Image analysis methodology to study the evolution of chromium penetration in chromium tannage

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ABSTRACT: The chrome tanning process is the main method employed to improve the hide stabilization, and chrome tanning in organic solvent medium has been tried by some authors, namely for ovine skins, but the process is not yet clear and fully understood. In recent years the application of image analysis methodologies to bioreactors is widely growing mainly on biomass and materials characterization. In the present work, the use of image analysis was employed to examine chromium penetration during bovine hide tannage in the presence of terpentine. Results showed that the overall chromium penetration rate was considerably faster in the first two minutes, becoming then much slower and linear until completion. Furthermore in the initial stages of penetration the chromium diffused much faster on the flesh that on the grain side of the hide. A second study performed on the flesh side only allowed to determine the chromium flux in the hide.

1 INTRODUCTION

1.1 *Tanning industry background*

The conversion of animal hides into leather is a classical method to dispose of organic waste products from the meat industry and, at the same time, to create commodities for the consumer. The essential step in leather manufacturing is the tanning process. Before the tannage process, hides are subjected to various preliminary cleaning processes. After the removal of different non-collagenous constituents by soaking and unhairing in alkaline medium the connective tissue is mechanically removed by fleshing, and some interstitial proteins are extracted by bating with mixtures of proteolytic enzymes.

Tanning with chromium is a process used since the end of the XIX century (Julien 1981). In this tannage process, the cleaned hide material, practically pure collagen, is brought into an acid medium by pickling and then stabilized with complex basic sulphates of trivalent chromium. The process is done in a water medium and is explained in detail by many authors (Martignone 1997, Adzet 1985, Heidemann 1993, Bienckiewicz 1983, Gratacós *et al*. 1962, Grasser 1934). Some processes have been tested and developed to increase the up-take of chromium by the hide with success, but there is still an important chromium discharge to the wastewater. The chrome tanning in an organic solvent medium is a possibility to reduce the chromium discharge, tried by some authors (Chagne *et al*. 1996), namely with ovine skins. The process is not well understood, mainly for bovine hides, and needs more investigation to have conclusive results. The aim of this work is to study the chromium penetration during the chromium tanning of bovine hides in the presence of terpentine

1.2 *Image processing and analysis*

Image processing and analysis have become nowadays a very important tool with a large field of applications. The image analysis systems strength resides on the ability to remove the subjectiveness of human analysis, the possibility to extract quantitative data that would be very difficult or impossible to obtain by other means and avoid tedious and time-consuming tasks to human researchers (Russ 1995, Gonzalez & Woods 1992). Furthermore, with the exponential increase in computer processing capabilities and affordability as well as better imaging systems, image analysis has became a standard routine in many day-to-day applications and scientific studies (Amaral *et al*. 2005, 2004a, b).

Image processing and analysis of grey scale images seems, therefore, as a quite appropriate methodology to allow the chromium penetration assessment. The image processing method must however take the highest care in the determination of the chromium penetration area within the hide

from the grey scale images. Therefore, the segmentation step emerges as a key stage in the correct chromium area assessment. Although many segmentation procedures could be considered it is recommended to use an automated or semi-automated algorithm. The resulting binary image may still require some cleaning such as debris removal, filling, etc, before the determination of the chromium penetration area.

2 MATERIALS AND METHODS

2.1 *Tanning procedure*

The hides were obtained from a lot of salted hides of 20-30 kg from Monteiro Ribas Indústrias (a Portuguese leather company from Oporto), at the lime splitted state with a thickness of 4.5 mm. All the used hide pieces, always from the same zone, near the back-bone, were first delimed and pickled by a conventional process: 400 g of pickled hide were weighed, sammed, cut in eight similar pieces, put into a small drum, with temperature control at a speed of 24 rpm. The hide pieces run at 30 ºC with 200% (w/w) of terpentine and 6% (w/w) of chromium salt and 0.8% (w/w) of sodium formiate.

Figure 1. Small drums.

2.2 *Image acquisition*

Each hide piece was immediately dried at 50 ºC in an oven, for 2 hours, and the chromium penetration was studied by image analysis: the image acquisition was performed by the visualization of a transversal cut of the hide piece in an Olympus SZ4045TR-CTV stereomicroscope (Olympus, Tokyo) at 40x magnification linked to a Sony AVCD5CE camera (Sony, Tokyo) and a DT3155 frame grabber (Data Translation, Marlboro). The images were digitalized with a size of 768x576 pixels and 256 grey levels by the software Global Lab Image 3.21 (Data Translation, Marlboro). An example of a sequence of images obtained from the hide pieces taken during the chromium penetration trials is presented in Figure 2.

Table 1. Penetration assays.

Sample	1	2	3	4	5	6	7	8
Time (min)	2	7	15	25	40	60	90	120

2.3 *Image analysis software*

An image processing and analysis software was developed in Matlab 5.3 (The Mathworks, Natick) in order to correlate the grey level intensities with chromium concentrations in the hide piece and assess the chromium concentration with time through the analysis of the chromium concentration gradient both in the grain and in the flesh side.

The software is divided in six stages: Image acquisition; image pre-treatment; image cropping; identification of chromium penetration areas; determination of the intensity values and gradient; binary image and data recording.

In the first stage the software allows the acquisition of the hide pieces in 8 bit format (256 colors) in a number of supported file types. Furthermore, the acquired image range is then set a minimum of zero and a maximum of one.

The second stage is the image pre-treatment where is first applied to the image a gray-scale opening with a 20x20 pixels mask. This procedure allows for the elimination of small peaks within both the chromium penetrated and the non-penetrated hide zones. Furthermore, an average filter of 20x20 pixels is applied to reduce the noise present in the image, mainly on the chromium gradient.

The next stage is the image cropping to establish the grain side and the flesh side. This is performed by simply applying a vertical image cut-off between the two zones and establishing a grain side sub-image and a flesh side sub-image. Care must be taken, therefore, on the image acquisition so that the hide is acquired in the upright position and centered with regard to the horizontal span of the image.

Next the chromium penetration areas must be identified to further determine their intensity values and gradient for both the grain and flesh side. In order to do so the image is analyzed row by row in the up-down direction. First the limits of the hide are determined based on their intensity differences from the homogeneous darker background. Then the limit of the chromium penetration is established given the pixels neighborhood differences between the changing intensity penetrated area and the constant intensity non-penetrated area.

Subsequently the intensity values and gradient of the chromium penetrated zones is determined for both the grain and flesh side. Upon the determination of the chromium penetration limits in the preceding stage, all the pixels between those two limits for each row are used with a twofold purpose: determine the average intensity of the penetrated

zone and the chromium gradient. For the determination of the chromium gradient the intensity pixel values and position are fed to a linear regression algorithm and the slope is calculated. Once this procedure has been performed for all the rows of the image an overall intensity gradient proportional to the chromium gradient can be determined.

Finally a binary image of the chromium penetrated zones for both the grain and flesh side is created and saved. The data of the average intensity values as well as the intensity gradient are also saved in text format.

3 RESULTS AND DISCUSSION

3.1 *Grain and flesh side penetration assay*

A study was performed on the hide chromium penetration from two opposite sides: Grain side and flesh side. An example of the images obtained in this chromium penetration study is presented in Figure 2.

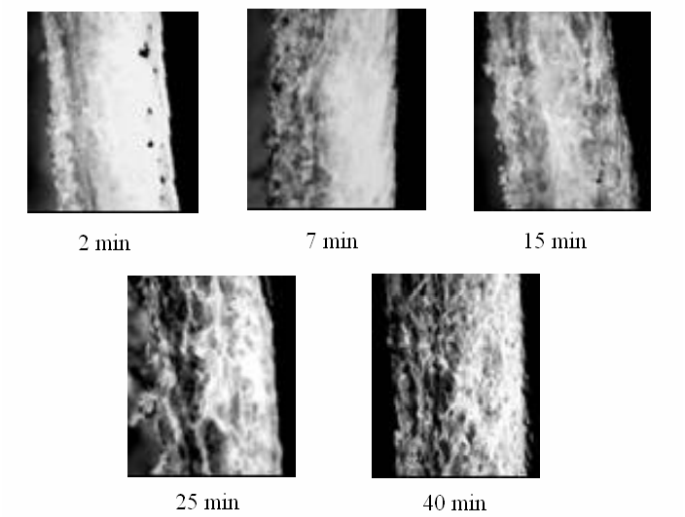

Figure 2. Images of the chromium penetration study from both the grain and flesh sides.

The obtained results in terms of normalized grayscale intensities are presented in Table 2 and their evolution with time in Figure 3.

Table 2. Normalized grayscale intensities with time.

Time (min)	Normalized grayscale intensity		
	Grain side	Flesh side	Total
2	0.02	0.25	0.27
7	0.02	0.30	0.32
15	0.21	0.20	0.41
25	0.42	0.12	0.54
40	0.33	0.37	0.70
60	0.50	0.50	1.00
90	0.50	0.50	1.00
120	0.50	0.50	1.00

The obtained results allowed to determine that the overall chromium penetration rate was considerably faster in the first 2 minutes and then much slower and linear until the complete penetration (normalized penetration of 1). The amount of time needed to the complete dissemination of the chromium in the hide was found to be 60 minutes in this assy. Furthermore, it could also be shown that, in the initial stage of penetration the chromium diffused much faster on the flesh side that on the grain side of the hide.

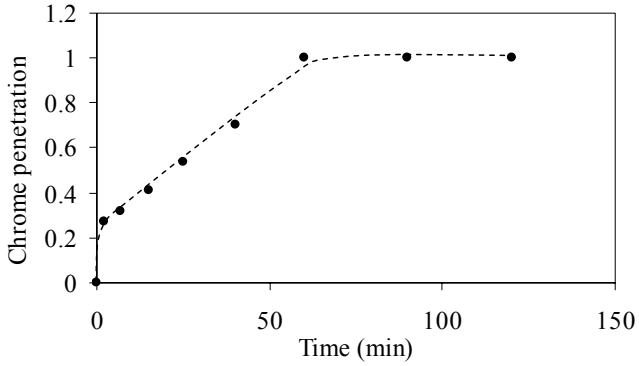

Figure 3. Evolution of the chromium penetration with time.

3.2 *Flesh side penetration assay*

Another study was performed on the chromium penetration by the flesh side and an example of the images obtained is presented in Figure 4.

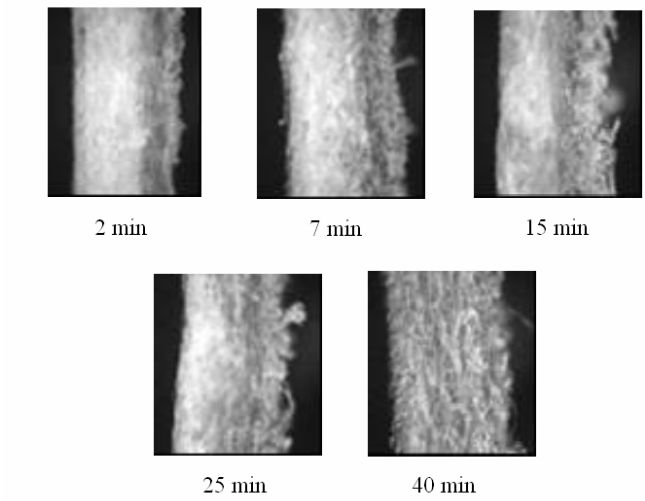

Figure 4. Images of the chromium penetration study from the flesh side.

This study was based on two fundamental assumptions:

The first assumption is that the average grayscale intensity found in the hide zone penetrated by the chromium, (C_β) is inversely proportional to the average of the chromium concentration in the hide, corrected by the hide average grey intensity.

The second assumption is that the relation between the gradient of the grayscale intensities in the hide near the periphery and in the penetration front, is proportional to the gradient of chromium concentration, but with opposite signs.

Table 3 presents the dependence of the penetrated hide grayscale intensity with time and the respective penetrated thickness (G_β) determined directly from the images.

Table 3. Normalized grayscale intensities and penetrated thickness with time.

Time (min)	C_β	G_β
2	0.671	0.00233
7	0.680	0.00263
15	0.643	0.00293
25	0.641	0.00238
40	0.563	0.00190

Figure 5 presents the correlation between the grayscale intensity and the assay time. From the analysis of this figure it was clear that the grayscale intensity (C_β) of the non-penetrated hide was, for this assay 0.7039, being hence the correcting intensity factor for the establishment of the intensity versus chromium concentration correlation.

Taking into account the second assumption, the chromium flux (chromium quantity penetrated by time) is proportional to the slope of the grayscale intensity correlation with time, and therefore proportional to 0.0033 min^{-1}.

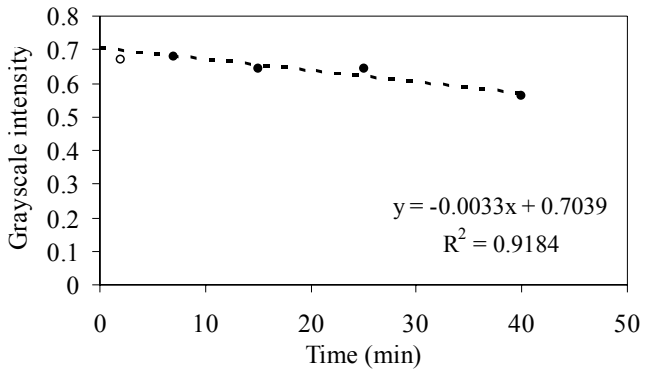

Figure 5. Grayscale intensity as a function of time.

4 CONCLUSIONS

The study performed on the hide chromium penetration from the grain and flesh sides allowed to establish that the overall chromium penetration rate was considerably faster in the first 2 minutes and then much slower and linear until complete penetration. It was also shown that, in the initial stage of penetration the chromium diffused much faster on the flesh side that on the grain side of the hide.

A second study was performed on the chromium penetration by the flesh side in order to determine chromium quantity penetrated by time (chromium flux) into the hide. The results have showed that the chromium flux, proportional to the slope of the grayscale intensity correlation with time, was found to be proportional to 0.0033 min^{-1}.

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