In the second system (i.e. with sulphoaromatic acid) there was also a change in the addition of chrome salt: the amount of added chrome salt (33% of basicity) was increased to 4% and the amount of added chrome salt (66% of basicity) was reduced to 2%. These modifications were carried out with the aim to obtain the maximum chrome fixing in the leather while resorting to the same amount of chrome salt addition in the process of tanning. A traditional tanning process was also conducted in order to contrast the results. In this case the leathers also came from a different batch and traditional tanning is necessary if we want to run objective comparisons with the other tests.

RESULTS AND DISCUSSION

Study of the influence of the temperature on the final leather and the float obtained

Both the results obtained from the first system of pickle-tanning and their standard deviations are detailed in Table IV.

The absorption of chrome by the leather was much greater (between 38 and 44 percent) than that using a traditional process, as can be inferred from the results obtained from the tanning process without float. Consequently, the total amount of chrome discharged decreased between 79 and 87 percent in the tanning processes without float, replicating the results obtained in an earlier study¹⁹. A decrease in the volume the residual float (between 79 and 83 percent) as well as in the amount of chlorides in that float (between 94 and 95 percent) was expected, since the initial addition in both cases was considerably lower than that of the traditional tanning process. This is simply a matter of proportion. However, the decrease in the amount of chrome in the residual float at a final temperature of 45°C (approximately 33 percent) is remarkable. Such decrease is maintained when the final temperature is 50°C.

The results obtained from the second system of pickle-tanning are detailed in Table V.

The absorption of chrome by the leather was much greater (around 25 percent) than that using a traditional process, as can be inferred from the results obtained from the tanning process without float. Consequently, the total amount of chrome discharged decreased between 95 and 97 percent in the tanning processes without float, replicating the results obtained in an earlier study²⁰. A decrease in the volume the residual float

TABLE IV
Physical and chemical properties analyzed (System I)

Final Temperature (°C)	30	35	40	45	50	Trad
TS (N/mm ²)	10.0±0.2	9.1±0.2	13.0±0.3	15.0±0.3	14.6±0.3	10.2±0.2
E (%)	35.5±1.4	28.6±1.2	38.5±0.8	33.3±1.3	32.3±1.3	35.3±1.4
TL (N/mm)	55.4±2.2	59.6±2.4	70.9±2.8	66.8±2.7	65.6±2.6	78.7±3.1
GCL (N)	400±24	387±23	471±23	198±10	394±19	317±16
GCD (mm)	14.29±0.36	12.00±0.30	13.23±0.33	11.54±0.28	13.24±0.33	11.74±0.29
LBL (N)	511±23	463±21	604±27	300±13	497±22	622±28
LBD (mm)	16.18±0.48	13.75±0.41	15.52±0.46	14.56±0.43	14.64±0.44	14.80±0.44
% Cr ₂ O ₃	4.5±0.1	4.6±0.1	4.4±0.1	4.6±0.1	4.6±0.1	3.2±0.1
Tg (°C)	116±1	116±1	116±1	116.5±1	116±1	109±1
Float volume (L/t hide)	197±14	214±16	233±15	197±13	241±16	1158±25
Chlorides float (kg/t hide)	1.55±0.01	1.69±0.01	1.84±0.01	1.55±0.01	1.90±0.01	30.70±0.12
Cr ₂ O ₃ float (kg/t hide)	1.23±0.01	1.10±0.01	1.30±0.01	0.80±0.01	0.88±0.01	6.13±0.09

TABLE V
Physical and chemical properties analyzed (System II)

Final Temperature (°C)	30	35	40	45	50	Trad
TS (N/mm ²)	14.5±0.3	11.3±0.2	11.0±0.2	11.3±0.2	14.0±0.3	10.2±0.2
E (%)	24.0±0.7	20.7±0.6	18.7±0.6	17.8±0.6	20.5±0.9	35.3±1.4
TL (N/mm)	82.7±4.9	59.4±2.6	67.5±3.3	83.9±3.7	84.5±3.9	78.7±3.1
GCL (N)	260±11	268±12	195±9	224±10	219±10	317±16
GCD (mm)	8.07±0.20	8.50±0.21	8.64±0.22	7.17±0.18	7.47±0.21	11.74±0.29
LBL (N)	422±21	374±19	312±15	409±21	343±15	622±28
LBD (mm)	10.59±0.32	10.69±0.32	10.58±0.31	10.31±0.30	10.37±0.41	14.80±0.44
% Cr ₂ O ₃	3.9±0.1	4.1±0.1	4.1±0.1	4.0±0.1	4.1±0.1	3.2±0.1
Tg (°C)	106±1	107±1	108±1	104±1	101±1	109±1
Float volume (L/t hide)	227±13	203±14	150±16	198±16	220±15	1158±25
Chlorides float (kg/t hide)	2.39±0.01	2.24±0.01	1.92±0.01	2.44±0.01	2.14±0.01	30.70±0.11
Cr ₂ O ₃ float (kg/t hide)	0.25±0.01	0.22±0.01	0.17±0.01	0.20±0.01	0.31±0.01	6.13±0.09

TABLE VI
Physical and chemical properties analyzed (System I)

Final temperature (°C)	50	55	60	Trad.
TS (N/mm ²)	11.0±0.2	9.7±0.2	13.8±0.2	15.0±0.3
E (%)	38.2±1.5	33.7±1.3	40.6±1.6	42.8±1.7
TL (N/mm)	65.6±3.9	63.3±3.8	83.9±5.0	85.2±5.1
GCL (N)	230±11	175±9	263±13	221±11
GCD (mm)	8.20±0.21	7.44±0.18	7.96±0.19	7.65±0.19
LBL (N)	320±14	280±12	378±17	341±15
LBD (mm)	10.40±0.31	10.07±0.30	10.24±0.30	10.40±0.31
% Cr ₂ O ₃	4.8±0.1	5.5±0.1	4.9±0.1	3.3±0.1
Tg (°C)	118±1	120±1	121±1	105±1
Float volume (L/t hide)	159±12	125±11	151±14	1162±24
Chlorides float (kg/t hide)	1.86±0.01	1.61±0.01	1.93±0.01	30.68±0.15
Cr ₂ O ₃ float (kg/t hide)	0.86±0.01	0.60±0.01	0.65±0.01	6.62±0.09

(between 80 and 87 percent) as well as in the amount of chlorides in that float (between 92 and 94 percent) was expected, since the initial addition in both cases was considerably lower than that of the traditional tanning process. Three further tests were conducted and their results compared to those of the traditional system of tanning. This was made so as to expand the study of the influence of the final temperature of tanning on the properties of the leather and on the exhaustion of the residual float.

Experimentation with increases in temperature in the study

The results obtained from the first system of pickle-tanning are detailed in Table VI.

The results replicated those in the previous test. Thus, and as compared to a traditional tanning process, (i) the increase in the absorption of chrome by the leather ranged from 45 to 67 percent; (ii) the total amount of chrome discharged decreased between 87 and 91 percent; (iii) the volumes of the residual float decreased between 86 and 89 percent; (iv) the amount of chlorides in the residual floats decreased between 94 and 95 percent. It can also be seen that if the final tanning temperature is increased to 55°C a significant decrease of chrome content in the residual float is obtained (a 30 percent decrease). Such decrease is confirmed when the final temperature is increased to 60°C.

The physical properties of the leather were not significantly altered despite a greater amount of chrome absorbed by the leather in the tests without float.

The results obtained from the second system of pickle-tanning are detailed in Table VII.

The results replicated those in the previous test. Thus, and as compared to a traditional tanning process, (i) the increase in the absorption of chrome by the leather ranged from 21 to 33 percent; (ii) the total amount of chrome discharged decreased between 91 and 95 percent; (iii) the volumes of the residual

float decreased between 84 and 87 percent; (iv) the amount of chlorides in the residual floats decreased between 92 and 94 percent. It can also be seen that if the final tanning temperature is increased to 60°C a significant decrease of chrome content in the residual float is obtained (a 35 percent decrease).

The physical properties of the leather were not significantly altered despite a greater amount of chrome absorbed by the leather in the tests without float.

As it can be seen in the results obtained, there is greater chrome absorption in the second experiment when working at 55°C and 60°C as compared to the first experiment. But since there was a change in the addition of chrome (i.e. the total amount of added chrome was increased) there was also an increase of chrome content in the residual float (about a 50 percent increase).

In view of the results obtained, further tests were carried out also, in order to obtain a greater exhaustion of the residual float. The modification that was introduced, which consisted of changing the system of addition of the basificant (MgO), was aimed at getting a slower dissolution of the basificant. By doing this, the basification would be more gradual and both the absorption and distribution of the chrome in the leather would also be greater. The next section comprises the discussion of the results obtained.

Study of the effect of the change in the basification system

The results obtained from the first system of pickle-tanning are detailed in Table VIII.

The results are very similar to those obtained in the previous tests except for the amount of chrome discharged in the residual float. Again, it can be seen how the decrease in chrome content in the residual float is significant when the final temperature is increased from 50 to 55°C (a 40 percent increase in this case). The results also indicate that the new system of basification leads to an increase in the

TABLE VII
Physical and chemical properties analyzed (System II)

Final temperature (°C)	50	55	60	Trad.
TS (N/mm ²)	17.0±0.3	18.0±0.3	17.0±0.3	15.0±0.3
E (%)	34.8±1.1	35.1±1.1	39.2±1.2	42.8±1.3
TL (N/mm)	97.7±3.9	98.7±3.9	106.3±4.2	85.2±3.4
GCL (N)	299±13	294±13	265±12	221±10
GCD (mm)	8.40±0.21	8.00±0.20	8.10±0.20	7.65±0.19
LBL (N)	388±17	404±18	512±23	341±15
LBD (mm)	10.26±0.26	10.42±0.26	12.29±0.30	10.40±0.26
% Cr ₂ O ₃	4.0±0.1	4.4±0.1	4.3±0.1	3.3±0.1
T _g (°C)	116.5±1	118±1	118±1	105±1
Float volume (L/t hide)	165±14	187±13	152±15	1162±24
Chlorides float (kg/t hide)	2.13±0.01	2.52±0.01	1.98±0.01	30.68±0.15
Cr ₂ O ₃ float (kg/t hide)	0.52±0.01	0.58±0.01	0.36±0.01	6.62±0.09

TABLE VIII
Physical and chemical properties analyzed (System I)

Final temperature (°C)	50	55	60	Trad.
TS (N/mm ²)	15.9±0.3	14.5±0.3	17.8±0.3	16.6±0.3
E (%)	40.8±1.6	32.6±1.3	52.0±2.0	48.6±1.9
TL (N/mm)	82.0±4.9	81.4±4.8	90.2±5.4	89.5±5.3
GCL (N)	333±16	317±19	356±21	337±17
GCD (mm)	8.79±0.22	8.04±0.20	10.32±0.25	9.24±0.23
LBL (N)	456±20	353±16	439±19	437±19
LBD (mm)	11.12±0.33	9.39±0.28	12.46±0.37	11.84±0.35
% Cr ₂ O ₃	4.5±0.1	5.0±0.1	4.6±0.1	3.1±0.1
T _g (°C)	119±1	117.5±1	118±1	106.5±1
Float volume (L/t hide)	137±14	145±13	151±15	1161±23
Chlorides float (kg/t hide)	1.67±0.01	1.68±0.01	1.33±0.01	23.74±0.12
Cr ₂ O ₃ float (kg/t hide)	0.45±0.01	0.27±0.01	0.23±0.01	5.76±0.08

TABLE IX
Physical and chemical properties analyzed (System II)

Final temperature (°C)	50	55	60	Trad.
TS (N/mm ²)	16.8±0.3	15.2±0.3	17.4±0.3	16.6±0.3
E (%)	43.8±1.3	38.9±1.2	48.8±1.5	48.6±1.9
TL (N/mm)	111.5±4.5	117.9±4.7	115.9±4.6	89.5±5.3
GCL (N)	435±19	397±17	400±18	337±17
GCD (mm)	9.78±0.24	10.08±0.25	10.63±0.26	9.24±0.23
LBL (N)	625±28	545±24	450±20	437±19
LBD (mm)	13.05±0.32	13.35±0.33	12.36±0.31	11.84±0.35
% Cr ₂ O ₃	3.9±0.1	4.0±0.1	4.0±0.1	3.1±0.1
T _g (°C)	111.5±1	113±1	114±1	106.5±1
Float volume (L/t hide)	162±15	154±12	123±14	1161±23
Chlorides float (kg/t hide)	1.77±0.01	1.82±0.01	1.74±0.01	23.74±0.12
Cr ₂ O ₃ float (kg/t hide)	0.13±0.01	0.06±0.01	0.05±0.01	5.76±0.08

absorption of chrome by the leather of between 45 percent and 61 percent depending on the final tanning temperature. The decrease becomes more relevant in the tests when the aforementioned final temperature is put up. Consequently, the amount of chrome discharged is much less than that of a traditional tanning process. In the case studied here, there was a 96 percent reduction.

As regards the physical properties that were measured, the results did not indicate significant differences when compared to the results obtained from the analysis of the leathers following the traditional process.

Finally, the experts that assessed the organoleptic properties of the leathers did not find any differences between the tanning without float and those following the traditional tanning process. Taking into account the physical tests conducted, the experts concluded that the leathers met the requirements necessary for sale.

The results obtained from the second system of pickle-tanning are detailed in Table IX.

The results are very similar to those obtained in the previous tests except for the amount of chrome discharged in the residual float. It can be seen how the decrease of chrome in the residual float is significantly high (a 54 percent decrease) when the final temperature is increased from 50°C to 55°C. The results also indicate that the new basification system leads to a decrease in the chrome discharged of between 98 percent and 99 percent depending on the final tanning temperature. As regards the physical properties that were measured, the results did not indicate significant differences when compared to the results obtained from the analysis of the leathers following the traditional process.

Finally, the experts that assessed the organoleptic properties of the leathers did not find any differences between the tanning

without float and those following the traditional tanning process except for the grain of the leather obtained that turned out to be a little rough. This means that the leathers obtained with this tested system can be used to produce most goods except those requiring high grain smoothness.

CONCLUSIONS

From an environmental point of view, the variation in both the final tanning temperature and the system of basification contributes in optimizing the two tanning processes without float and with low salt addition.

When comparing the results obtained from the two new formulations tested with those of a traditional tanning process, it can be seen that there are decreases between 86 and 89 percent in the residual float discharged, between 92 and 94 percent in the amount of chlorides discharged and between 92 and 99 percent in the amount of chrome discharged.

The two types of tanning processes developed in this study help to obtain leathers commercially accepted. However, the leathers obtained by using the sulphoaromatic acid are not appropriate for manufacturing those goods characterized by the smoothness of their grain.

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REFERENCES

1. Thanikaivelan, P., Rao, J.R., Nair, B.U. and Ramasami, T.; Underlying principles in chrome tanning: Part II. Underpinning mechanism in pickle-less tanning, *JALCA* **99**, 83, 2004
2. Saravanabhavan, S., Aravindhan, R., Thanikaivelan, P., Chandrasekaran, B., Rao, J.R. and Nair, B.U.; An integrated eco-friendly tanning method for the manufacture of upper leather from goatskins. *JSLTC* **87**, 149, 2003
3. Abdelmalek Roula, On theory and practice of chromium oxide tanning process, Proceedings of XXVI IULTCS Congress, Capetown, 2001
4. Simpson, C.M., Poole, J.M. and Money, C.A., Improved chrome liquor recycling, Proceedings of XXVI IULTCS Congress, Capetown, 2001
5. Lucas, M. and Langerwerf, J.S.A., Reduction of chrome and sulphate emission of chrome tanning by relatively simple in process measures, Proceedings of XXVI IULTCS Congress, Capetown, 2001
6. Muralidharan, C., Sundar, V.J., Sundara Rao, V.S. and Ramasami, T.; Two stage tanning - A new approach for chrome management, *JALCA* **96**, 61, 2001
7. R+D Department, SETA, S.A., Brazil; Rationalisation of the

- tanning process: avoiding pickling and basification; *World Leather*, **13** (6), 67, 2000
8. Cranston, R.W., Glesiner, R.W., Macoun, R.G., Simpson, C.M., Cowey, S.G. and Money, C.A., The total recycling of chromium and salts in tanning liquors, Proceedings of XXIV IULTCS Congress, London, 1997
9. Kellert, H-J. and Trommer, B.; Comparison of tanning methods from an ecological view-point (Part 1), *Leather* **201**, 37, 1999
10. Trommer, B. and Kellert, H-J.; Ecological Comparison of tanning methods (Part 2), *Leather* **202**, 54, 2000
11. Aloy, M. and Vuillermet, B.; Membrane technologies for the treatment of tannery residual floats; *Ind. du Cuir* **9802**, 43, 1998
12. Srivastava, S.L.; Chrome recycling, *J. Ind. Leat. Techn. As.* **41**, 253, 1991
13. Boast, D.A.; An investigation into differences in properties of leathers produced from chrome recycling and conventional chrome tannage, *JSLTC* **73**, 164, 1989
14. Chandra Babu, N.K., Ramesh, R., Rao, N.S., Rao, J.R., Ramasami, T., Covington, A.D., Langerwerf, J.S.A. and Walker, W.P., High exhaustion near to zero waste, chrome tanning methodologies, Proceedings of XXIII IULTCS Congress, Friedrichshafen, 1995
15. Fuchs, K., Kupfer, R. and Mitchell, J.W.; Glyoxilic acid: An interesting contribution to clean technology, *JALCA* **88**, 402, 1993
16. Franke, H., Possibilities for a better chrome fixation in the process of the chrome tannage and wet finish, Proceedings of XXI IULTCS Congress, Barcelona, 1991
17. Mayer, A.K.; Reduction of chromium in the effluent by use of a high-exhaustion chrome tannage with Baychrome 2403, *JALCA* **76**, 35, 1981
18. Luck, W.; Chrome tanning processes with particularly good exhaustion, *JALCA* **75**, 378, 1980
19. Morera, J.M., Bacardit, A., Ollé, L., Costa, J. and Germann, H-P; Study of a chrome tanning process without float and with low-salt content compares to a traditional process. Part I, *JALCA*, *accepted and publication still pending*
20. Morera, J.M., Bacardit, A., Ollé, L., Costa, J. and Germann, H-P; Study of a chrome tanning process without float and with low-salt content compares to a traditional process. Part II, *JALCA*, *accepted and publication still pending*
21. Palop, R.; Reducción de la salinidad en el proceso de piqué curtición; Proceedings of LAQEIC Congress; Pamplona, 2001
22. Ciba-Geigy, S.A; Curticiones al cromo de alto agotamiento y baja salinidad: nuevo concepto de piquelado; Jornada Técnica de Curtición y Medio Ambiente, AQEIC; Puerto Lumbreras, 1995
23. Morera, J.M., Química Técnica de Curtición, Ed. EUETII-ESAI, Igualada, 2000
24. Soler, J., Procesos de Curtidos, Ed. EUETII-ESAI, Igualada, 2000
25. Adzet, J.M., Química Técnica de Tenería, Ed. EUETII-ESAI, Igualada, 1985
26. Heidemann, E.; Fundamentals of Leather Manufacturing, Ed. Roether K.G., Darmstadt, 1993
27. O'Flaherty, E; The Chemistry and Technology of Leather, R.E. Krieger Publishing Company, Malabar, 1978
28. Soler, J, Morera, J.M., Almendros, J.F. and Martínez, M.; Variaciones en la curtición al cromo. Proceedings of Symposium Internacional de Curtición al Cromo, Igualada, 1992