

Sustainable and environmentally friendly production of leather

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Focus of the leather producing industry is the transformation of untreated skins that are brittle under dry conditions and may rot under wet conditions into durable, imperishable leather by processes which incorporate tanning agents into the hides. The traditional processes comprise a multitude of different steps (up to 70), are time-consuming and water intensive. An accrual of 20 to 40 t of wastewater per tonne of hides is typical. About three fourth of the wastewater contain less critical compounds like salts and surfactants, while one fourth of the wastewater may contain metal cations and/or organic tanning agents.

In order to intensify the processes of leather formation a new method of high-pressure-impregnation was developed. The impregnation steps are carried out in aqueous systems in the presence of pressurized carbon dioxide, which may be either in its liquid, gaseous or supercritical state. The processes are considerably accelerated. Tanning for instance is achieved already after a few hours, if the process is operated at elevated pressure between 30 and 100 bar, while the traditional process may take some ten hours. Similar acceleration was found for other steps like washing, pickling or defatting of the treated hides. The water consumption can be reduced to about one fourth of the traditional method (Weidner and Geihlsler, 1995).

An overview of results achieved in lab and pilot scale will be given. Process principles will be described and the acceleration of the tanning process will be demonstrated. In lab scale traditionally tanned hides were produced. With a standardized experimental approach, the time dependency of the ion content in the tanning liquid was measured when tanning was performed in the presence of CO₂. Moreover, the influence of CO₂ pressure on the tanning time and the influence of the concentration of the tanning agent were investigated. Based on this lab-scale results experiments in pilot scale were performed. The upscale-factor based on the mass of treated hides was 400%. A quality control of the leathers produced showed high quality.

1 Introduction

More than 2800 tanneries in the European Union produce more than 210 million m² of leather every year. This means an average turnover of 8 billion Euros. The structure of most of the tanneries is traditional. The tanning formulas have been developed over generations and each tannery has its own formula to get its best leather quality. The tanner defines leather quality by optic and haptic impressions.

The basic questions at the beginning of the research were how to produce leather in lab scale, how to define the quality of the leather and how much time would it take to produce good leather quality. Without this knowledge it is not possible to define if the CO₂ process is more effective than the traditional process.

2 Materials

2.1 Hide

The hides used were goat hides because they fit well with chrome as tanning agent. Hides are a natural product and therefore each hide is different. In order to keep the variation of the matrix as small as possible all experiments were carried out using the same hide of one individual animal. The part of the hide used was the best part, the so-called croupon.

2.2 Pickle- and tanning solution

The hides' preparation was done in a solution called pickle-solution, which consists of water, formic acid, oil of vitriol and salt. The solution is lucent and the pH-value is between 2 and 3. The tanning solution is gained by adding chrome salt (8 wt.-%) and sodium hydrogen carbonate (until a pH-value of 4 is reached) (Heidemann, 1992).

2.3 Tanning agent

The tanning agent used was chrome salt called "Chromsal B" produced by Bayer. It is a powder and a good complexing agent with a high rate of hydration in the aqueous solution.

3 The tanning process

The conversion from raw hides into leather comprises up to 70 steps. The major processes are curing, soaking, flesh removal, hair removal, scudding, deliming, tanning, dyeing, rolling and finishing (Yigit and Bitlisli, 2006). In the following the focus will be on the tanning step.

The production of leather depends on the generation of complexes between the tanning agent and the skin collagen. The stability of the leather can be ascribed to the strong chemical bonding between the collagen fibers of the skin ridge and the tanning agent. Collagen fibers consist of proteins and have different binding sites available. The binding sites used differ depending on the respective tanning agent (mineral, vegetable and synthetic tanning agent) (Reich, 2005). The different binding sites are shown in figure 1.

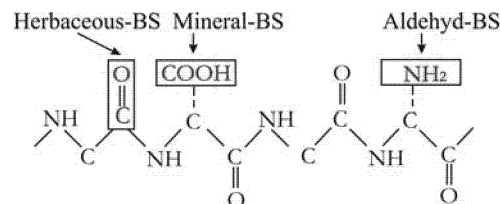


Figure 1: Binding sites (BS) of the collagen for different tanning agents (Moog, 2005)

The carboxyl groups are the important binding sites for the mineral tanning agents (like chrome) (Silvestre, 1994). These binding sites have to be prepared for the tanning step and the collagen has to be activated. This is achieved by a pickle-solution right before the tanning takes place. During the pickle process hair and epidermis are removed from the hide at a pH-value of 2.5. Proteins are hydrolyzed and washed out. Collagen fibers gain more space and therefore the leather is gaining softness. Due to the low pH-value

the collagen starts to swell. The swelling is limited and kind of controlled via buffering salts (Stather and Pauligk, 1961).

The basis for the tanning solution is the pickle-solution. 10 times more chrome solution (wt.-%) than hide is used for the tanning was used for this research. For a good tanning the pH-value has to be raised to 4 (Loewe, 1959). At a pH of 2.5 only some carboxyl groups (Mineral BS) of the skin collagen are ionized (Cuq et al., 1999). By raising the pH-value to 4 a maximum binding of chrome and collagen can be reached. Under these conditions 3.8 wt.-% chrome in skin can be reached. Experimentally it was found, that at least 3 wt.-% of chrome have to bind into the skin for producing leather of good quality (Heidemann, 1997). The binding of chrome and carboxyl groups generates chrome complexes under formation of water and sulphuric acid. The mechanism is shown in figure 2.

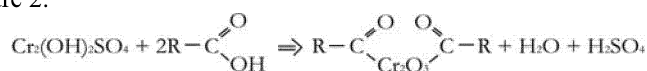


Figure 2: Accumulation of a chrome complex

The tanning is carried out in rotating tanning drums. Conventional tanning takes approximately 24 to 35 hours. The products of chrome tanning are called “wet blue” because of their blue color. Tanning is a major step but until finally “leather” is generated, some more finishing and fattening steps are required (Covington, 1997).

4 Analysis for leather quality assessment

The 3 wt.-% criterion (Cr in skin, Heidemann, 1997) is the basic criterion for reaching good leather quality. In industry the leather quality is assessed by a professional tanner mainly via qualitative criteria (Smoothness, hand feeling etc). Typically this requires large pieces of skin. In order to save resources and money, samples in our lab-scale experiments are small (Ø 2 cm). These samples can not be assessed by traditional optic or haptic properties. Therefore the 3 wt.-% criterion is used, which allows to apply an ICP (Inductive Coupled Plasma) for a first indication of the leather quality.

In a typical lab-scale experiment a 2 cm piece of leather was put in a high pressure view cell with a volume of 63 ml. Then tanning solution was added (Mass ratio Solution/hide = 10/1). After a defined contact time the solution was removed and its chrome content was analyzed. Prior to ICP the used tanning solution was diluted with water at a ratio of 500/1 and 1000/1. From the chrome content in the solution and the mass balance of the process it was calculated how much chrome has been incorporated into the hide. The so determined concentration was compared to the 3 wt.-% criterion, thus indicating the percentage of chrome in the hide.

5 Tanning in lab scale

5.1 Traditional tanning

The tanning of skin in lab scale is necessary because it has to be shown that it is possible to tan leather and to measure how long it takes to reach the 3 wt.-% criterion. In industrial scale 24 hours is given as the average time needed to reach a good leather quality (Suzuki et al., 2000). Therefore, the experiments in lab scale were also carried out for 24 hours, expecting that a reduction of time might be possible due to the higher surface-to-edges-ratio of the small pieces used in lab scale. The average surface-to-edges-ratio in industrial scale is 167 while the ratio used in lab scale was 2.5. Two tanning experiments were carried out every hour. So in total 48 experiments were carried out for 24 hours of tanning. The ratio of masses between skin and tanning solution was 1/10 (wt.-%).

Results are shown in figure 3. The starting concentration of the solution is 14 g/l. The concentration of the solution (left diagram, upper curve) decreases over time until 11.5 g/l is reached after 24 hours. The calculation of the chrome content in leather is shown in the lower curve.. It is rising fast over the first 4 hours. After 4 hours 4 mg of chrome in the leather is reached, equivalent to an average increase of 1 mg/hour. Between 4 and 17 hours only a moderate rise of the chrome content is measured. After 17 hours a chrome content of 6 mg is reached which is equivalent to an average increase of 0.15 mg/hour. Then the content rises again faster until after 24 hours a chrome content of 12.8 mg is reached (0.97 mg/hour between 17 and 24 hours)

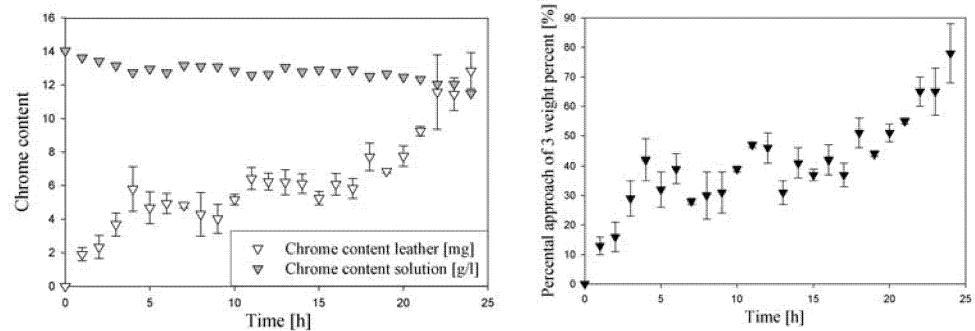


Figure 3: left: Cr content of leather and solution using traditional tanning
right: Percentage approach of good leather quality using trad. tanning

These data have been compared to the 3 wt.-% value suggested by Heidemann (right diagram). Values below 3 wt.-% indicate a non-sufficient amount of bound chrome, leading to low leather quality. Again, 4 values are calculated for each hour which was averaged and for which the standard deviation was calculated. After 3 hours of tanning 29% of the aimed chrome content is reached. Between 3 and 20 hours the values are still rising but the variation is broad. After 20 hours 50% of the aimed value is reached and the rising is faster. 78% of the aimed chrome content in the leather is reached after 24 hours of traditional tanning in lab scale. The aimed value is not achieved. It can be estimated that approximately 28 hours of tanning are needed to reach 100%.

5.2 Carbon dioxide tanning

The tanning under the influence of compressed CO₂ was carried out in the same high pressure view cell as the traditional tanning. The cell has an internal volume of 63 cm³ and is suitable for 175 bar and 180°C. Figure 4 shows the setup schematically.

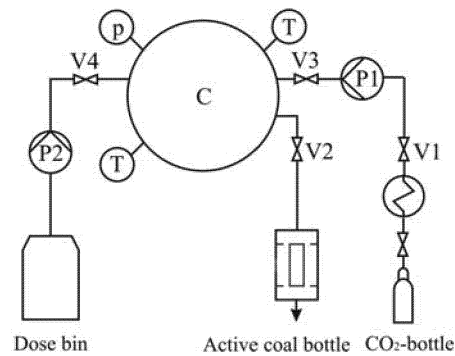


Figure 4: Set up of the high pressure view cell

Again a piece of skin was put into the cell. The cell was closed and the tanning solution was added using the dose bin. Subsequently CO_2 was added by a continuous working pump. A CO_2 cooling system upstream of the suction side prevents cavitation. When the desired pressure is reached, the valves are closed. The pressure is indicated by a digital manometer. The cell can be heated by two heating rods. These heating rods are integrated in the casing of the cell. The phase behavior can be observed through two sapphire windows on opposite side of the cell. The cell content can be stirred.

The tanning experiments were carried out at 100 bar and 30°C . The stirrer was driven by 50 r/min (the same speed was used in the traditional tanning experiments (stimmt das?). Five minutes before the experiment ended, the cell was depressurized slowly. The measured time started with first contact of hide and tanning solution and ended with the last contact when the tanned hide was taken out of the cell. A maximum of 7 hours tanning time was applied.

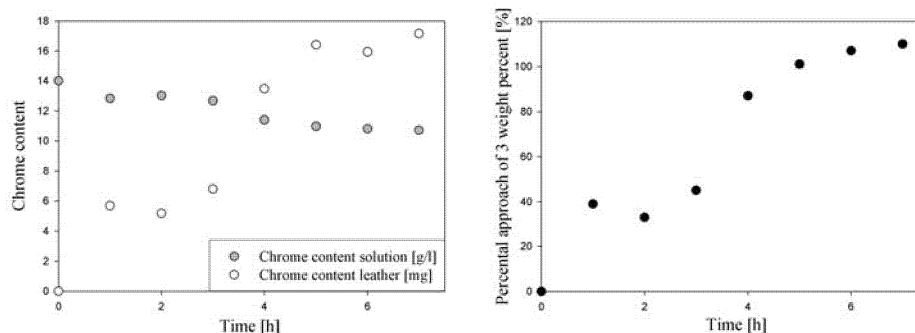


Figure 4: left: Cr content of leather and solution using CO_2 tanning
right: Percentage approach of good leather quality using CO_2 tanning

The results are shown in figure 4. The grey circles show the decrease of Cr content in the solution from 14 to 11 g/l (left). The calculation of the Cr content of the skin shows a comparable behavior to the traditional tanning (left, white circles). The time needed to reach the same content as in traditional tanning is shortened considerably. Furthermore, it can be observed that a boundary value is reached. In figure 4 (right) the results with

respect to the 3 wt.-% value are shown. 50% of the required chrome content is reached already after three hours. After 4 h 87% can be achieved and after 5 h 100% are exceeded. The value rises above 110% after 7 h.

5.3 Comparison of the methods

In this article just the 3 wt.-% criterion is compared because it is rather simple and fast to be determined. The 3 wt.-% criterion is fulfilled after 4 to 5 h using CO₂ as auxiliary substance and after 28 h or more when applying traditional tanning methods. The time saving is significant.

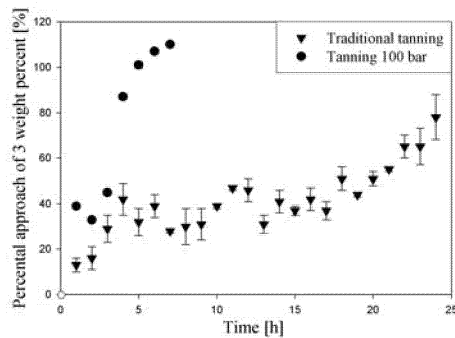


Figure 5: Comparison of the 3 wt.-% criterion

The comparison of the traditional and CO₂-supported tanning shows comparable results. Looking at the diagrams a trend over the tanning time can be seen. It can be divided into 4 sectors. In the first sector a really quick rise of the chrome uptake of the hide takes place. The second sector is characterized by only a moderate uptake velocity and in the third sector again a quick rise of the chrome uptake velocity is measured. The longest period of time is needed for the second step. Regarding the CO₂-supported tanning a fourth sector can be identified. Here a boundary value is approached.

The fast rise in the first sector is probably caused by fast binding of the chrome on the surface of the hide. The speed of uptake in the second sector may be dominated and controlled by the diffusion of the chrome into the hide. Due to a small diffusion rate in this sector a strong variation of the data is measured. The fluctuation is caused by the natural variations of the hides used. Each hide has a different allocation of pores and follicles resulting in different diffusion rates. The third sector is characterized by a renewed rise of the chrome uptake velocity, indicating an increase of the diffusion rate. This increase could be caused by the swelling of the hide. Hides in an aqueous solution are swelling, which widens the pores and follicles. Wider pores and follicles can be penetrated by molecules/particles which are too big for non-expanded pores and follicles. When most of the available collagen carboxyl groups have been reached by the chrome the last sector (sector 4) is reached. This sector is characterized by the approximation to boundary value, which corresponds more or less to 100% of chrome binding.

The first 3 sectors were observed both for the traditional and the CO₂-supported tanning. Only the time needed to pass the sectors is different. The sectors in the CO₂-supported

tanning are passed much quicker. The quicker pass of the sectors can be explained by an improved diffusion or an accelerated reaction. The first tests suggest that the hides' swelling is strongly affected by the CO_2 . The relation between CO_2 , swelling and the faster chrome uptake will be investigated in future work.

6 Tanning in pilot scale

The tanning in pilot scale was realized in a 20 l autoclave. Inside the autoclave a rotating cage assures that CO_2 efficiently reaches the surface of the skin after dipping into the tanning solution. The mass ratio (skin to solution) was also 1/10. The mass of skin was 2 kg (lab scale about 5 g). This means a scale up of about 400%.

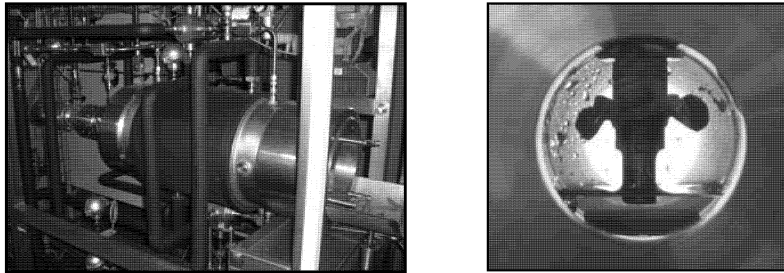


Figure 6: Autoclave, volume 20 l (left) and high pressure cell, volume 63 ml (right)

A first result is shown in figure 7. A comparison is made and shown in figure 7. 3 wt.-% of chrome in skin can nearly be reached after 6 hours. This means a reduction of process time by about factor 5. The shown result was measured twice.

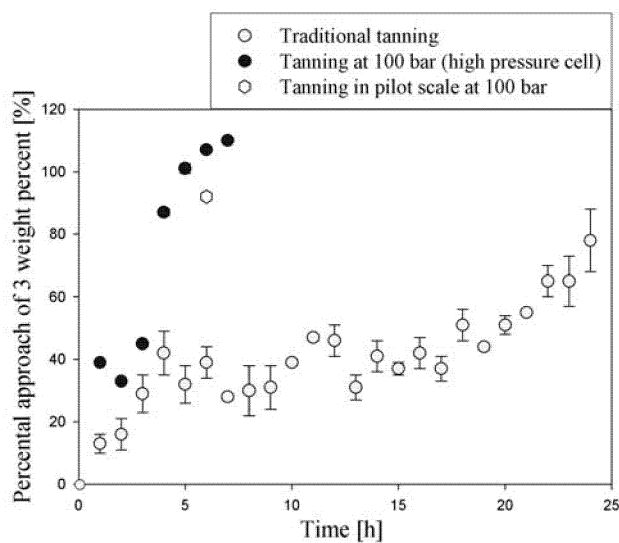


Figure 7: Comparison of tanning in lab and pilot scale

7 Conclusions

The tanning of hides under the influence of compressed carbon dioxide shows that the tanning time can be reduced from approx 28 to 5 hours. The measured curves of uptake of chrome show characteristic shapes, indicating 4 different sections. Explanations of the underlying chemical and mass transfer mechanisms are suggested. First investigations show that results from lab-scale are confirmed in pilot scale. Future work aims on continued pilot scale tanning, the improved understanding of the underlying transfer processes, being the basis for modeling the production process and on using other tanning agents (alumina and biobased).

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