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# Minimization of the environmental impact of chrome tanning: a new process reusing the tanning floats

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ABSTRACT

A chrome tanning process which allows the reuse of tanning floats has been developed. The most commonly used chromium salts were replaced by highly masked and basified ones. This substitution eliminates basification operation and prevents pH change and the considerable neutral salts concentration increase in the tanning float. Consequently, tanning float can be reused several times. An optimum chromium salt concentration in the tanning float between 10% and 12.5% has been determined. It has been shown that the number of times the tanning float can be reused depends on the quality of the leather grain to be manufactured. In the best case, a saving of 18 L of water per kilogram of tanned leather is calculated. This means savings of 90% of water normally used.

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## 1. Introduction

Currently, minimizing the environmental impact of tanning processes is the goal of many researchers (Gutterres et al., 2010; Li et al., 2010; Galiana et al., 2011; Jian et al., 2011; Hu et al., 2011).

One of the environmental problems inherent in the chrome tanning is the residual float generated. Specifically, 70% of total chrome (III) is discharged during this process (IULTCS, 2008). This entails using large quantities of water that will end up being transformed into highly contaminant wastewater (Simpson et al., 2001; Saravanabhavan et al., 2003; Thanikaivelan et al., 2004). Data provided by various prestigious international organizations (FAO, 2010; IULTCS, 2008) allow deducing that approximately 17 million $m^3$ of contaminated water is released yearly, with contents 0.04Mt Cr (III) approximately. This calculation is based on the pollution values from tannery processes under good practice conditions. Therefore, it is reasonable to assume that wastewater and chromium released in tanneries are much higher than the amounts mentioned above. It is important to note that the consumption of water per kilogram of tanned hide or skin can vary dramatically depending on the hide or skin type: from 2 L to obtain bovine leather for shoes to 20 L for double-face fur.

Different solutions have been proposed in order to minimize this problem, but without rejecting the use of chromium salts as a tanning material, because of the unique properties that these salts confer on the leather. The reason is that these salts give the leather unique properties. One of these solutions is recycling tanning floats (Cranston et al., 1997; Aloy et Vuillermet, 1998; Tobin and Roux, 1998; Song et al., 2000; Scholz and Lucas, 2003). However, this solution entails some drawbacks. If a standard process is followed, tanning with the most commonly chromium salts used (33% basicity) to fix the chromium in the collagen fibres of the hide, a pH increase, known as basification within tanners, is necessary (Heidemann, 1993; Morera, 2000). This process is done either by adding an alkali (solid or liquid) to the float or using self-basifying chromium salts in which the alkali is already built in. In any case, the residual float cannot be reused directly, because its characteristics (e.g. pH or higher amount of neutral salts in the float) are not appropriate to begin the tanning process because the leather obtained would present a poor appearance and would not meet the required physical properties. One possible partial solution is to adjust the tanning float to the appropriate conditions prior to tanning (e.g. lowering the pH with acid). This solution has several drawbacks. Among them, it is a cumbersome process and the addition of alkalis and acids leads to increase even more the amount of salts in the float. This result in a decrease of the organoleptic properties of the leather grain's obtained.

A possible alternative to avoid the basification is the replacement of the most commonly used chromium salts by highly masked and basified ones (66% basicity). The interaction between an unmasked

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chromium salt of 33% basicity and the collagen carboxylic groups is shown in Fig. 1. To increase the chromium salt basicity means replacing water groups in the chromium complex by hydroxyl groups. Then, larger complexes with more atoms of chromium are made. Therefore, more chromium can be fixed in the hide. Moreover, masking means the replacement of water groups in the chromium complex by organic groups (e.g. acetate). This implies higher stability of the chromium complex with respect to a pH increase, reducing the risk of precipitation of chromium salt in the tanning float instead of their absorption in the hide. To work at higher pH values means having more carboxylic groups (P-COO$^{\Theta}$) in the side chains of collagen, the protein of the hide. Therefore, by increasing the number of points where links between the hide and the chromium complexes can be established, more chromium can be fixed in the hide.

Therefore, if chromium salts of high basicity are used to tan, it is not necessary to increase the pH of the tanning float. This prevents the alkali addition each time a batch of skins is tanned and its resulting increase in pollution load.

Consequently, these salts allow, under certain operating conditions, the direct reuse of the tanning float, without cumbersome adjustments of pH. Another feature of such salts is that tanning with temperatures at or above 50 °C, the hide absorbs significantly higher amounts of chromium than if the tannage is done at lower temperatures. However, these chromium salts have also incorporated other salts (e.g. sodium sulphate). The consequence is that the amount of salts in the tanning float will increase each time the float is reused. This will increase the final amount of salts in the leather and an important decrease in the organoleptic properties of the grain. However, the increased concentration of salts in the float will be gradual and the same float can be reused several times without affecting the quality of leather obtained. This is especially true in those leathers in which the grain quality is relatively important, such as double-face leathers, splits, pigment finished leather, etc.

The aim of this study is to develop a tanning system with a highly masked and basified chromium salt and examine both the evolution of the tanning float, reusing it several times, and the leathers obtained, in order to determine the advantages and the limitations of such system.

## 2. Materials and methods

### *2.1. Material*

The tanning process was carried out in a stainless steel tank with a stirring paddle attached. The capacity of the tank is 8 L and also incorporates an electrical resistance and a thermostat to control the temperature of the tanning float. The tests were carried out using pieces of split pickled bovine hide (pH = 3.5; 300 mm × 300 mm × 3 mm approx.). A commercial chromium salt (20% $Cr_2O_3$ and 66% basicity) was used to tan. Laboratory grade chemicals were used for analysis.

### *2.2. Methodology*

The research was carried out in two stages. In the first stage, the appropriate concentration of the tanning float was determined. In the second stage, changes in the tanning float and changes in the leathers obtained, related with the number of times the tanning float had been reused, were investigated. For both stages the same tanning procedure was followed.

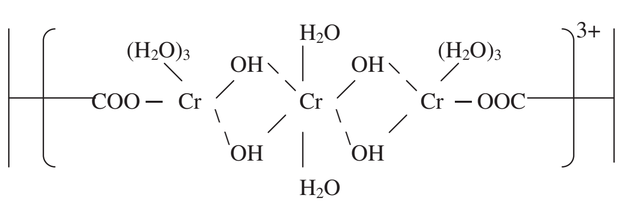


**Fig. 1.** Reaction between the chrome complexes and the collagen carboxylic groups.

#### *2.2.1. Tanning float preparation and tanning methodology*

To prepare the tanning float, the required amount of chromium salt was dissolved in 5 L of water. Once prepared, the solution was left to stand for one week in order to stabilize it. Once prepared and pH controlled, the tanning float was introduced in the stainless steel tank. The stirring paddle was started both to maintain the homogeneity of the solution and to give it a slight mechanical effect. The electrical resistance was started and the thermostat was graduated at 50 °C. Finally, the piece of hide was submerged and left in the tanning float for 3 h. Then, the piece of hide was taken out, washed slightly, let inside a plastic bag for a week and dried.

#### *2.2.2. Determination of the tanning float appropriate concentration*

Five tanning processes with different concentrations of chromium salt were carried out. The chromium salt concentrations tested were 10%, 12.5%, 15%, 17.5% and 20%. The percentage indicates the ratio weight of salt/water volume. The objective was to determine the appropriate chromium concentration of the tanning float for carrying out the tests of the second stage of experimentation.

#### *2.2.3. Reuse effect on the leather and on the tanning float*

Twenty successive tanning processes were carried out in the same float. The chromium concentration in the initial float was chosen from the results of tests carried out in the first stage of experimentation. The influence of certain physical, chemical and organoleptic properties on the leathers obtained and on the evolution of the tanning float was determined in order to assess the number of the tanning float possible reuses. The relevant analysis was performed after 1, 5, 10, 15 and 20 tanning processes.

#### *2.2.4. Chemical analyses and physical test*

Float samples collected for analysis were filtered through a filter paper and the corresponding analyses were performed. The chemical analyses and physical tests carried out, with the methods followed, are detailed below:

- ISO 2419:2006. Sample preparation and conditioning (ISO, 2006).
- ISO 2418:2002. Sampling location (ISO, 2002).
- ISO 3380:2002 (modified). Determination of shrinkage temperature up to 100 °C. Method was modified replacing water by glycerine (ISO, 2002a).
- ISO 5398:2007. Determination of chromium oxide content (ISO, 2007).
- ASTM D-5356-93. Standard test method for pH of chrome tanning solutions (ASTM, 2010).
- ASTM D-3898-93. Standard test method for chromic oxide in basic chromium tanning liquors (ASTM, 2009).

**Table 1**
Results of physical tests and chemical analysis performed on the leather and on the tanning float.

| Chromium salt in tanning float (%) | Final pH of the tanning float | Shrinkage temperature (°C) | $Cr_2O_3$ in leather (%) |
|---|---|---|---|
| 10 | 3.42 | 118 | 2.6 |
| 12.5 | 3.42 | 128 | 4.4 |
| 15 | 3.42 | 131 | 4.2 |
| 17.5 | 3.42 | 127 | 4.3 |
| 20 | 3.41 | 126 | 5.3 |

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