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Sustainable leather management: a mass balance benchmark of different chromium tanning technologies

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Abstract

Chrome tanning remains the best known available technology to thermally stabilize collagen, the main structural protein of any hide or skin. Multiple research studies of all mineral tanning processes over several years have shown that Cr III sulfate performs best due to two key reasons: 1. The Cr III ion forms an extremely stable complex with the inner structure of the protein triple helix, and 2. The tanning production process of penetration and fixation is easily controlled.

Tanners have traditionally focused, arguably quite logically, in the first instance on the quality of the resulting wet blue and crust leather and thus designed the process accordingly. This unfortunately has resulted in tanning processes commonly not being optimized in terms of efficiency and sustainability. Approximately only 40% of the initially offered amount of chrome tanning material (CTM) ends up in the final leather. The remainder (i.e. up to 60%) of the CTM is either washed during processing, or is in the solid waste, mainly shavings. Recycling is possible for most of this "waste." Chrome containing sludge can be safely, legally and usually economically disposed of, so it is acceptable from an environmental perspective. However, from a sustainability point of view (and most probably also from a longer-term economic view), this endless "dumping" of finite resources needs to be questioned, and the sooner the better.

In the following article, two alternatives to the "standard" chrome tanning process are discussed. High-exhaustion technology and/or hybrid tanning technology would lead not only to a major improvement in the mass balance for chrome tanning material, it would also in turn be of immediate benefit in terms of the public perception of the leather sector and most probably also critical for the long-term future of the entire tanning industry.

Keywords chromium, tanning, mass balance, effluent, waste, exhaustion.

1. Introduction

The main "operating" step in leather manufacturing is the tannage, which stabilizes the collagen and chemically converts this protein into leather. Due to the ideal chemical characteristics of chromium in the valence state III, this element can enter inside the triple helical structure of collagen where it uses its special complexing and cross-linking behavior to stabilize the protein matrix. The geometric dimensions of the resulting Cr(III) complex fits in perfectly with the surrounding 3-D protein structure of the collagen. The macroscopic result is a significant increase of the denaturation point (= shrinking temperature) of the leather above 100 °C that can only be achieved with a chrome tanning material (CTM) and not with any other metal tanning agent on its own. Decades of research were necessary to understand the ideal, complex chemistry of chrome tanning scientifically and several theories have been developed which explain the different phenomena of this process step. One famous theory is the principle of covalent tanning with chrome tanning materials (CTM) within the link-lock mechanism (1). Another important and fundamental finding is the principle of olation/oxolation of metal ions (2).

1.1. The principle of olation

Reference is often made to the cross-linking of CTM, and rather less frequently to olation, a type of “in-situ” inorganic polymerization (3), but this is still fundamental and critical for understanding the tanning process. At a low pH (i.e. “pickle”) many metal ions exist in solution as complexes with a low molecular weight that are unreactive or rather less reactive to collagen. As the pH increases (i.e. “basification”), these complexes start to react with each other to form larger molecules (metal ion oligomers) with higher reactivity towards the collagen subunits, up to a level where they become insoluble. The tendency is to form bigger molecules rather than cross-linking collagen, up to a level where no reaction with the protein takes place anymore, and the ability to steer this with suitable ligands depends on the nature of the metal. Here, only chrome(III) has the right pH-dependent balance between increasing both molecular weight to the right size and reactivity toward collagen, also steering this easily with suitable ligands like sulfate or acetate.

1.2. Other mineral tanning technologies

It is known that other metals can provide a stabilization effect such as aluminum, zirconium or iron, to name the most important ones in order of tanning power. The stabilization effects follow a different mechanism as described in (1) and even the pH-dependent olation/oxolation phenomenon (3) has different (for leather tanning unfavorable) characteristics. Subsequently, all these alternative metal tanning systems result also in a lower denaturation point of the resulting substrate. So far, no alternative tanning agent for leather exists that fulfills the unique property profile of CTM. Therefore, non-chrome systems usually require some degree of “compensation” especially in the retanning step. This results in additional amounts of conventional retanning chemicals being required, thus changing sustainability profile and haptic and technical performance, although application-wise a chrome-like character is possible.

1.3. Advantages and challenges of the chrome tanning process

The chrome tanning process is the dominant tanning system also because it is a relatively easy, stable and robust process. It results reliably in a safe, high-performance technical substrate. The speed of penetration of CTM can be easily steered via simple measures and controlled even visibly. The following process step involving the cross-linking reaction of the chromium in the leather can again mainly be managed by pH adjustment with harmless basification agents. Thus about 85% of the world’s leather production is still based on chrome-tanned leather, and this has been the case for more than 100 years and is expected to continue in the foreseeable future.

To continue the future-proof development of chrome tanning both in general and especially from a sustainability point of view, a closer look at two important aspects is required. First: process rules to avoid the formation of Cr VI in leather. Second: process concepts to increase the utilization of CTS further in order to keep the release of chromium into the effluent to an absolute minimum.

For the first topic, clear process rules to be followed have already been established and are well known as a best available technology (3). In order to have a closer look at the second topic, a simple mass balance needs to be performed to compare different chrome tanning process alternatives.

2. Mass balance of different chrome tanning processes

Here, the mass balance of three different process alternatives is compared and all should result, with relatively minor adjustments of the retanning recipe, in similar crust articles:

1. Standard chrome tanning
2. High-exhaustion chrome tanning
3. Hybrid tanning – wet white pre-tanning with high-exhaustion re-chroming

2.1. Standard chrome tanning process

In a standard chrome tanning operation, initially up to 8% of CTM is offered (in relation to pelt weight – Table 1), corresponding to an absolute amount of 17-20 kg Cr2O3 based on 1,000 kg pelt. About 60% of this chromium will be chemically fixed (via covalent bonding) to the protein while approx. 40% remains still unfixed (either in the float or in the liquid within the leather matrix after the tanning operation). During the subsequent washing and processing steps (samming, retanning), about 40% of the initially offered CTM will be washed out in the effluent and should be separated by further treatment. In a modern tannery operation, the majority of this discharge could be separated and recycled. However, good equipment and especially proper and intensive quality controls of the recycled chrome material are necessary to ensure that the quality of the wet blue is comparable to the usage of only CTM from a reliable supplier. If the chrome is not recycled it must be safely and legally deposited at appropriate, usually municipal, approved facilities.

Furthermore, up to approx. 20% of the initially offered CTM will end up in the solid waste as shavings. The majority of the chrome in the shavings will either end without a specific functional requirement in an upstream basic raw material (e.g. for construction or energy generation) or again end up on as waste in a landfill.

Considering these two "losses" in a normal retanning process, without additional re-chroming only around 40% of the initially offered amount of CTM ultimately ends up in the final leather. From this remaining chromium in the final leather matrix only a very small part (some ppm) is not strongly bonded and can be extracted with artificial sweat from the dried crust leather. This is what is usually referred to as the "leachable" chrome part.

	Standard chrome tanning	
offering for 1.000 kg splitted pelt:	*6-7 % CTS on pelt = **17-20 kg Cr2O3***	7% 6% *unbonded* *bonded*
tanning float:	*~10-20% = **1.5-4 kg Cr2O3** - recyclable*	20%
samming/washing:	*~10% = **2kg Cr2O3** - recyclable*	10%
shaving	*~ **5 kg Cr2O3** content difficult to recycle*	20%
~ 500 kg wet blue (shaved)	*~ **9-10 kg Cr2O3** content*	
retanning:	*~10% = **2 kg Cr2O3** - difficult to recycle*	10%
~250 kg dried crust (~220 qm)	***~7.5 kg Cr2O3***	40%
extractable range (100 - 400 ppm)	***0.1-0.4 kg Cr3O3** / 250 kg crust based on wb*	

***Table 1**: Mass balance of a standard chrome tanning process*

2.2 High-exhaustion chrome tanning process

As an alternative to standard chrome tanning processes, in Table 2 the mass balance of a typical high-exhaustion chrome tannage is illustrated. The sustainability is considerably improved, because the majority of chrome originally offered ends up in the leather. Furthermore, this process can be run with the same equipment as the standard chrome tanning process; no special investment needs to be made and in principle every tannery worldwide should be able to switch to a high-exhaustion process.

As less chromium will be washed out into the effluent with this high-exhaustion process, the initial offer can be reduced down to 4.5 - 5% (based on pelt weight). This alone represents an almost quarter reduction in CTM use compared to the standard process. Through the addition of special fixing agents – high-exhausting chrome tanning agents – the exhaustion can be improved significantly, not only in the tanning, but also in the retanning process step. Subsequently, the resulting amount of chrome in the raw effluent is so low that most legal requirements for the chromium content of the discharge can be met without any problem. This process also results in a high score in the Leather Working Group (LWG) audit, which requires an uptake of at least 97%. The total amount of chromium in the final leather is comparable to the standard chrome tanning process. The key difference is that the unfixed proportion, which normally gets washed out during processing and ends up in the effluent in the standard process, is effectively eliminated.

	Cr3O3 balance	**High Exhaustion Tanning**
offering for 1.000 kg splitted pelt:	*4 - 5% CTS on pelt* *= **14 - 16 kg Cr2O3***	4.8% *bonded*
plus High Exhausting Chrome agent incl. samming	*<3% = **< 0,4kg Cr2O3** - recyclable*	
shaving	*~ **5 kg Cr2O3** content difficult to recycle*	
~ 500 kg wet blue (shaved)	*~ **9 kg Cr2O3** content*	
plus High Exhausting Rechroming agent	*~5% = **0,5-1 kg Cr2O3** - difficult to recycle*	
~250 kg dried crust (~220 qm)	***~8 kg Cr2O3***	
extractable range (100 - 400 ppm)	***0,1-0,4 kg Cr3O3** / 250 kg crust based on wb*	

Table 2: *Mass balance of a high-exhaustion chrome tanning process*

2.3 Hybrid tanning technology – wet white pre-tanning followed by high-exhaustion re-chroming

With the term "hybrid tanning technology" we refer to the combination of wet white pretanning with a synthetic tanning agent. For the most sustainable wet white technologies (e.g. ref. 3) there is even no need to pickle. Obviously, no chromium can end up in the effluent, or any by-products such as shavings; the process up to the wet white intermediate stage is completely free of chrome.

In order to get a similar intermediate like a wet blue, the retanning process then has to start with a re-chroming step. A high-exhausting re-chroming agent is added, approx. 5-7% based on shaved wet white weight, which correlates to only around 2-2.5 kg absolute Cr_2O_3 based on 1,000 kg split pelt. (Shaved wet weight has about 30-50% of the weight of a pelt, depending on water content and shaved thickness.)

With a special fixing re-chroming agent the exhaustion in this process step is extremely high. Close to 100% of the initially offered Cr_2O_3 ends up in the crust leather, with only a tiny amount of Cr_2O_3 washed out in the retanning floats. Visible for all by their lack of color, these floats are correspondingly virtually colorless and transparent. After re-chroming, the typical organic retanning process completes the process, usually with only slight adjustments in the recipe being necessary in order to reach a similar crust to that achieved with a traditional wet blue intermediate.

	High-exhaustion rechroming
offering for 1.000 kg splitted pelt:	*5-7% RC on* ***ca. 2-2,5 kg Cr_2O_3***
tanning float:	
samming/washing:	
shaving	
~ 500 kg wet blue (shaved)	
retanning:	***< 0.5 kg Cr_2O_3***
~250 kg dried crust (~220 qm)	***ca. 2 kg Cr_2O_3***

Table 3: *Mass balance of a hybrid tanning process – wet white pre-tanning followed by a high- exhaustion re-chroming process.*

2.4 Discussion of the three chrome tanning processes

The comparison of the mass balances of the three tanning processes show that, from a sustainability point of view, the two suggested alternative processes are more favorable compared to the standard chrome tanning process. Since there are so many parameters that can influence the outcomes, such as local conditions, recipes, raw material quality, beamhouse preparations, etc. we have purposely entered only rough numbers for chromium content in the effluent. However, many production-scale examples have shown that running a high-exhaustion process already reduces the chromium content of the effluent to such an extent that in most cases the effluent can be discharged directly to a wastewater treatment plant without any pre-treatment or chrome separation required. Also in the case of sludge, it has such a low chromium content that it is not considered to be a hazardous chemical (according to most of the legal requirements). This already is a considerable process achievement.

In our industry today there still remains the issue of Cr-containing shavings, which concerns massive volumes. The ultimate sustainable process and best available compromise where you still have all the advantages of a chrome-tanned article without this issue is considered to be the “hybrid tanning process.” Zero chrome in the effluent and the shaving byproduct is obviously guaranteed during a wet white pre-tanning step. With the use of a special high-exhausting re-chroming agent, the leather will virtually fix all offered active chromium ions afterwards; therefore nearly all offered amounts of chromium will end up in the final leather sold, and not in any waste.

3. Conclusion

Stainless steel can be produced only with chromium, i.e. there is no other element in the periodic system which gives a similar stabilization of the iron. Similarly in leather making there is no other known technical possibility of stabilizing the protein than in a chrome-tanned leather. There are different ways to chrome tan a leather. In order to strive for the best available sustainability performance it has been shown that the two proposed alternatives to standard chrome tanning would provide an interesting sustainable opportunity: either a high-exhaustion chrome tanning process including a downstream use for the wet blue shavings, or – even better – a wet white retanning process followed by a shaving and a re-chroming step of the shaved material. In both cases the overall material mass balance would be improved. Depending on adjustments in the retanning process. even the resulting final crust in all three articles would be comparable.

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