

# TANNING USING BASIC CHROME SULFATE OBTAINED FROM ASH PRODUCED IN THE THERMAL TREATMENT OF LEATHER WASTES

by

ALINE DETTMER\*, KEILA GUERRA PACHECO NUNES, MARILIZ GUTTERRES<sup>a</sup> AND NILSON ROMEU MARCÍLIO

*Federal University of Rio Grande do Sul, Chemical Engineering Department,*

*Laboratory of Waste Treatment (LPR),*

*<sup>a</sup>Laboratory for Leather and Environment Studies (LACOIRO),*

RUA ENG. LUIZ ENGLERT, s/Nº, CEP. 90.040-040, PORTO ALEGRE—RS, BRASIL

## ABSTRACT

Tanning is the process which converts hide (putrescible) into leather (non-putrescible) material. Tanning wastes contain chrome that is classified as hazardous; consequently, finding satisfactory treatments or proper disposal is a fundamental necessity. Few studies on alternatives treatments for these wastes have addressed the thermal treatment of shavings and trimmings generated during the production process. The ash obtained in this process is rich in chromium oxide, which can be recovered and reused in the tanning process. Firstly, the method consists of obtaining sodium chromate, followed by the production of basic chromium sulfate that can be applied in leather tanning. Preliminary tests were carried out utilizing the tanning salt solution obtained from the ash in tanning hide powder experiments. Two simultaneous analyses were carried out using the product obtained in the laboratory and a commercial product sample, to confirm the efficacy of the salt obtained from the ash. Secondly, the sulfate obtained in the laboratory was applied in the tanning of hide samples, and again two simultaneous analyses were carried out. The results obtained in this work were satisfactory and the typical characteristics of tanned hides were achieved, that is, the hydrothermal stability of the tanned samples and their structure modification (distance between fibers) verified using electron microscopy.

## RESUMEN

El curtido es el proceso que convierte la piel (putrescible) en el material cuero (no putrescible). Los residuos de curtido contienen cromo, que está clasificado como peligroso, y en consecuencia, la búsqueda de tratamientos satisfactorios o disposición apropiada es una necesidad fundamental. Pocos estudios sobre tratamiento de alternativas para estos residuos han abordado el tratamiento térmico de virutas y recortes generados durante el proceso de producción. La ceniza obtenida en este proceso es rica en óxido de cromo, que puede ser recuperado y reutilizado en el proceso de curtido. En primer lugar, el método consiste en la obtención de cromato de sodio, seguido de la producción de sulfato básico de cromo que se puede aplicar en el curtido de cuero. Las pruebas preliminares se llevaron a cabo utilizando la solución de sal curtiente obtenida de la ceniza en pruebas experimentales de curtido sobre polvo de cuero. Dos análisis simultáneos se llevaron a cabo utilizando el producto obtenido en el laboratorio y una muestra del producto comercial, para confirmar la eficacia de la sal obtenida de las cenizas. En segundo lugar, el sulfato obtenido en el laboratorio fue aplicado en el curtido de muestras de cuero, y nuevamente dos análisis simultáneos se llevaron a cabo. Los resultados obtenidos en este trabajo han sido satisfactorios y las características típicas de los cueros curtidos se lograron, es decir, la estabilidad hidrotérmica de las muestras curtidas y su modificación de la estructura (distancia entre las fibras) fue verificada utilizando microscopía electrónica.

\* Corresponding author e-mail: alinedet@enq.ufrgs.br, mariliz@enq.ufrgs.br, Tel.: +55 51 3308 3956; fax: +55 51 3308 3277.  
Manuscript received December 5, 2009, accepted for publication April 19, 2010

## INTRODUCTION

Environmental awareness and concern continue to increase and affect more and more people worldwide. This is due, in part, to the implementation of international environmental treaties associated with pollution reduction and the introduction of stricter laws that impose restrictions criminal fines and other punishments on polluters. This has stimulated research studies seeking more efficient production processes with less environmental impact. The proper waste treatment and disposal have received particular attention. The activities related to hide and leather processing produce a considerable environmental impact, as they require high quantities of water and toxic products such as chromium and sulfides, besides generating considerable amount of organic wastes. Only about 25% of the initial raw material (raw hides) is transformed into leather, and wastes are consequently created in different forms.<sup>1</sup>

To enable leather to be used as a raw material in the fabrication of many consumer goods (footwear, bags, car upholstery) it passes through different processes and transformations. The process that transforms hide into leather is called tanning. The most common tanning salt is basic chrome sulfate. The principal characteristics of leather achieved by chromium tanning are: a hard fixed collagen matrix which is solid against wet and dry heat and enzymatic attack, besides being thermally and mechanically resistant.<sup>2</sup> This fixation is attributed to the formation of cross-links with the tanning substances in the protein matrix. Due to the unique characteristics of leather obtained by chrome tanning, this method is the preferred choice in the tanning industry. This tanning process generates solid wastes containing trivalent chromium, classified as hazardous that require prior treatment and/or adequate disposal. A considerable quantity of leather wastes is also created in the footwear and handcrafted goods industries; at this point, the waste is composed mostly of tanned shavings that can no longer be utilized. In Brazil,<sup>3</sup> the majority of tanned wastes are disposed of to landfills and only about 3% are recycled. Thermal treatment is an alternative method for the purification of such residues.

Many different methods to treat leather wastes have been developed.<sup>4-8</sup> Several studies related to the treatment of waste from the footwear industry have been carried out in the Laboratory of Waste Treatment (LPR) at the Federal University of Rio Grande do Sul.<sup>9-13</sup> The principal research line is thermal treatment, which permits energy generation and chromium recovery from the ash which contains from 50 to 60% of chromium oxide ( $\text{Cr}_2\text{O}_3$ ) by weight. This material can be utilized as a raw material to obtain sodium chromate, which is the precursor of basic chromium sulfate. The tanning salt obtained from the ash can be applied in hide tanning. The tanning power of basic chromium sulfate obtained in the laboratory was evaluated in preliminary tests using hide

powder, and the optimum conditions were later evaluated in the tanning of intact hide samples.<sup>13</sup>

Hide powder has been produced in the last hundred years to analyze the tanning capacity of vegetable extracts. Due to the satisfactory uniform distribution of powdered hide sample, it has a tendency to have large contact surface and fast water absorption.<sup>14</sup> Hide powder is standard, particularly in terms of its associated absorption characteristics.<sup>15</sup> The absorption characteristics of hide powder are considered standard.

The aim of this study is to apply a tanning solution recycled from the ash after thermal treatment of footwear industry wastes in hide tanning. Consequently, the waste generated by the industry can be reused and it is possible to close the cycle and decrease significantly the impact of tanneries on the environment.

## MATERIALS AND METHODS

### Materials

The basic chromium sulfate used to tan the hide powder and the intact hide samples was obtained according to a previously described method,<sup>16</sup> where basic chromium sulfate was recovered from the ash through oxidation (obtaining chromium VI) and then reduced using sodium sulfite. Freiberg hide powder was used, with the characteristics shown in Table I.

**TABLE I**

### Freiberg hide powder characterization

pH	5.2–5.6
Chromium oxide content	< 0.5%
Ash content	< 0.9%

### Hide powder tanning

Comparative tests were carried out on the tanning salt obtained in the laboratory and the commercial salt sample. For this procedure, a solution of commercial basic chromium sulfate was prepared with the same concentration of chromium oxide ( $\text{Cr}_2\text{O}_3$ ) present in the experimental recycled solution. The method used for the hide powder tanning analysis was that described by Oertel.<sup>17</sup> The suspension containing the tanning agent and the hide powder was incubated with continuous shaking for 2 hours, at 25°C, in a shaker. The different solution of basic chromium sulfate with different basicity values (18 and 35% of basicity) were used to evaluate the influence of basicity on the chromium fixation to the protein. The basicity of the commercial product was verified through analysis as 33%.

The influence of heating and alkali addition to the suspension obtained at the end of the tanning process was evaluated considering the influence of these parameters on chromium compound hydrolysis. Three tests for each of the two tanning agents, the commercial chromium salt and the one recovered from the ash were performed. After two hours of mixing at 25°C, the succeeding steps were followed for each test:

- Test 1—withdrawn from the shaker, taken at  $t = 2$  h;
- Test 2—with addition of sodium bicarbonate, taken after 3 h;
- Test 3—without addition of sodium bicarbonate, taken after 3 h.

The temperature was adjusted to 50°C and the suspension remained shaking for one more hour. The suspension was then filtered and the hide powder formed a tablet. The pH of the residual bath was measured for the three tests. The quantity of chromium oxide,<sup>18</sup> the quantity of ash<sup>20</sup> in hide powder and the quantity of chromium oxide in the residual bath<sup>19</sup> were determined. Samples of hide powder tanned separately with the two tanning agents were observed using scanning electron microscopy (SEM).

### Hide sample tanning

The tests were conducted in a laboratory drum (cylindrical rotating reactor, used for hide and leather processing). Samples of pickled hides, acidified and ready to receive the tanning agent, were obtained from the tannery. The times required and chemical reagents used are described in Table II.

For proper diffusion of chromium compounds, the chrome tanning process needs a minimum duration of 6 hours. It is necessary that the tanning salt penetrates well through the fiber structure to avoid superficial tanning. For comparative analysis, three tanning tests were performed simultaneously on each of the two tanning agents, using commercial basic chromium sulfate (BCS) (A) and BCS obtained from the ash in the laboratory (B). The test results are tabulated in Table III.

In the first tanning test, 1.56% chromium oxide (W/W) of the hide sample by weight was used. The time required for tanning was six hours. In the second and third tanning tests, the amount of chromium oxide was increased to 2.08% of the hide sample by weight. The time required for tanning also increased, due to the utilization of a laboratory drum system; where, at this scale, there is less mechanical action on the hide compared to an industrial system. The time required for tanning was 24 hours, to guarantee the diffusion of the

**TABLE II**

### Formulation used for the steps of hide tanning and basification

Step	Reagent	Quantity (%)*	Time
Tanning	Chromium oxide ( $\text{Cr}_2\text{O}_3$ )	1.56 or 2.08	6 h
Basification	Magnesium oxide	0.2	20 min
	Magnesium oxide	0.2	20 min
	Magnesium oxide	0.15	20 min

\* The reagent weight used was set as a percentage of the hide sample weight % (w/w)

**TABLE III**

### Hide sample tanning tests

Test	% $\text{Cr}_2\text{O}_3$	Tanning time	Basification time
1	1.56	6 h	2 h
2	2.08	24 h	24 h
3	2.08	24 h	24 h

**TABLE IV**  
**Results obtained for hide powder tanning**

Test	Basicity of BCS (%)	Heating	Alkali added	pH of tanning solution after 2 h stirring	pH after alkali addition	Final pH	% of Cr <sub>2</sub> O <sub>3</sub> in hide powder	Ash in hide powder (%)
1*	18	Yes	Yes	3.81	4.08	3.38	2.98	5.54
2*	18	Yes	No	3.82	-	3.26	2.98	5.20
3*	18	No	No	3.82	-	-	1.70	4.27
4*	35	Yes	Yes	3.89	4.26	3.66	4.20	6.64
5*	35	Yes	No	3.92	-	3.46	3.70	6.72
6*	35	No	No	3.96	-	-	2.35	4.67
7**	33	Yes	Yes	3.46	3.92	3.37	4.60	5.77
8**	33	Yes	No	3.45	-	3.14	4.30	5.19
9**	33	No	No	3.66	-	-	2.60	2.78

\*The tests were performed with BCS recovered from the ash of thermally treated leather wastes.

\*\*The tests were performed with commercial BCS.

**TABLE V**  
**Results for chrome-tanned (wet-blue) hide samples**

		Shrinkage (%)	Cr <sub>2</sub> O <sub>3</sub> in leather (%)	Soluble Cr in leather (%)	Ash content (%)	Residual Cr <sub>2</sub> O <sub>3</sub> tanning solution (g/l)	Wet-blue pH	Wet-blue difference cipher
1	A	5.45	2.41	0.135	9.34	5.00	-	-
	B	10.91	1.95	0.230	16.01	5.90	-	-
2	A	0.00	5.33	0.525	12.59	3.08	3.75	0.70
	B	0.00	2.88	0.770	28.87	6.08	3.82	0.76
3	A	0.00	5.93	0.910	13.64	4.16	3.61	0.78
	B	0.00	3.99	1.085	23.93	4.90	3.85	0.67

A—Commercial BCS

B—BCS obtained from the ashes in laboratory

tanning salt. Through the mechanical action the diffusion/penetration rate of chromium is maximized.<sup>21</sup>

The next step is called basification where the fixing of the tanning salt in the hide occurs, through an increase in its basicity. Alkaline compounds were added to the tanning bath, until the pH reached values of around 4. Usually, after the basification process in tanneries, the drum continues to rotate for an additional 1–2 hours. In the first tanning test, after reaching the ideal pH, the system was heated and the temperature was adjusted to 50°C. The process was then allowed to continue for 2 hours. In the second and third tanning tests, the system was heated and the basification time was increased to about 24 hours.

After fixing the tanning salt, the tanned hide samples were withdrawn from the drum and aged at room temperature for 72 hours, allowing the reactions between the fiber structures and tanning agent to occur in order to obtain the final tanned leather sample. The residual tanning solutions were collected for analysis. Subsequently, a leather shrinkage test was carried out to evaluate the hydrothermal stability of the leather product.

A rectangular piece was taken from the tanned hide and the dimensions recorded, then the sample was immersed in boiling water for 2 minutes. The sample dimensions were measured again to monitor the leather shrinkage. The ideal retraction is less than 2% by sample size. The quantities of soluble chromium,<sup>22</sup> chromium oxide<sup>18</sup> and ash<sup>20</sup> in the leather were determined. The residual tanning solutions were analyzed and the quantity of chromium oxide<sup>19</sup> was assayed. The tanned leather samples were observed under a scanning electron microscope.

## RESULTS AND DISCUSSIONS

### Hide powder tanning

The results obtained for the hide tanning powder are shown in Table IV.

According to Table IV, the basicity is fundamental in good fixation of chromium compound to the protein. Solutions with 33% basicity (pH about 3,2) are considered ideal, having good diffusion activity at the beginning of the tanning process. While raising the tanning salt basicity the level of fixation in the hide increased and thus the tanning power was improved. The chromium salt basicity is increased by adding alkaline compounds until basicity values of between 45–50% are reached.<sup>23</sup> The use of the BCS solution with 18% basicity led to lower chromium fixation compared to the solution characterized by its higher basicity (33–35%).

The positive effect on chromium fixation of the tanning system with heating and alkali addition was verified. After

heating only, the quantity of chromium fixed to the protein increased, but when heat and an alkali were both applied to the system the quantity of fixed chromium increased further. Only the solution with a basicity of 18% showed no variation in the quantity of chromium oxide when submitted to heating and alkali addition, this effect being related to the basicity not being ideal.

The decrease in the solution pH values at the end of tanning process led to the hydrolysis of chromium compounds. Chromium salts in solution undergo hydrolysis releasing acid radicals into the bath, resulting in an increase in the solution acidity as well as the chromium complex basicity. Also, the hydrolysis increases with temperature, volume of water used and alkali addition.<sup>24,25</sup>

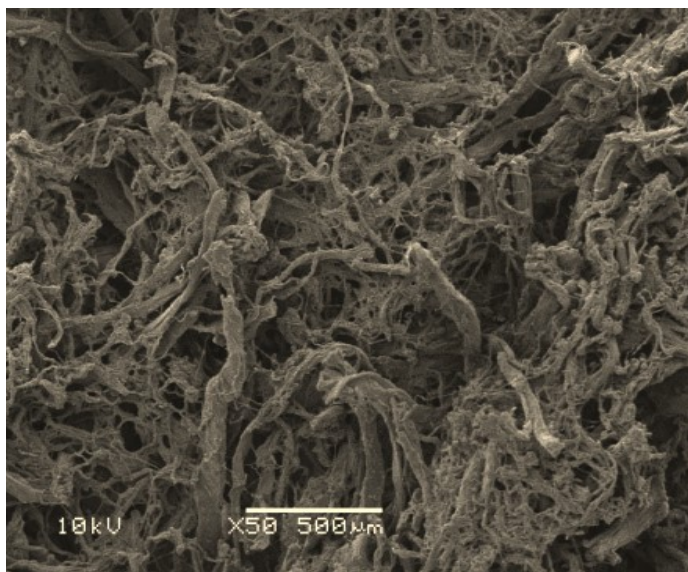
The recycled tanning solutions obtained in the laboratory were found to have greater ash content than the tanning solutions made from the fresh commercial salt. The solution used to obtain the BCS in the laboratory could contain impurities introduced into the solution during the sodium chromate preparation process,<sup>13</sup> and the reduction reaction of hexavalent chromium in the laboratory was carried out with sodium sulfite, an inorganic compound. Furthermore, the experiments that showed greater chromium fixing also had higher ash content, due to the increased fixation of the tanning salt.

### Tanning of hide samples

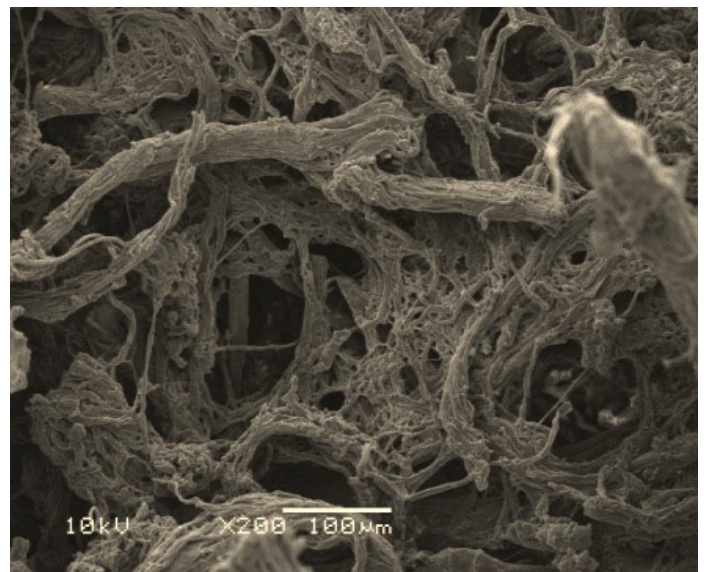
Table V shows the results obtained when the samples of leather were submitted to retraction tests and the results for the quantities of chromium oxide and soluble chromium, amount of ash in the wet-blue leather, the concentration of Cr<sub>2</sub>O<sub>3</sub> in residual tanning baths and the pH and difference cipher for the wet-blue leather.

For the three experiments, only number 1 failed to reach the desired levels of hydrothermal stability. However, in this case, although a smaller quantity of chromium was fixed to the tanned hide using BCS recovered from the ash, the tanning process was successful in conferring some hydrothermal stability to the hide. The absence of shrinkage in tests 2 and 3 could be attributed to the increase in chromium available and to the longer processing time (tanning and post basification), allowing greater diffusion and fixation of tanning agents to the protein. The retraction temperature and the quantity of chromium fixed to the hide increases with the tanning time.<sup>21</sup> The increases in hydrothermal stability are attributed to the tanning agent complexation through cross linking.<sup>23</sup>

The main difference between the results obtained for leather tanned with the BCS recovered from the ash and the commercial BCS is the quantity of soluble chromium and the quantity of chromium oxide present in the hide samples. Also, there is a significant difference related to the ash content. The increase in the amount of chromium oxide (% Cr<sub>2</sub>O<sub>3</sub>) in

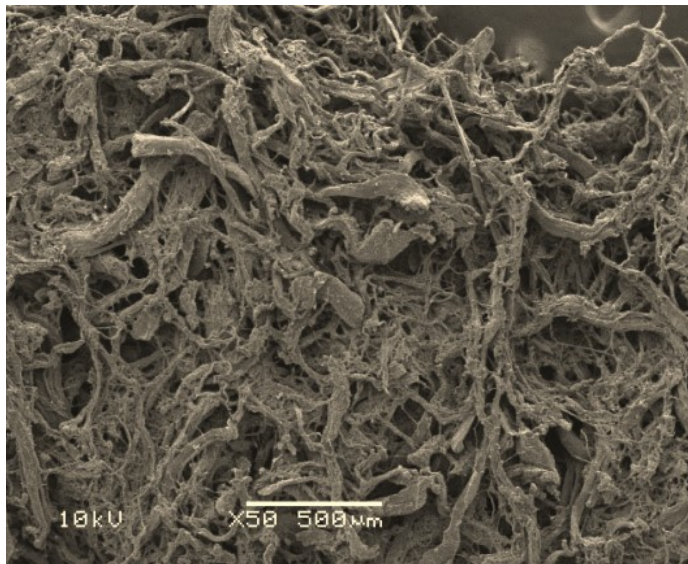


(a)

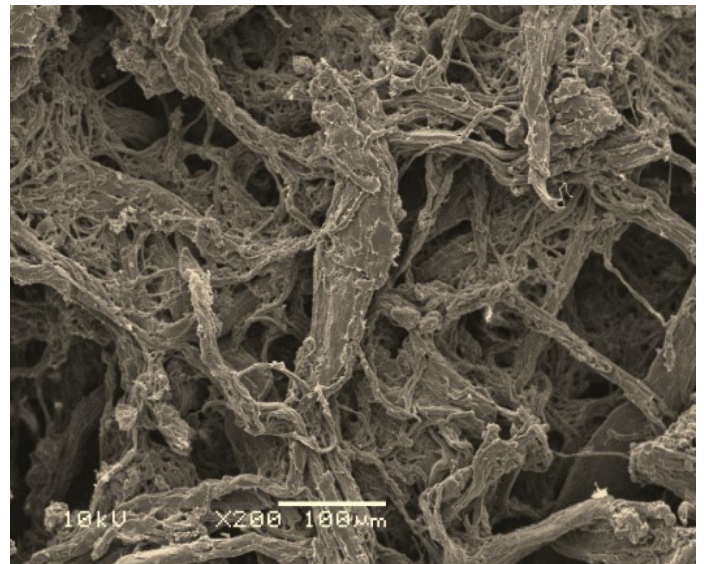


(b)

Figure 1. SEM of hide powder tanned with commercial BCS, with magnifications of (a) 50X and (b) 200X



(a)



(b)

Figure 2. SEM of hide powder tanned with BCS obtained in the laboratory, with magnifications of (a) 50X and (b) 200X

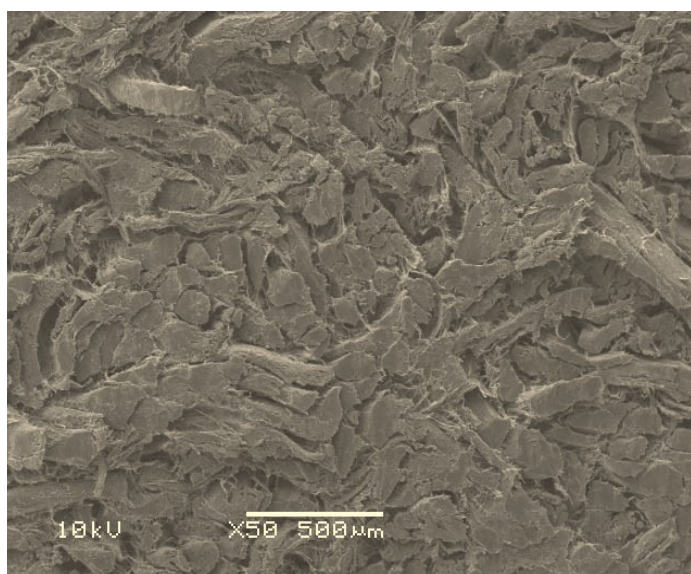
experiments 2 and 3 occurred due to the higher concentration of chromium available (from 1.56 to 2.08%). Also, the tanning time was extended from 6h to 24h, and the fixation period was longer (post basification from 2 h to 24 h), allowing a better diffusion through the fibrous structure and better tanning agent fixing to the protein. This could have directly influenced the increase in absorption of chromium in tanned hide samples.

For experiment 1, the quantity of chromium in the residual tanning solution was similar for the two products, which confirmed the results for quantities of chromium oxide in the hide that also showed similar values. For experiment 2, a larger

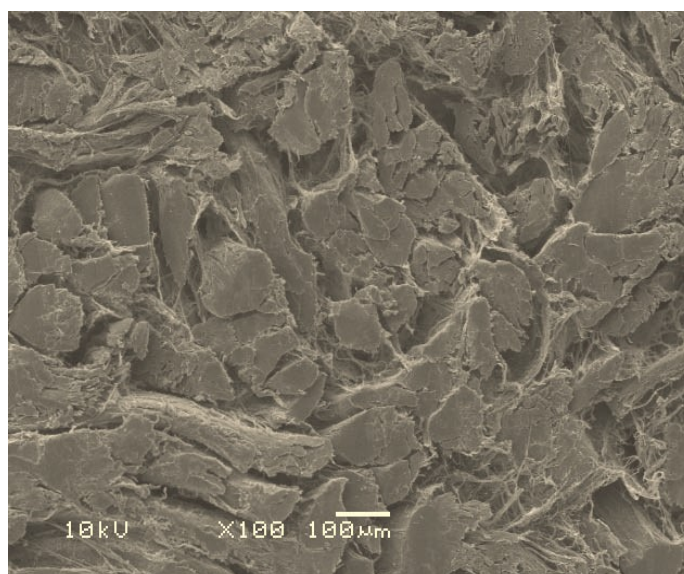
quantity of chromium oxide in the residue of the tanning solution obtained in the laboratory was registered, which is in agreement with the result obtained for chromium oxide fixed to the hide, commercial BCS showing a higher level of fixation.

The tanning solutions showed closer chromium oxide concentrations for experiment 3. Although the content of chromium oxide for the sample tanned with commercial BCS was higher, the sample tanned with recycled BCS also showed a satisfactory chromium oxide level, that is, higher than 3.5% according to leather specifications.

Increasing the quantity of chromium oxide caused an increase

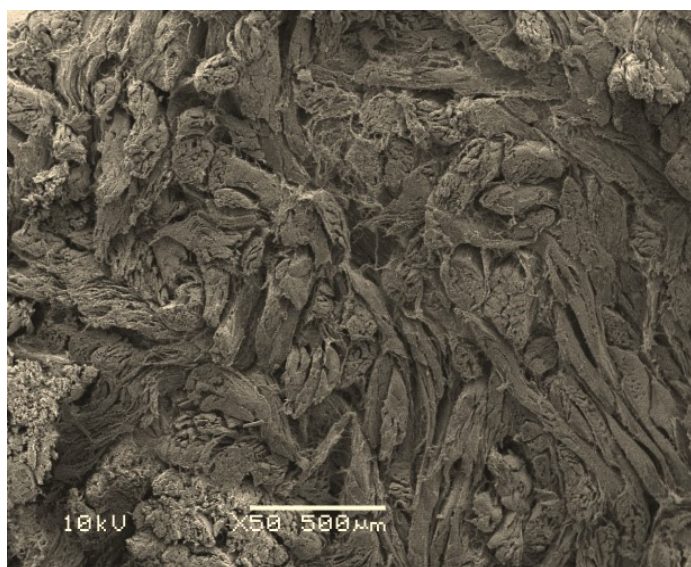


(a)

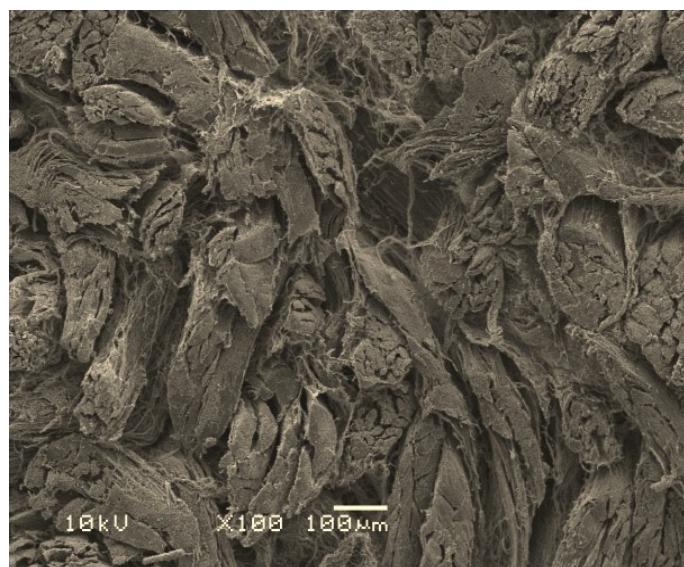


(b)

Figure 3. SEM of hide samples tanned with commercial BCS, with magnifications of (a) 50X and (b) 100X



(a)



(b)

Figure 4. SEM of hide samples tanned with BCS obtained in the laboratory, with magnifications of (a) 50X and (b) 100X

in the quantity of soluble chromium. None of the methods were able to fix all the chromium added. The rate of chromium absorbed by the hide is generally related to the quantity of carboxyl ions available. An increase in quantity of chromium oxide may lead to an increase in the quantity of chromium fixed in the hide. However, an increase in the available chromium may lead to a decrease in the percentage of chromium fixed to collagen if the quantity of carboxyl ions remains unchanged<sup>21</sup>. The samples tanned with the BCS obtained in the laboratory had a higher quantity of soluble chromium, since this product had different characteristics, being obtained from a residue and using process different from the industrial ones.

Samples 2B and 3B had very high ash contents, the ideal value being less than 12%. This increase in ash content may occur either due to the higher amount of chromium added during the tanning process, or the higher amount of chromium in the samples. For the samples tanned with the commercial product (1A, 2A, 3A) the quantity of ash increased with that of chromium in the tanned hides. For the experiments 2A and 3A the quantity of ash remained slightly above the ideal value, due to the longer processing time (tanning and post basification), which enables greater incorporation of tanning salts into the leather. An excess of ash can cause spots on the leather and can also affect subsequent steps such as dyeing. In addition, an excess of salts may cause crystallization on the

leather surface or in the structure, causing fiber rupture and loss of resistance.<sup>24</sup> In the tanned leather, the pH and the difference cipher were also analyzed, but only for experiments 2 and 3. The difference cipher is related with the type of acid used during the pickling step as well the type of chromium salt used during the tanning process. A difference cipher above 0.7 indicates the presence of strong inorganic acids. The pH remains above the minimum (3.5) for all samples, indicating that the basification was satisfactory, and thus contributed to the fixation of chromium to the protein structure. The values for the difference cipher were within the acceptable limit (below 0.7), indicating that the acids used during pickling were strong acids.

### Scanning electronic microscopy (SEM)

Figures 1 and 2 show the surface of the hide powder samples. The images obtained were similar for the two tanning solutions, the commercial BCS and that obtained in the laboratory, confirming the result obtained for the chemical analysis, i.e., chromium fixation was detected in both samples. The distance between the fibers can be observed, a characteristic afforded by the fixation of tanning agent in the structure avoiding the effect of fiber gluing.

Figures 3 and 4 show the samples of hides tanned with commercial tanning salt and that obtained in the laboratory.

The distance between the fibers can be observed in Figures 3 and 4, which indicates an alteration in the structure caused by the fixation of chromium in leather samples. The tanned fibers are clearly separated and individualized as a consequence of the action of the tanning agent fixed in the structure which prevents the approximation between them, resulting in a porous and stable structure.<sup>2</sup>

### CONCLUSIONS

The results show that hide tanning can be carried out with basic chromium sulfate obtained from the ash of the thermally treated leather wastes. Hydrothermal stability and the modification of the structure (distance between fibers) observed by electron microscopy are two of the most important characteristics of chromium-tanned leathers that were attained by using the recycled basic chromium salt obtained in the laboratory. Further research could therefore provide the means to produce leather similar to that obtained using the commercial chromium salt. Thus, wastes from the leather and footwear industries, which are classified as hazardous can be treated and return as a recovered product to the leather production process, minimizing or annulling the impact of these wastes in the environment. In this way, such wastes will not be disposed of in landfills, companies generate no environmental passives and the energy generated by combustion of the wastes, for example, can be used to generate steam.

### REFERENCES

1. Aquim, P. M. Mass Balance: tool for optimization of tanning and beamhouse processes. Master's Thesis, Federal University of Rio Grande do Sul, Porto Alegre, 2004.
2. Gutterres, M. Tanning effect on dermis structure, *Leather Magazine* **16**, 56–59, 2003.
3. Godinho, M., Marcilio, N.R., Masotti, L., Martins, B.C., Ritter, D.E., Wenzel, B.M.; Formation of PCDD and PCDF in the Thermal Treatment of Footwear Leather Wastes. *J. of Hazardous Materials* **167**, 1100–1105, 2009.
4. Brown, E.M., Taylor, M.M. and Marmer, W.N.; Production and Potential Uses of Co-Products from Solid Tannery Waste. *JALCA* **91**, 270–276, 1996.
5. Taylor, M.M., Diefendorf, E.J., Brown, E.M. and Marmer, W.N.; Characterization of Products Isolated by Enzyme Treatment of Chromium-Containing Leather Waste, *JALCA*, **87**, 380–388, 1992.
6. Veeger, L.; Ecological Procedure to Solve the Tannery Problems, *JALCA*, **88**, 326–329, 1993.
7. Jian, S., Wenyi, T. and Wuyong, C.; Ultrasound-Accelerated Enzymatic Hydrolysis of Solid Leather Waste, *J. of Cleaner Production* **16**, 591–597, 2008.
8. Erdem, M.; Chromium Recovery from Chrome Shaving Generated in Tanning Process. *J. of Hazardous Materials* **129**, 143–146, 2006.
9. Godinho, M., Marcilio, N.R., Lansarin, M.A.; Kinetic Parameters for the Reactions of Leather Shavings with Oxygen and Carbon Dioxide. *JALCA* **102**, 175–181, 2007.
10. Godinho, M., Marcilio, N. R., Faria Vilela, A.C., Masotti, L., Martins, C. B.; Gasification and Combustion of the Footwear Leather Wastes, *JALCA* **102**, 182–190, 2007.
11. Vieira, M. S.; Chromium Recuperation from Ashes of Footwear Wastes Incineration for Sodium Chromate Obtaining. Master's Thesis, Federal University of Rio Grande do Sul, Porto Alegre, 2004.
12. Pereira, S. V.; Chromium Recovery from the Ash from Incineration of Waste Leather for the Production of Sodium Chromate. XXIX Congress, IULTCS-103<sup>rd</sup> ALCA Annual Convention, USA, 2007.
13. Dettmer, A.; Chromium Recuperation from Ashes of Thermal Treatment of Footwear Industry Wastes for Tanning Hides. Master's Thesis, Federal University of Rio Grande do Sul, Porto Alegre, 2008.
14. Gutterres, M.; The Science in course of leather technology, *Tríplice Environment Solutions*, p. 505, 2008.
15. Heidemann, E.; Tanning Theory: Structure Location, Darmstadt, 2003.
16. Dettmer, A., Nunes, K.G.P., Gutterres, M., Marcilio, N.R.; Production of basic chromium sulfate by using recovered chromium from ashes of thermally treated leather, *J. of Hazardous Material* **176**, 710–714, 2010.
17. Oertel, H.; Model experiments on hide powder. International Union of Leather Technologists and Chemists Societies—IULTCS Congress, London, 1997.

- 
18. ASTM D 2807-93 (Re-approved 1998)—Annual Book of American Society for Testing and Materials Standard, Test Method for Chromic Oxide in Leather (*Perchloric Acid Oxidation*), p.280-282, 1998.
  19. ABNT—NBR 13.341—Brazilian Technical Standardization Association, Tanning and Retanning Residual Baths—Determination of chromium oxide quantity, 1995.
  20. ASTM D 2617-96—Annual Book of American Society for Testing and Materials Standard, Test Method for Total Ash in Leather, p. 272–273, 1998.
  21. Covington, A.; Chrome Management, XII Congresso Latinoamericano de Químicos y Tecnicos de la Industria del Cuero, Colombia, 1995.
  22. ABNT—NBR 14.176—Brazilian Technical Standardization Association, Leather—Determination of soluble chromium, 1998.
  23. Hoinacki, E., Moreira, M.V., Kiefer, C.G.; Basic Manual of Leather Processing, Porto Alegre: SENAI/RS, p.402, 1994.
  24. Reich, G.; From Collagen to Leather—The Theoretical Background, Ludwigshafen, BASF Service Center Media and Communications, p.337, 2007.
  25. Footwear, Leather and Components, Setor Couro Publicações, p.105, 1992.
-