High Pressure Tanning – New Process Principle from Lab-Scale to Industry

Renner M. *, Weidner E., Geihsler H.
Fraunhofer Institute UMSICHT
Osterfelder Str. 3
46047 Oberhausen - Germany
E-mail: manfred.renner@umsicht.fraunhofer.de, eckhard.weidner@umsicht.fraunhofer.de

The tanning trade is a world wide organized industry. Most of the skins are produced in the USA, Argentina, the former states of the USSR and the EU. The trade of skins is global and the EU and China are net-importers. China is the largest producer of leather followed by the EU. Every year leather amounting to an area of 13 700 km^2 (for comparison: Belgium 30 000 km^2) is produced and just the intermediate product raw leather has a turnover of 45 billion US $.

The leather producing industry is time and water intensive. Up to 70 different steps are necessary to produce leather. Most of them are carried out in aqueous systems with lots of chemicals. For the production of one tonne of leather it is common to use 2 500 kg chemicals, 75 to 250 m^3 water, 45 to 210 GJ energy and 2 200 to 3 600 kg solid waste. Most of this waste is contaminated with chromium because 90 % of all leathers are produced using chrome-III-salts.

The research of Fraunhofer UMSICHT is focussed on cattle skin and chrome tanning, because in this sector the interest in alternative processes is great. The highest quality of leather can only be produced by using chrome. The toughest leathers are produced of cattle skin. There is a change of opinion in the industry because consumers are asking for environmental friendly alternatives to conventionally tanned leathers.

In 2007 the research started in lab scale. The experimental series showed that it is possible to reduce process time about factor 6 from 30 to 5 h using compressed CO_2 at 100 bar. The lecture will give an overview on the most important results and how emission spectrometry was used to detect the leather quality of 2 cm samples. In pilot plant scale the experimental series were carried out in a 20 L autoclave starting at 300 bar in a rotating drum. A scale up from 2 cm samples to 0,75 m^2 was possible. The time needed to produce high leather quality could be reduced to 2.5 h at pressures below 60 bar. This was possible by reducing process water and giving the CO_2 a large area for penetration. The amount of chrome containing water could be reduced by more than 90 % compared to conventional industrial processes. This means a reduction of sewage water from 1.5 to 2 tonnes per tonne of leather to less than 100 kg.

In autumn 2010 a new plant at the premises of Fraunhofer UMSICHT will make it possible to tan up to 15 complete cattle skins in a 1 400 L autoclave. This means a weight of more than 500 kg and an area of 50 m^2 per process circle.

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* To whom all correspondence should be addressed

1. INTRODUCTION

In the tanning process, highly rot-susceptible, untreated skins or furs are processed to become a durable material, the leather, which can be used to manufacture different products. The entire process includes a series of complex chemical reactions and mechanical processing steps, whereby the tanning represents the fundamental process stage that provides the leather with durability and its typical character. The quantity of untreated furs and skins is determined by the animal stocks and slaughtering volumes and depends in the first instance on meat consumption.

Worldwide, the USA, Argentina, the former USSR and the EU possess the largest stocks of cattle. Lamb skins stem primarily from New Zealand, Australia, the Middle East and the EU. The EU is a net importer of both cattle skins and lamb skins, which indicates the need for corresponding storage facilities and means of transport for the raw materials, which are normally conserved in salt.

After China, the EU is the world's second-biggest producer of leather [1]. China produced a surface area of 613 million square meters in 2006. China's production capacity has almost doubled since 1998. The EU member states together produced approx. 325 million square meters in 2006 (Brazil 153 million m^2). In terms of employment figures, production and turnover, Italy is the most important production site in Europe with 15 % of world production of bovine and calf leather and 65 % of the leather volume produced in the EU [2]. The total turnover of the industry for leather as a semi-finished product is put at US$ 45 billion. A steady growth of the production in Asia can be seen, attributed to lower labour costs, but also supported by less stringent environmental regulations.

Leather manufacturing is an industry sector intensive in both raw materials and work. The raw materials account for 50 % to 70 % of the production costs, wages for 7 to 15 %, chemicals approx. 10 % and energy 3 %. The costs of environmental protection measures in European tanneries are estimated at about 5 % of their turnover [2].

The leather producing industry is a segment with high potential for environmental pollution. The effects on the environment include not only transport and concentration of classic pollutants, but also use of certain chemicals, such as biocides, surface-active substances and organic solvents. Tanneries in Europe normally feed their wastewater into large sewage plants, which are either municipal sewage works or, in the case of large tanneries, proprietary systems. Most tanneries connected to the public sewage system have various forms of wastewater treatment systems that may cover mechanical, chemical or even biological treatment [3].

Worldwide, more than 90 % of all tanneries are using chrome-III salts as tanning agent. For one tonne of finished leather, one can generally put the key substances used in the tannery sector at 2 500 kg of chemicals, 75 to 250 m^3 water, 45 to 210 GJ energy and 2 250 to 3 650 kg of solid waste (e.g. cutting waste, shavings, dust, sewage sludge etc.) [4].

This brief overview of the industry, the costs structure and the substances employed is intended to show the potential for an intensified and environmental friendly process.. The high usage of fresh water, mostly drinking water, and the strong contamination of that water are of influence on the perception of leather as a "natural product". The new process principle described in the following combines the advantages of the conventional method with the possibility of a massive saving in process time needed and water used.

2. CONVENTIONAL TANNING PROCESS

The tanning of animal skins is a labour-intensive and time-consuming process. Tanning requires incorporation of tanning agents into the skin. These tanning agents can be divided into three groups, vegetable, mineral and synthetic agents. During tanning cross-bonding between skin collagens via the tanning agent must be achieved. Thus the cross-links are fortified compared to original skins, resulting in a durable and stable product – the leather. The processes will be described below in more detail for chrome-III, as this tanning agent is used to produce more than 90 % of all leather because of the high leather quality that can be achieved [5].

The skins produced in an abattoir are usually salted and dried for the transport to tanneries or are transported chilled. In this way the skins are conserved for a long period. The subsequent process is defined to a large extent by the structure of the skin. In a tannery, the skins are washed and softened at the beginning of the production cycle. The aim of this working stage is to wash out the salt and to adjust moisture. This so-called **softening** is carried out at a pH value of 7 to 9. In the next step, the **liming**, the fatty top skin is destroyed and the hairs are removed from the skin by adding lime and sulphur compounds. Proteins are washed out and the breaking of polypeptide groups creates higher fibre mobility. The aim of this and the subsequent working steps is to expose the skin collagen and ease penetration of the tanning agents into the skin. The high alkalinity of the lime (pH >10) is strongly reduced for the next working step, the **pickling** process. This is essential because the skin swells at a high pH value and that swelling can lead to destruction of the collagen chains. During the pickle, the skin is prepared for the tanning process at a pH value of 2.5 (8 to 20 hrs). The lime residues are thus removed and the diffusion capability for the tanning agents is increased further [6]. The next step is the **tanning**, taking place in rotating tanning tanks over a period of 12 to 20 hours (in some cases even weeks). During the tanning process, the skins are brought into intensive contact with liquid containing a tanning agent, usually a solution of water and chrome-III salts. During this stage, the pH value is elevated from 2.5 at the beginning of the process to 3.8 at the end of the process [7] [8]. This permits optimum penetration of the tanning agent at a low pH value and by steadily elevating the pH value the tanning agent bonds with the reactive groups of the skin collagen, the carboxyl groups, in the skin [9]. The tanning can be called successful if 3 % by weight of chrome has been enriched within the leather [10]. This concentration is used as the fundamental criterion to define high leather quality for the trials on a laboratory scale [11].

3. TANNING UNDER THE INFLUENCE OF COMPRESSED CO_2 IN BENCH SCALE

3.1 Preliminary tests

Preliminary qualitative tests have shown that time can be saved in the tanning process under the influence of compressed carbon dioxide. It could also be demonstrated that certain working steps in the tanning can be combined in one stage [12].

Based on these preliminary findings, quantitative experiments on laboratory scale were designed to verify the time saving and to establish an analytical method for indicating the quality of tanning. Conventional standard testing methods, which are realised above all via haptic impression of the leather produced, could not be applied, as the technology at the beginning of the project only permits tanning of small samples.

To quantify the acceleration, classical tanning has been performed in laboratory scale. The time dependency of the measured chrome content in leather was used as reference value. Subsequently tanning under the influence of compressed carbon dioxide was carried out in the same plant under comparable conditions. The chrome content in the leather was calculated from analysing the chrome content in the tanning solution by means of emission spectrometry.

3.2 Substances used

The tanning processes on a laboratory scale were carried out with goatskin. The pieces of skin were taken from a croupon section (skin from the animal's back) as the skin at this point displays a rather regular pore distribution. Bovine skin was used for the trials on a pilot plant scale. Based on this much thicker skin, the aim was to secure the feasibility of the new method. The tanning solution consisted of water, chrome-III salt, salt, formic and sulphuric acid.

3.3 Quality evaluation of the leather samples

Developing a quantitative method for determination of leather quality was a core element of the research project. In industry this is normally carried out by the tanner. The very traditional structure of the tanning trade is characterized by legacy values and knowledge passed down over generations. One of those legacy values is the method to evaluate leather quality. This quality evaluation is based upon the haptic perception of the tanner. This means that the leather quality is mainly based upon subjective impressions. The tanner takes the freshly produced leather in his hands and judges whether the leather quality is good or bad. No quantitative evaluation of the leather quality is normally carried out at this part of the standard tanning process.

An indication for the tanning success and indirectly for the quality of the leather is the chrome content. By measuring the chrome content of the tanning liquid via emission spectroscopy (ICP EOS) and a mass balance, the chrome concentration in the leather was quantitatively determined. For that purpose, small samples from the tanning solution are diluted (1/500 and 1/1000) and then injected into the plasma of the ICP. Via the chrome content of the tanning solution the quantity of chrome in the leather was calculated. According to Heidemann, a chrome content of at least 3 % by weight is a key condition for good leather quality. The results shown below represent the percentages to which this criterion is met, e.g a value of 80 % means, that the leather contains 2,4 wt.-% of chrome.

3.4 Conventional tanning

Literature indicates tanning times for complete skins of approx. 12 to 24 hrs [13]. This value cannot be applied for laboratory trials without further consideration. As already mentioned, small pieces of skin (Ø 2 cm) are used. In contrast to the complete skin, the punches have a comparatively large edge surface relative to the surface of the skin. During tanning, chemicals are penetrating both via the edge areas and the skin surface. Because of the high ratio of skin to edge surface area when tanning complete skins, the diffusion path via the edge surface is negligible in an industrial scale, while in lab this was not yet studied. For that reason, we experimentally have determined the tanning time needed for the punches during classic tanning

Trial preparation. The trial preparation takes place immediately before the tanning so that the skin parts do not dry out. Figure 1 shows the substances and apparatus used. The skin to be tanned is stamped out using a hollow punch with a diameter of 20 mm. The skin is then weighed and the mass of the chrome solution to be used is calculated in a ratio of 1/8 (skin/tanning solution) and weighed out.

Conduct of trial. The skin was placed with the tanning solution in a sealable glass, to prevent any evaporation of liquid. A 6 mm long agitator inside the glass served to mix the tanning solution. The speed was set to 50 $^{1}/_{\text{min}}$. The pieces of skin were taken out of the glass at the end of the trial.

Figure 1: Skin (Ø 2 cm), ratio solution to skin, tanning glasses

Analysis. As already described, diluted mixtures of the “spent” tanning solutions were collected and tested for their chrome content. The measurements result in a concentration of chrome in the solution which is expressed in grams per litre.

Evaluation of trials and discussion. Results shown in Figure 2 were calculated in that the dispersed chrome quantity was defined as a percentage of the leather weight in order to relate it to the 3 weight percent criterion of Heidemann (percental approximation to 3 weight percent). Each of the points shown in the graph is the result of four measurements per hour, from which the mean value and the standard deviation were determined. After 3 hours, 29 % of the chrome mass to be reached in the skin has been dispersed in the skin. Between 4 and 17 hours the values remains nearly constant. An increase to 50 % is apparent after 20 hours. By 30 hours the value rises to 100 %. Under ambient pressure full tanning of the leather samples is achieved after 30 hours.

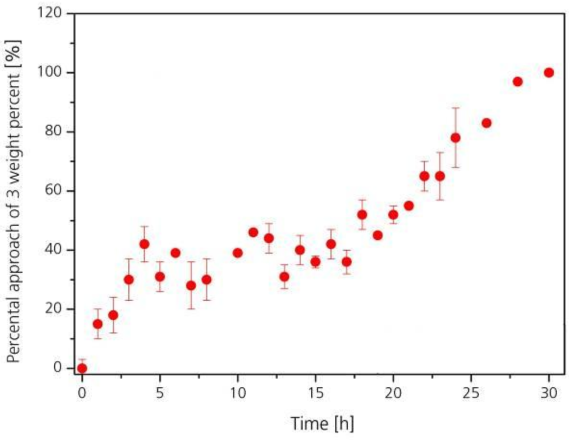

Figure 2: Percental approximation of the chrome content to 3 weight %

3.5 Tanning under the influence of compressed carbon dioxide

The tanning under the influence of carbon dioxide was carried out on a laboratory scale in a high-pressure viewing cell with the same mass ratios as in the previously described non-pressurized experiments. The high-pressure viewing cell has an internal volume of 63 cm^3 and a maximum operating range up to 175 bar at 180 °C. Figure 3 shows the build-up of the equipment used. Tanning times have been varied at a pressure of 100 bar..

The pressure was built up by means of a pump. Once the desired pressure was reached, the valves were closed. Two heating elements integrated in the outer wall of the container heated the high-pressure viewing cell (not includes in the illustration). The interior of the cell can be observed via two windows on the front and rear sides. A stirrer is mounted on the viewing cell.

Trial preparation. At the beginning of the trial preparation, the mass of the skin fragment to be tanned and the mass of the tanning solution were determined. The piece of skin was then laid in the opened viewing cell. The viewing cell was then sealed. The viewing cell was inerted by filling it with carbon dioxide at 50 bar and then releasing it.

Conduct of trial. The tanning solution was poured into the viewing cell. The tanning time was measured from the first contact with the tanning solution. After sealing the viewing cell, the pressure was elevated to the desired level by pumping in compressed carbon dioxide. The tanning sessions looked at here were carried out at 30 °C and 100 bar. The stirrer inside the viewing cell was set to 50 $^{1}/_{\mathrm{min}}$.

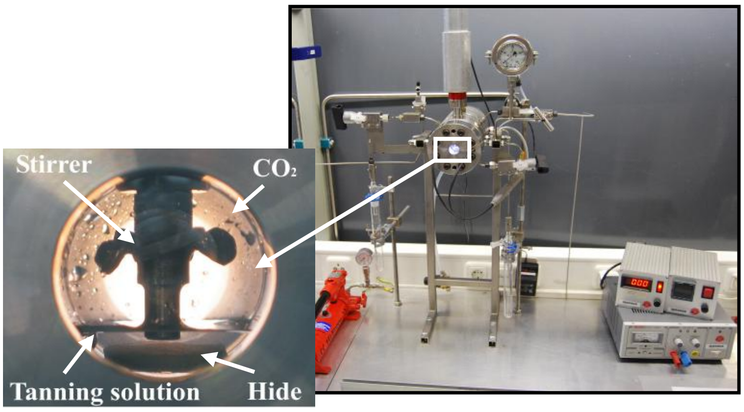

Figure 3: High-pressure viewing cell system (left: view into the viewing cell)

Evaluation of trial and discussion. The results shown in Figure 4 indicates the comparison of the tanning time of the conventional and carbon dioxide-assisted method. The tanning at 100 bar shows a similar characteristic to the conventional tanning, but in much shorter time intervals. After an initial, rapid, increase to 40 % of the required chrome content after one hour, the increase stagnates. Subsequently it rises further. 85 % of the criterion is met after a tanning time of 4 hrs, and 100 % after 5 hrs. The chrome content then approaches a threshold at 129 %. This equates to a chrome content of 3.6 %. This measured value is also confirmed in the literature for the conventional tanning process and demonstrates the comparability between laboratory scale and tanning on an industrial scale.

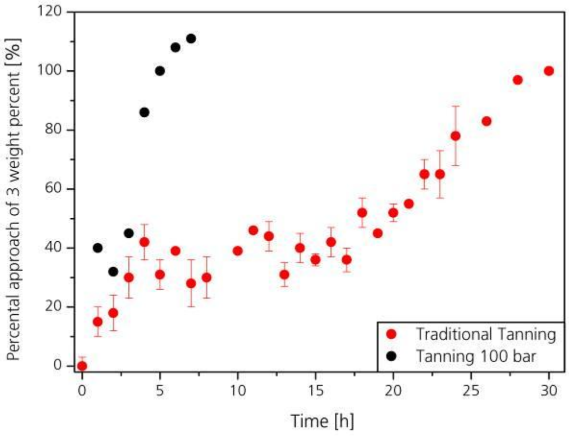

Figure 4: Comparison of the percental approximation of the chrome content to 3 weight %

The tanning can be accelerated by a factor of 6 through the influence of compressed carbon dioxide. In the next step, this result was verified in pilot plant scale and additionally the possibility of saving water investigated.

4. TANNING UNDER THE INFLUENCE OF COMPRESSED CO_2 IN PILOT PLANT SCALE

The trials on a laboratory scale have shown that accelerated tanning under the influence of compressed carbon dioxide is possible. In order to implement a process industrially, material samples must be produced that have a representative size. Particularly in the very traditional tanning industry, customers can be convinced only via product samples that can be evaluated by touch.

For the tanning on a pilot plant scale, a new system was built up at Fraunhofer UMSICHT. This system shown in Figure 7 allowed leather to be tanned in a rotating 20 L basket up to a pressure of 320 bar and a maximum temperature of 60 °C. The size of the leather amounts to approx. 0.7 m^2. Rotation of the basket is essential in order to fold and unfold leather and thus to expose each surface element to the tanning solution and CO_2.

4.1 CO_2 assisted tanning at high surplus of tanning solution

Figure 5 shows selected results of the series of trials to determine the minimum process pressure needed. The goal of the trials was, to confirm the results achieved on a laboratory scale and, to determine suitable parameters for the tanning process. Tanning time is shown on the x-axis and the process pressure on the y-axis. The tanning sessions that produced high leather quality are shown in the form of big points, and those that produced lower quality in the form of small points. The tanning sessions were carried out at the same mass ratios of tanning solution to skin as on laboratory scale. The basket rotation was set to 10 revolutions per minute and thus the skin was contacted with the tanning solution in a similar mode like in the conventional process. The graph shows that high leather quality can be produced within 2.5 hrs at 200 and 300 bar. Three hours were needed at 100 bar. By these investigations a threshold time that could not be shortened was found. It also became apparent that, at 300 bar, no significant reduction of the tanning time compared to 100 bar can be achieved.

4.2 CO_2 assisted tanning at low amounts of tanning solution

The results shown in Figure 6 were determined in a modified process. This method is characterized by a substantially lower time than the conventional method and in parallel by a significant saving in chrome-laden wastewater.

For this new method, the skins are brought into contact with only as much liquid as they can absorb. The liquid contains a sufficiently high chrome concentration to saturate the collagen bonding sites. During the high-pressure process, the liquid is absorbed by the skin and the chrome ions diffuse to the reactive points (carboxyl groups) of the skin collagen. Figure 6 shows the influence of pressure and time. The tanning time in hours is shown on the x-axis and the process pressure on the y-axis. The values for 100 bar were taken from Graph 5 and indicate the difference in the results to the tanning with high surplus of tanning solution. The trials carried out at 20 bar of carbon dioxide and below failed to produce a high leather quality. A threshold pressure could be identified at 30 bar. The overlapping of small and large points at a tanning time of 2 hours and 30 and 50 bar shows that those trials were strongly influenced, e.g. by the starting material. Depending on whether the skin stems from a neck or loin section, for example, the qualities can vary. Tanning success can be assured for all investigated types of leather at 2.5 hrs tanning time.

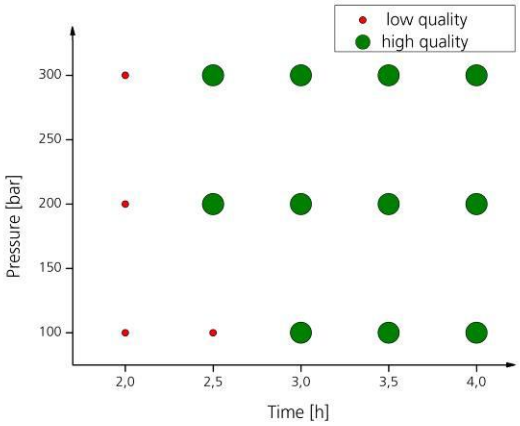

Figure 5: Results of tanning in pilot plant scale

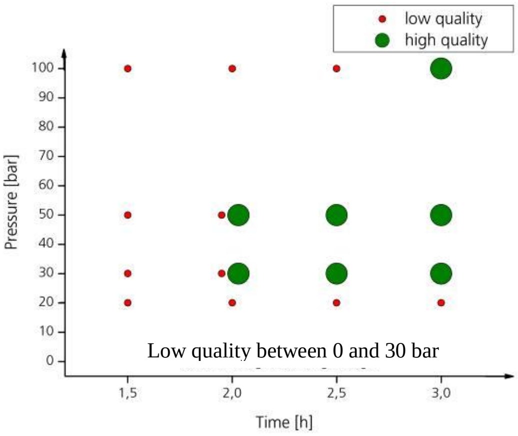

Figure 6: Reduction of time and pressure using less water

The reduction in wastewater can be stated at over 90 % with this approach. With a conventional tanning process, approx. 1.5 to 2 tonnes of chrome-laden water are needed to produce one tonne of leather. The new method produces less than 100 kg of wastewater per tonne of leather.

The again reduced process time can be attributed to the greater surface area, resp. contact surface, for the carbon dioxide. With the approach described in section 4.1, major parts of the skin were immersed in the tanning solution. The pore structures of the skin [14] could not be diffused as quickly by the carbon dioxide to the extent that occurs with the approach as described in this section.

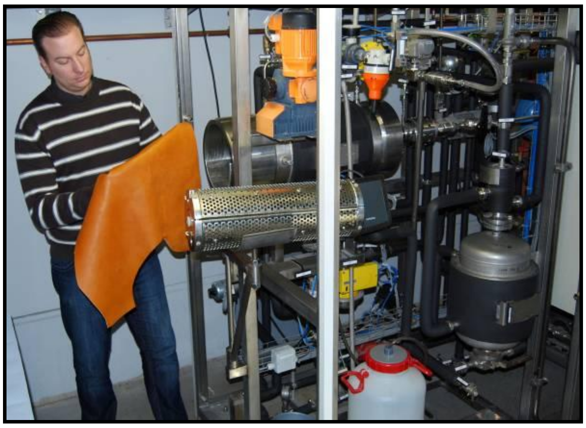

Figure 7: 20 L, 320 bar high pressure tanning equipment

Figure 8: Examples for high pressure Cr tanned leathers

5. CONCLUSIONS

It was demonstrated that it is possible to improve the conventional and proven technology for tanning of leather with the help of compressed carbon dioxide. By using carbon dioxide as an additional process medium, the tanning time was shortened by a factor of 4 to 8 (12 to 20 hrs to 2.5 hrs) and over 90 % of the wastewater was saved.

Within the context of a follow-up project supported by the Federal Ministry for Education and Research in Germany, a system will be built up on a pilot scale at Fraunhofer UMSICHT. In late 2010 it will be possible to tan up to 15 complete bovine skins in a 1 400 litre high-pressure system. This equates to a mass of over 500 kg and a leather surface area of over 50 m^2 per session. That system is intended to show how efficiently leather can be produced with the new technology. It will also be possible for potential users to test the new technology with their products and thus facilitate implementation in the industry significantly.

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