

Taking tanning to the next level with an improved pickle product

Dr. Volker Rabe, Maurice Aertse, Thomas Schneider - Lanxess

Introduction

The dominant chrome tanning process currently used at the present time is simple, fast, reliable and highly efficient. Over past decades there have been countless initiatives to find alternatives, however chrome tanning remains the primary method for over 85% of the leather produced today. This long and continuing success is due to many reasons, not only those mentioned above but also its high adaptability. Over time, the focus has been developed and enlarged significantly. Starting from a focus on producing the optimum quality of leather, it became more and more a holistic view, including the environmental aspects of production. Although state-of-the-art chrome tanning is already at a very high level of performance in this respect, research at Lanxess is being continued in order to further optimise it, which will make this tanning method attractive and reliable in the foreseeable future and beyond.

Challenges for chrome tanning

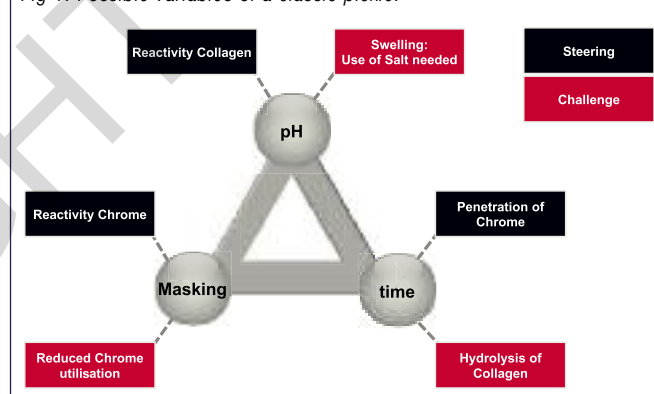
Requirements for chrome tanning still include high process efficiency, reuse of tanning floats, superior prevention of Cr (VI) formation in leather and solutions for the issue of chrome-tanned shavings issue. For many of these points, there are already solutions available such as basifying agents for high exhaustion tanning⁽¹⁾ or products which provide protection against Cr (VI) formation⁽²⁾.

Salinity is a further critical issue and so the reduction of salt used in the pickling process is a key challenge in the leather industry. The pickle-free X-Crust process (X-Tan organic tannage, followed by reduced offer re-chroming) has been successfully run in production at various tanneries and provides a more optimised solution to salinity issues⁽³⁾. However, as a leading manufacturer and developer of chrome tanning products, Lanxess has continued to research further alternatives to offer comprehensive solutions to fit all tanneries.

The pickle

The pickling process before tanning has two key aims. First, complete the deliming process and, second, prepare the hide and/or skin for chrome tanning. The typical pickle process has three key variables of pH, degree of masking, and time. These variables have an influence on each other and can be adjusted according to the requirements of the intermediate wet blue and/or end leather. (Fig 1) Each new pickle product must ensure the same high quality of wet blue that is achieved with the industry standard, while also avoiding or reducing the challenges of the traditional system. Additionally, the process must remain safe, simple and robust.

Fig 1: Possible variables of a classic pickle.



Challenge: Salt content in the pickle

In order to understand how the pH value controls the reactivity of collagen and why salt is needed in the pickle, the structure of the skin must be examined at the molecular level (Fig 2). For the sake of clarity, the carbonamide groups -CO-NH- are dots and only the relevant amino acid residues

Fig 2: Simplified schematic representation of the skin at the molecular level during the tanning process.

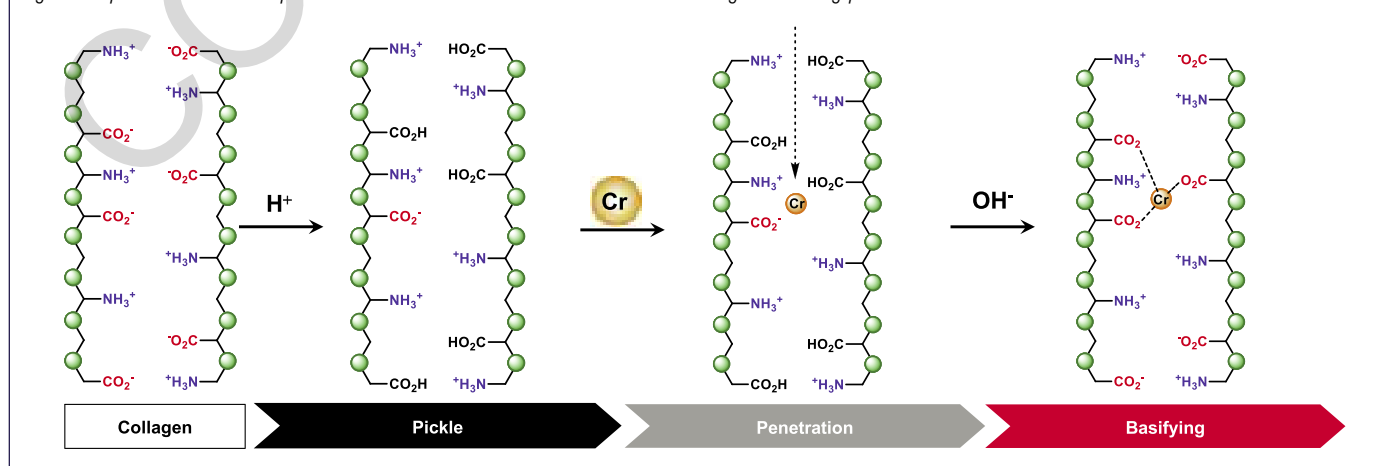
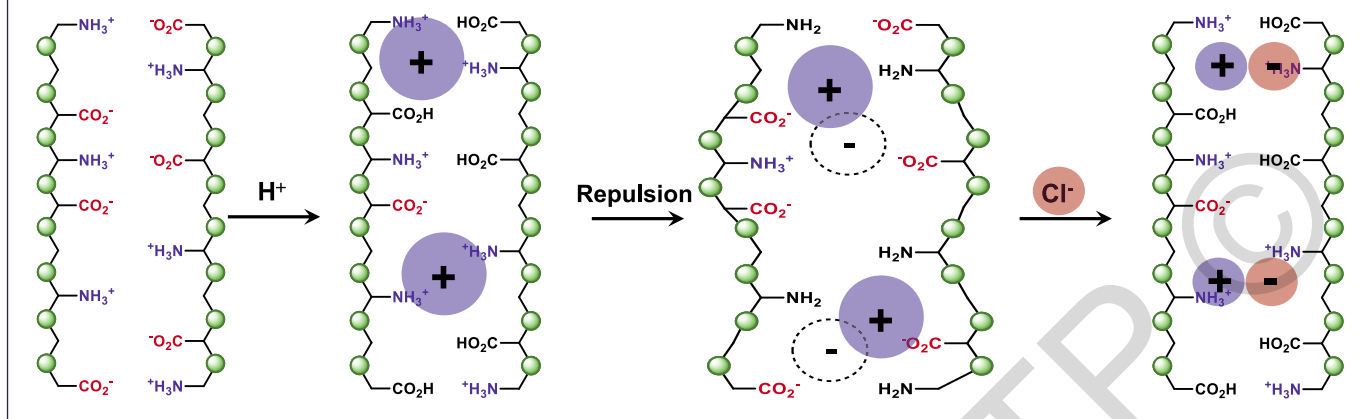




Fig 3: Swelling due to one-sided loading and compensation by salt in the pickle.



important for tanning are shown. In collagen, the number of positive amino groups is equal to the number of negative carboxyl groups, all charges are balanced at a pH value of about 5.5 and the collagen can be seen as neutral.

By lowering the pH value, the carboxyl groups are protonated, i.e. the number of possible binding groups for the chromium complexes is reduced, thus lowering the reactivity of collagen to the chromium tanning agent. This reduction is reversed in the basification step by increasing the pH value. The pH value is therefore an easily controllable, but very effective, parameter for chrome tanning.

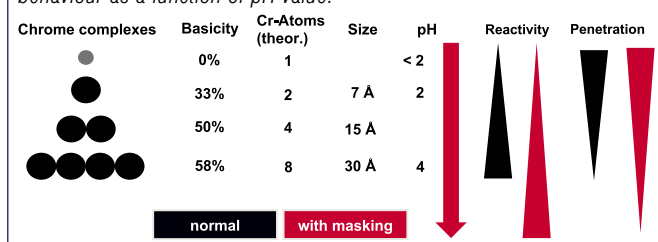
The protonation of the carboxyl groups creates a one-sided positive charge in the collagen. Due to the charge, the protein chains repel and swelling occurs measurably by an increase in pelt thickness⁽⁴⁾. In the classical pickle, salt is used to balance the partial charges with the Cl ions (Fig 3).

Another way to balance the charge and reduce swelling is to use non-swelling acids⁽⁵⁾. The disadvantage of most of these acids is that penetration is not fast or uniform enough⁽⁶⁾. Therefore, previous systems were often limited to split and thinner skins.

Masking: Control of the reactivity of the chrome tanning agent

The most common chrome tanning agents have a basicity of approximately 33% and are available in simplified form as di-nuclear chrome complexes in solution. The reactivity of this complex towards the skin is low, but the penetration speed is fast or sufficiently uniform. When the pH value is increased, these complexes polymerise with each other and form larger molecules. This increases the reactivity towards the collagen but reduces the penetration speed. This applies up to the point where the complexes become completely insoluble. For pure chromium sulphate, this point is about pH 4.5 (Fig 4).

Fig 4: Schematic representation of chromium complexes and their behaviour as a function of pH value.



The values shift when masking agents are added to the chromium complex. The masking substances are deposited around the chromium complex like a protective shield, slowing down the growth of the molecule size, increasing the stability against higher pH values, and lowering the reactivity of the chromium tanning agent against the collagen. This can be used for a salt-reduced pickle. By using enough masking agent, a sufficient penetration of the chrome is possible even at higher pH values⁽⁷⁾ like >4.5, where the swelling is greatly reduced⁽⁸⁾. The problem is that at these high pH values the penetration speed of the masking agent is very slow and therefore, the pickling time is very long. Also, with unsplit and thick hides a large quantity of masking agent has to be added and thus the utilisation of the chrome tanning agent significantly decreases. For this reason, these systems are usually limited to split and thinner hides.

Time: The challenge of collagen hydrolysis

A factor that is often underestimated despite its strong influence on the quality of the leather is the hydrolysis of collagen. This degradation of the collagen chains by H⁺ ions leads, depending on the degree of looseness, to reduced physical values and even visible damage of the finished leather. The degree of damage strongly depends on the temperature of the liquor and the duration of the pickle, and to a lesser extent on the pH value (Fig 5). This means that the longer the pickle process and the warmer the float, the stronger the attack on the collagen. Some tanneries attempt to counter this problem with the addition of ice. The thicker the hides, the longer the process, and attempts to shorten it can quickly lead to quality issues.

Fig 5: Increase in dissolved organic molecules ("degradation level") in the pickle as a function of time and temperature with the same pH value.

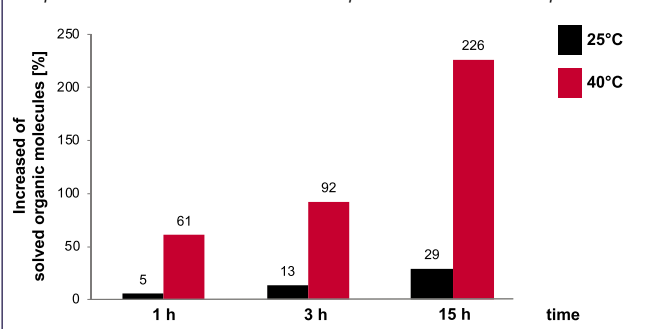




Fig 6: Recipe of a conventional tanning (left) and a chrome tanning with Blancorol HP (right).

Process	%	Products	°C	dil.	Min	Remarks	Pic
Pickling	40	Water	20				
	5,0	Salt			15	6°Bè	
	+	0,5	Formic acid	1:5	15		
	+	0,4	Sulphuric acid	1:10	30		
	+	0,5	Sulphuric acid	1:10	270	pH 3,3; Cut 100%	
+	6,0	Chromosal B			120		
+	0,1	Preventol U-Tec G			30		
+	0,5	Blancorol BA-I			420	t : 40°C pH 4,0	
Drain						Drain	
Wash	100	Water	25		10		
Unload							
					Time 16 h 10 '		

Process	%	Products	°C	dil.	Min	Remarks	Pic
Pickling	40	Water	20				
	3,0	Salt			15	4°Bè	
	+	0,5	Formic acid	1:5	15		
	+	0,8	Blancorol HP	1:10	30		
	+	0,8	Blancorol HP	1:10	60		1
						Cut >50% blue	
+	2,0	Chromosal B			60		2
+	3,5	Chromosal B			60	pH 2,5	3
+	0,1	Preventol U-Tec G			30		
+	0,5	Blancorol BA-I			420	t : 40°C pH 4,0	4
Drain						Drain	
Wash	100	Water	25		10		
Unload							
					Time 11 h 40 '		

Lanxess solution: Blancorol HP

When developing the new pickle product, the primary focus was on reducing both the salt and the process time whilst maintaining the leather quality even for very thick unsplit hides, avoiding hydrolysis and increasing chrome utilisation. The process remains with comparable robustness and the same controls known from the classical system.

This was achieved by combining all existing concepts in one single product:

- Control of collagen reactivity through low pH value;
- Use of non-swelling acids to minimise the amount of salt required;
- Use of masking agents to ensure a good penetration of the chrome tanning agent even at higher pH values inside the skin.

Blancorol HP: Practical experience

To demonstrate the feasibility of Blancorol HP, unsplit Scandinavian bull pelts, of the weight class 30 kilogrammes, were divided, with one half tanned with a classic pickle and the other half using Blancorol HP (Fig 6).

It is important to note that both pelts were delimed completely until the phenolphthalein indicator was colourless. This is particularly important for the Blancorol HP process, as otherwise a time delay in chromium penetration might occur. For this reason, the deliming process must be carefully controlled.

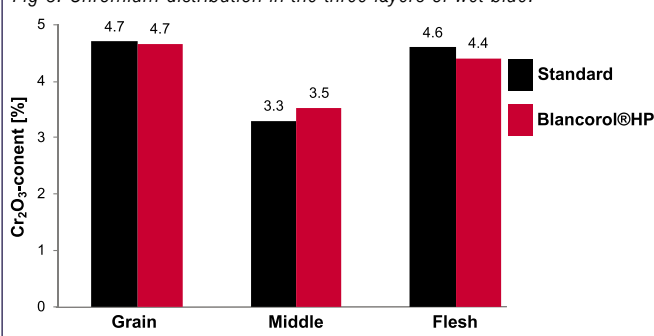
The first offer of Chromosal B was added to the new pickling process after 90 minutes when the inner part of the pelt was still > 50% blue (Fig 7, Pic 1). The addition of the second offer of Chromosal B took place after a further 60 minutes (Fig 7, Pic 2). Two hours after the first addition of the chrome tanning agent, penetration was almost complete with only a small white stripe visible inside the skin (Fig 7, Pic 3). When the classical pickle is through after five hours, the Blancorol HP process has already been basified for two hours (Fig 7, Pic 4).

The resulting wet blue sides were split into three layers and the chromium content measured (Fig 8). Surprisingly, despite the early addition of the tanning agent, a somewhat better chrome distribution was found compared to normal chrome tanning. This demonstrated good penetration of the chrome

Fig 7: Images during pickling and tanning to check penetration behaviour (indicator: Bromocresol Green).

Total time	Conventional Pickle	Blancorol HP-Process	Process
Pic 1 90 min			60 min after Blancorol HP
Pic 2 150 min			60 min after 1. Rate Chrom B.
Pic 3 210 min			60 min after 2. Rate Chrom B.
Pic 4 300 min			120 min after starting Basifying

Fig 8: Chromium distribution in the three layers of wet blue.



despite the initially very high pH value inside the skin.

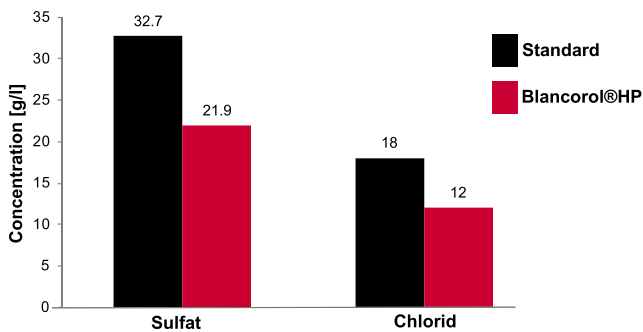
Also by the use of 0.5% less Chromosal B in the Blancorol HP pickle, the same chromium content was measured in the wet blue as in the standard process. Consequently, there is also, less chromium in the wastewater (Fig 9) with Blancorol HP.

Fig 9: Chrome content in the floats and wet blue.

Standard		Blancorol HP	
Cr ₂ O ₃ Float	Cr ₂ O ₃ Wet Blue	Cr ₂ O ₃ Float	Cr ₂ O ₃ Wet Blue
1.6 g/l	4.2 %	1.0 g/l	4.2 %



Fig 10: Decrease in ion concentration through the use of Blancorol HP in the tanning liquor.



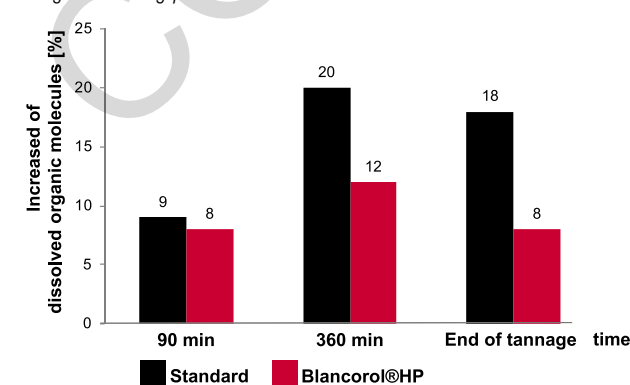
By using 40% less salt, the chloride content in the effluent could also be reduced and the sulphate content also decreases by saving chrome tanning agents and sulphuric acid (Fig 10). This reduces the TDS (total dissolved solids) by 30%.

Fig 11: Thickness change of the skin as a measure for the swelling during the pickling process.



By measuring the increase in thickness of the pelts during the Blancorol HP pickle and comparing it with the classical system, the effective suppression of swelling by the non-swelling acids at a float density of 4° Bé is demonstrated (Fig 11).

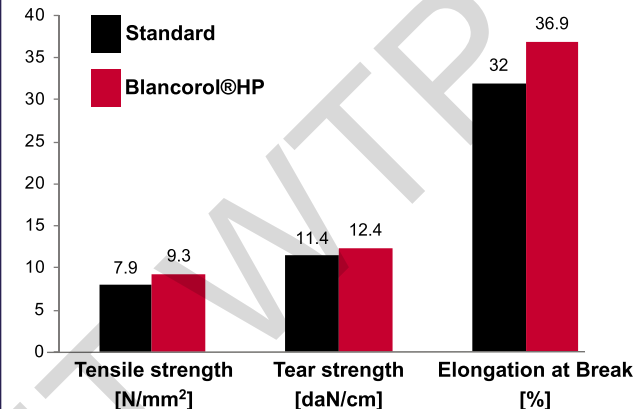
Fig 12: Dissolved organic molecule content ("degradation level") during the tanning process.



As a consequence of the reduced collagen hydrolysis during the Blancorol HP process, less dissolved organic molecules are measured than in a standard tanning process, which clearly indicates a lower level of damage to the natural collagen structure (Fig 12).

The resulting leathers are firmer, fuller and tighter. This is confirmed by the measured physical values of tensile strength, tear strength and elongation at break of the leather. All results show higher values (Fig 13).

Fig 13: Increase in physical values due to use of Blancorol HP Pickle.



Blancorol HP: Bulk trials

These good results have already been proven on an industrial scale through several trials. One example is the tanning of 16 tonnes of raw hides from southern Europe. The main challenge was the use of "surface water" with an initial temperature of 25°C. This, together with the high thickness of the hides, meant that slight adjustments to the recipe were necessary:

- The two additions of Blancorol HP were increased to 1% each;
- The running time after the second chromium addition had to be adjusted to 240 minutes.

It should be mentioned that the chrome was completely penetrated in the coupon (butt) 120 minutes after the second chrome addition (Fig 14, Pic 3), but in order to also achieve

Fig 14: Images during pickling and tanning to check penetration behaviour (indicator: Bromocresol Green).





Fig 15: Picture of thickest part of the wet blue and splits at 2.4 millimetres or 1.5 millimetres.



Fig 16: Advantages of the Blancorol HP process compared to a classic pickle at a glance.

Handling	Performance	Sustainability
Time saving Process time for pickle and tanning can be substantially decreased	Higher physical properties Less hydrolysis, resulting in tighter and fuller leather with measurable improved physical values	Higher Exhaustion Higher utilisation of the chrome tanning material with a better distribution in the cross-section of the pelt
Robust & Easy Same controls as in a normal process with less risk of chrome stains at higher end pH	Improved Appearance Colour of resulting wet blue is nicely blue	Clean Waste Water Significantly reduced salt-freight (particularly chloride, sulfate) and Chromoxide in the effluent

complete penetration in the cheeks, an additional 120 minutes running was done (Fig 14, Pic 4).

The final wet blue pieces were split at the thickest parts to 2.4 millimetres and 1.5 millimetres respectively. In all cases the splits showed good chrome penetration and were no different to the normally used tanning with overnight pickling (Fig 15).

With Blancorol HP, the overall process time from pelt to wet blue was reduced from 48 hours to 24 hours. The wet blue showed a remarkably uniform blue colour. The resulting leathers were firmer, fuller and tighter due to reduced hydrolysis. Most importantly, Blancorol HP has been proven to work for very thick, unsplit raw hides, which is a clear indicator of the robustness of a tanning system.

In summary, Blancorol HP provides an improvement in terms of handling, performance and sustainability (Fig 16).

Summary

With Blancorol HP the traditional tanning process can be taken to the next level. This is achieved the first time by combining all the existing concepts to improve the pickle in only one product. All pickle parameters (pH, masking agent and time) have been taken into account and the associated challenges for the tanning process have been minimised. This improves both the quality of the wet blue and the resulting leather through reduced hydrolysis. Furthermore, the overall tanning is also improved from an environmental

point of view by reducing the salt load and chrome content in the floats. A further advantage is the significant reduction of the required process time while maintaining the robustness and production reliability of the standard tanning system. This is shown by the comparison in the tanning of thick, unsplit hides, which succeeds with minimal adjustments to the pickle process. The Blancorol HP product thus meets all the defined targets in order to provide chrome tanning with a further product solution for improving the system.

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