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 18L of

water per kilogram of tanned leather is calculated. This means savings of 90% of water normally used.

Keywords: Tanning industry, Chrome tanning, Tanning wastewater, Residual float, Wastewater minimization.

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 2L to obtain bovine leather for shoes to 20L 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 chromium salt of 33% basicity and the collagen carboxylic groups is shown in Figure 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 ($P\text{-}COO^{\ominus}$) 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 additon 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 50ºC, 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 8L 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; 300mm X 300mm X 3mm 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.

2.2.1. Tanning float preparation and tanning methodology

To prepare the tanning float, the required amount of chromium salt was dissolved in 5L 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 50ºC. Finally, the piece of hide was submerged and left in the tanning float for three hours. 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 degree 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, 2009a).
- ASTM D-3898-93. Standard test method for chromic oxide in basic chromium tanning liquors (ASTM, 2009).
- ISO 4684:2005. Determination of volatile matter. (ISO, 2005).
- ISO 4047:1977. Determination of sulphated total ash and sulphated water-insoluble ash. (ISO, 1977).
- Float density. Directly measured with a densimeter.

3. Results and Discussion

3.1. Determination of the tanning float appropriate concentration

Results are shown in Table 1. Both the shrinkage temperature and chromium content absorbed by the hide increase when the concentration of chromium salt increases from 10% to 12.5%. In contrast, an increase of this concentration does not cause changes in the properties analyzed. The adequate concentration of chromium salt sought would be any value between 10% and 12.5% because, for most industrial goods, a 4% Cr_2O_3 content in leather is enough. A concentration of 12% chromium salt was chosen to perform the tests to assess the number of the tanning float possible reuses (explained in section 2.2.3). This concentration ensures obtaining leathers with a high tanning degree.

3.2. Reuse effect on the leather and on the tanning float

From the results obtained, some additional calculations were made to better interpret the reuse effect. The organic matter in the tanning float was calculated using formula *(1)*:

Organic matter (%) = Total Solids (%) – Ashes (%) *(1)*

Where: Total solids: Porcentaje del baño curtiente que queda en forma sólida después de calentarlo a 103ºC and Ashes: Parte del baño curtiente que queda en forma sólida después de calentar los Total solids a 600ºC.

Where: Total solids: Porcentaje of the tanning float which remains as solid after heating at 103ºC and Ashes: Part of the tanning float which remains as solid after heating the Total solids at 600°C.

The inorganic matter (except the chromium oxide) in the tanning float was calculated using formula *(2)*:

Inorganic matter (%) = Ashes (%) – Cr_2O_3 in float (%) (2)

Results are shown in Table 2.

Depending on the number of reuses of the tanning float, the results can be explained as follows:

3.2.1. Shrinkage temperature and chromium in leather

The shrinkage temperature remained almost constant in all the leathers while its chromium content increased as more reused was the tanning float. During the first five float reuses, the hide absorbed approximately the same amount of chromium. By increasing the number of reuses, the hide increased the absorption of chromium, but not its fixation. Two facts support this conclusion. The first is the constant values of the shrinkage temperatures. The second is that when the first five samples were immersed in water to soak and subsequently measure the shrinkage temperature, no change in colour of the water was observed while, from sample 11 to 20, the water was tinted green, becoming darker. A likely explanation for this effect is that when the number of float reuses increases, the float volume decreases, probably due to a simple effect of evaporation. The increased absorption of chromium by the hide is due to the increased concentration of chromium in the tanning float. However, its fixation is limited because it depends on the chemically reactive groups the hide has.

3.2.2. Evolution of the tanning floats composition

Chemical analyses carried out allow distinguishing three parameters: chromium, organic matter (coming from the masking compounds of the chromium salt) and inorganic matter (coming from inorganic salts such sulphates incorporated into the chromium salt). When increasing the number of reuses of the tanning float, the values of the three parameters increase exponentially, following the same trend.

Very similar values of chromium oxide and organic matter were obtained. But the exponential growth of inorganic values was much faster. This growth trend is represented in Figure 2.

Therefore, as the tanning float is reused, chromium content, inorganic and organic matters increase. This increase is also due to the decrease in the amount of water in the float. However, proportionally, the absorption of chromium and masking agents by the leather is superior to that of inorganic matter. Consequently, the inorganic matter in the tanning float presents a greater exponentially increases.

It is also important to note that when the tanning float sample reused 20 times was filtered, prior to its analysis, it began to crystallize almost immediately. Two types of fully differentiated crystals were obtained: green and white ones. This phenomenon was less pronounced in the float samples reused 15 and 10 times and almost zero in both the float sample reused 5 times and in the float sample used in the first tanning. The different types of crystals are explained according to the chromium salt used, that contains 20% of chromium oxide and a large amount of other salts (e.g. sodium sulphate) that precipitate as white crystals.

Another parameter that was monitored was the density of the floats. The results were consistent with those cited in the preceding paragraphs. Indeed, the density also increased exponentially when the numbers of reuses of the tanning float increased.

Finally, the pH variation of the tanning float was also logical; the tanning float was acidified each time it was reused. By increasing the chromium compounds concentration in the float, the pH was decreased.

3.2.3. Organoleptic control of the leather pieces obtained

The grains of the leather pieces obtained after tannage in floats reused up to five times had a good fineness of grain. In the pieces obtained in subsequent tanning processes a worsening of the grains was observed; they lost fineness and became rough. After the tenth tannage, the leather pieces presented salt efflorescence. This efflorescence increased as tanning float is reused. This loss of fineness of grain and the subsequent salt efflorescence appearance are the result of progressive increase in the concentration of inorganic matter (e.g. sulphates) in the tanning float. A higher concentration of inorganic matter in the float implies more absorption of the pieces of leather and thus more salt will precipitate and more salt efflorescence will appear.

Given these results, it is clear that what mainly limits of the tanning float reuse is the amount of inorganic salts in the chromium salt. Depending on the type of leather you want to make will vary the number of possible float reuses. The maximum savings in water consumption (90%) will be achieved in the manufacture of leathers that require a large consumption of water and those which the appearance of the grain is not important. For example, extrapolating the results to the tanning of sheepskins for a double-face fur, a saving of 18L of water per kilogram of tanned leather is calculated. This figure was calculated taking into account that 20L of water per kilogram of skin are commonly used in this type of tanning. Therefore, if the traditional way to tan is followed, without recirculating the tanning float, and assuming that 1 kg of skin is tanned in each tanning float, 200L of water are needed for tanning 10 kg of skins. If the proposed new method is followed using the same tanning float for ten consecutive tannages, only 20L of water is needed to tan 10 kg of skin because it will not be necessary to change the tanning float. Therefore, to tan the same amount of skins, with the new proposed method 90% less water than tanning with the traditional method is used.

In this case, although the float is recirculated, the amount of chromium discharged is the same as when using the traditional method. Chromium supply in the traditional method is ten times smaller (Soler, 2002) than chromium supply in the new method tested. By reusing the float 10 times, total chromium discharge per kilogram of sheepskin is the same in both working systems. However, the proposed new tanning method generates nine times less wastewater, thus dropping water treatment costs significantly.

In addition to significant water savings, the proposed tanning method presents another environmental benefit: by not adding alkalis to the tanning float the amount of salts in wastewater substantially decreases and treatment in the sewage plants is easier.

4. Conclusions

With the chromium salt used and in test conditions, tannage can be done without the basification operation. Leather can be easily obtained with chromium content and shrinkage temperature exceeding usual commercial requirements. The tanning float can be reused several times depending on the quality of the leather grain to be manufactured. For all these reasons, the tested tanning method can be used to save water, especially for the goods in which the appearance of the grain is not important, for example in the cases of double-face furs, pigment finished leather or splits.

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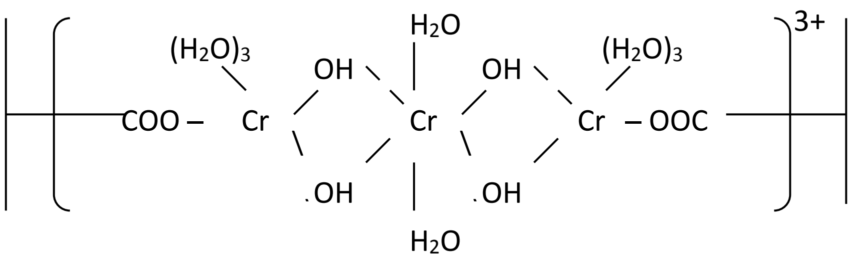

Fig. 1. Reaction between the chrome complexes and the collagen carboxylic groups

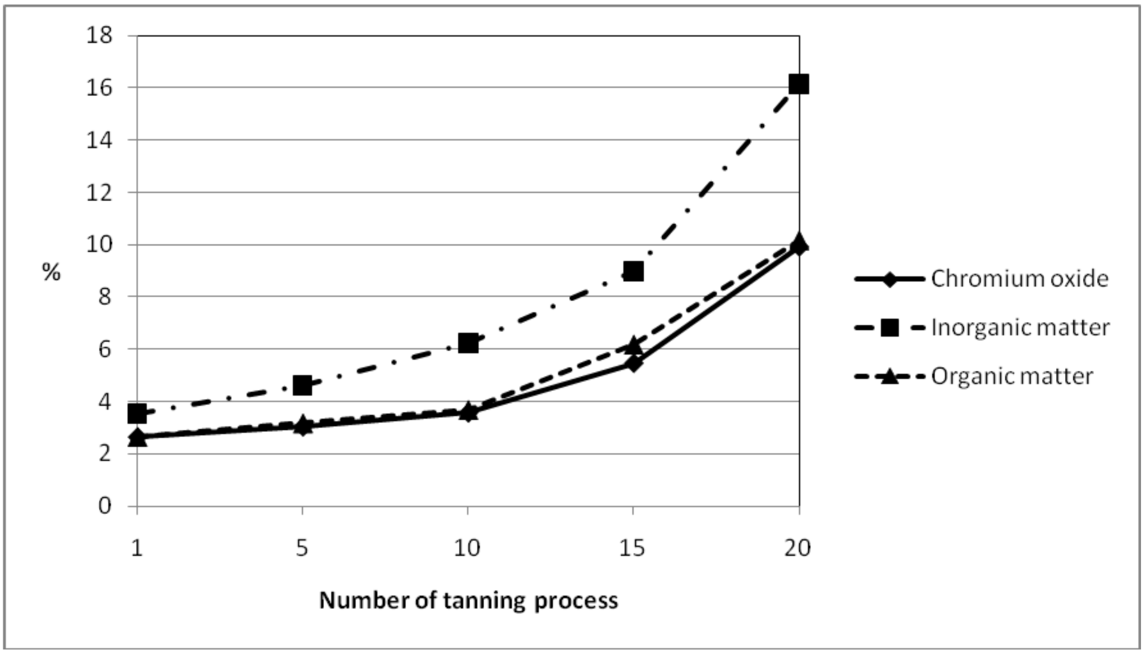

Fig. 2. Evolution of the tanning floats composition

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 (ºC)	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

Table 2

Results of physical tests and chemical analysis performed on the leather and on the tanning float

Number of tanning process	1	5	10	15	20
Shrinkage temperature (ºC)	125	125	126	126	126
Cr_2O_3 in leather (%)	4.8	4.9	5.4	5.6	7.3
Cr_2O_3 in float (%)	2.7	3.1	3.6	5.5	9.9
Total dried solids (%)	8.9	10.9	13.5	20.6	36.2
Ashes (%)	6.2	7.7	9.8	14.4	26.0
Final float pH	3.60	3.62	3.57	3.51	3.31

Float density (g/mL)	1.06	1.08	1.10	1.16	1.33
Organic matter (%)	2.7	3.2	3.7	6.2	10.2
Inorganic matter (%)	3.6	4.6	6.2	9.0	16.1