



Glutaraldehyde: Proven technology for white metal-free leathers

Part 2 of 2: The versatility of glutaraldehyde in leather making

C. Gabagnou, F. Döppert, D. Herta, M. Hess, J.T. Pelckmans, J. Christner, J. Fennen
TFL Ledertechnik AG

Part 1 of this paper, published in December/January 20015/16 and entitled Pre-tanning with modified glutaraldehyde, describes the theory and practice of glutaraldehyde tanning, ecological and toxicological aspects, and pre-tanning including a guideline formulation.

In this paper, Part 2, the study expands upon the versatility of this product, and includes two guideline processes for the retanning and fatliquoring of automotive and footwear leathers.

3. The flexibility and advantages of leathers pre-tanned with glutaraldehyde

Every tanning method has its own characteristics regarding the process, the type of leather produced, costs, eco/tox considerations, etc. As the vast majority of leathers produced today are chromium tanned, it is evident that chromium tanned leather is the reference technology.

Chromium-free leathers based on glutaraldehyde tanning have so far been commercially successful mainly in the field of automotive leathers. The better performance of chromium-free vs. chromium tanned leather regarding dry shrinkage behaviour has been one of the factors favouring this tanning method in this sector. In recent years, non-automotive applications of wet-white technology have become more common in the business, but they are still seen as the exception rather than the rule. This dominance of the automotive sector has led to some common misconceptions regarding glutaraldehyde tanning.

3.1. PROCESSING FULL SUBSTANCE MATERIALS

Automotive leather is almost without exception made from lime split pelts. In this situation there is only a relatively low thickness substrate to achieve full penetration of glutaraldehyde. It is therefore often assumed that it is not possible or not reliable to achieve penetration and tannage with glutaraldehyde on full substance hides. However, trials with both sides and examples of regular production prove that this is in fact absolutely feasible.

To achieve a good penetration of the tanning agent, it is important to select a significantly masked glutaraldehyde and otherwise follow the standard conditions of tanning with glutaraldehyde. For example:

- A bath pH of 2.5 to 3.0 after pickling
- A yellow cross section with bromo-cresol-green
- A temperature of approximately 25°C during pickling and pre-tanning

- A bath pH of 4 to 4.5 after basifying
- A green cross-section with bromo-cresol-green.

Comparison trials between a short process with a penetration time of 4 hours and a long process with a penetration time of 8 hours using a 4% glutaraldehyde offer showed that both are suitable to achieve full penetration. This was proven by splitting the wet whites produced into three layers and measuring the shrinkage temperature of each layer. There was neither a difference between the different layers of one side, nor a difference between the two sides.

3.2 RETANNING AND FATLIQUORING WET-WHITE FROM GLUTARALDEHYDE PRE-TANNAGE

Retanning and fatliquoring techniques are fully established for these leathers. Examples of outline formulations for automotive and shoe nappa leathers are set down respectively as *Panels 9* and *10*.



Panel 9: Automotive leathers (FoC): Retannage and fatliquoring				
Material: Bovine glutaraldehyde tanned. Shaved 1.1 mm				
Process	%	Product	Time	Required
<u>Wash</u>				
Add	300	Water 30°C	10 min	
Add	0.3	Emulsifier ⁽¹⁾	60 min	pH 5.0
Add	5.0	Phenolic tanning agent ⁽²⁾ (high tanning capacity)		
Drain,				
<u>Neutralisation</u>				
Add	100	Water 30°C		
Retannage	2.0	Sodium formate	30 min	pH 5.3
	8.0	Tanning agent ⁽³⁾ (Low phenolic and formaldehyde)		
	3.0	Dispersing acrylic polymer ⁽⁴⁾		
	3.0	Synthetic/natural fatliquor ⁽⁵⁾ (lightfast)	20 min	
	3.0	Hollow sphere polymer ⁽⁶⁾		
Add	15.0	Phenolic tanning agent ⁽²⁾ (high tanning capacity)		
Add	15.0	Tanning agent ⁽³⁾ (Low phenolic and formaldehyde)	90 min	
<u>Dyeing</u>	3.0	Synthetic/natural fatliquor ⁽⁵⁾ (lightfast)	20 min	
Add	3.0	Profile dyestuff ⁽⁷⁾ (High fastness)		
		(+ run overnight on automatic settings)		
Add	2.0	Formic acid (85%)	40 min	pH 3.9
Drain, wash 300% water 45°C/10 min, drain				
<u>Fatliquor</u>				
Add	100	Water 45°C		
Add	12.0	Synthetic/natural fatliquor ⁽⁵⁾ (lightfast)	60 min	
Add	3.0	Butylacrylate polymer ⁽⁸⁾	30 min	
Add	6.0	Tanning agent ⁽³⁾ (Low phenolic and formaldehyde)	20 min	
Add	1.0	Formic acid (85%)	20 min	
Add	1.5	Formic acid (85%)	30 min	pH 3.5
Drain, wash 300% water 45°C/10 min, drain				
Pile overnight, set, vacuum dry (45°C/5 min), hang dry free of tension, stake, mill.				
Key - (1) Barron SAF, (2) Sellatan MBS gran, (3) Sellatan WL-W liquid, (4) Magnopal DP, (5) Coripol ESU, (7) Sella Fast (Beige) HF-G, (8) Magnopal SFF.				

Panel 10: Shoe nappa leathers (FoC): Retannage and fatliquoring				
Material: Bovine glutaraldehyde tanned. Shaved 1.1 mm				
Process	%	Product	Time	Required
<u>Wash</u>				
Add	300	Water 30°C		
Add	0.3	Emulsifier ⁽¹⁾	20 min	pH 4.9
Drain,				
<u>Neut/retan</u>				
Add	100	Water 30°C		
Add	10.0	Tanning agent ⁽²⁾ (Low phenolic and formaldehyde)	30 min	
Add	1.0	Sodium formate		
Add	0.3	Sodium bicarbonate	20 min	pH 5.6
Add	4.0	Polymer ⁽³⁾ (Filling and softening)		
Add	2.0	Natural/synthetic fatliquor ⁽⁴⁾	20 min	
Add	3.0	Synthetic/natural fatliquor ⁽⁵⁾ (lightfast)		
Add	16.0	Tanning agent ⁽²⁾ (Low phenolic and formaldehyde)		
Add	16.0	Tanning agent ⁽²⁾ (High astringency)	90 min	pH 5.3
Add	3.5	Dyestuff	40 min	pH 5.0
		(+ run overnight on automatic settings)		
Add	100	Water 45°C		
Add	1.5	Formic acid (85%)	30 min	pH 4.0
Drain, wash 300% water 45°C/10 min, drain				
<u>Fatliquor</u>				
Add	100	Water 45°C		
Add	0.5	Sodium bicarbonate	10 min	
Add	4.0	Polymer ⁽³⁾ (Filling and softening)		
Add	8.0	Natural/synthetic fatliquor ⁽⁴⁾	60 min	
Add	6.0	Synthetic/natural fatliquor ⁽⁵⁾ (lightfast)	20 min	
Add	6.0	Low phenolic and formaldehyde tanning agent ⁽²⁾	30 min	
Add	1.5	Formic acid (85%)	30 min	pH 3.3
Add	1.5	Formic acid (85%)	30 min	
Drain, wash 300% water 45°C/10 min, drain				
<u>Fixation</u>				
Add	200	Water 50°C		
Add	1.0	Cationic fixing agent ⁽¹⁰⁾	20 min	
Drain, wash 200% water 25°C/10 min				
Pile overnight, set, vacuum dry (1.5 min/45°C), hang dry, stake, kiss plate				
Key - (1) Barron SAF, (2) Sellatan WL-W, (3) Magnopal IPF, (4) Coripol AV, (5) Coripol ESU, (6) Sellatan HAT liquid, (7) Sella Fix E				



3.3. HEAT AGEING OF GLUTARALDAHYDE/CHROMIUM-FREE VS CHROMIUM TANNED LEATHERS

It is often said that wet white/chrome free leathers has less favourable heat ageing properties than wet blue. This appears to be the case according to the details illustrated in *Panel 11*.

Here, compared to the pelt it is made from, a piece of glutaraldehyde tanned wet white has a lower rating, whereas chromium tanning improves the rating.

However, wet white and wet blue are not the relevant materials to be tested. This is because the retanning process will have a decisive influence on the fastness properties as well.

With a proper selection of retanning agents – avoiding naphthalene based syntans and vegetable extracts – the retanning will improve the heat resistance drastically. In fact, starting from the same pelt, a chromium-free leather retanned with phenolic syntans and polymers and a similarly treated chromium tanned one will show the same heat resistance properties as shown in *Panel 12*.

Overall, although it is correct to say that wet white has a lower heat resistance than wet blue, this has no influence on the crust stage. Here, the chromium-free and chromium tanned leather show the same performance as shown in *Panel 13*.

3.4. WATERPROOFING OF GLUTARALDAHYDE TANNED LEATHERS

Due to the reaction with the amino groups in collagen, wet white tanned with glutaraldehyde carries more negative charges than chromium tanned leather, where the carboxylic groups form a complex with the metal. Hydrophobing agents are more difficult to fix, and the material is in general more hydrophilic. It is therefore more difficult to achieve a high waterproofing performance on chromium-free leathers than it is for chromium tanned leathers.

But it is not impossible to achieve a hydrophobing effect that is sufficient for the majority of waterproof articles. This does, however, require a metal capping – for example with zirconium salts.

Also a hydrophobing agent is required that is based on functionalised silicones, with an acrylic polymer supporting the waterproofing effect, and an auxiliary for improved distribution and fixation of waterproofing fatliquors, applied in a washing bath before capping. Employing these techniques, values of 20,000 Maeser flexes and 240min in the Bally penetrometer are consistently achievable.

4. Summary

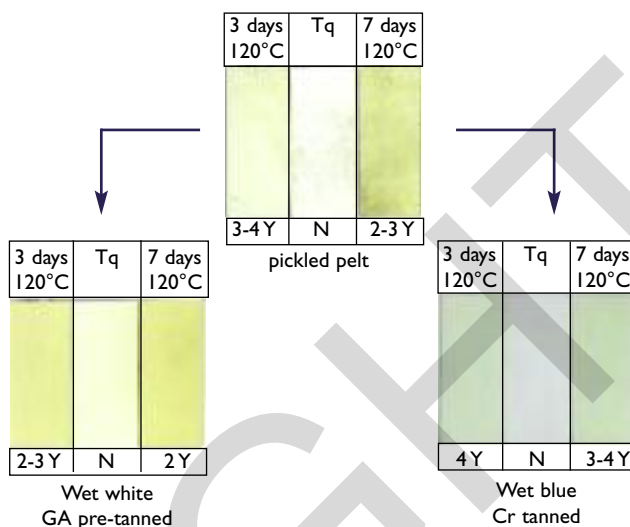
Tanning with modified glutaraldehyde is a proven and efficient technology, viable for tanneries equipped with standard machinery. The process is reliable, consistent and economically feasible. There are no restrictions to the use of glutaraldehyde as a tanning agent, and with proper processing there is no detectable glutaraldehyde in the final leather. Consequently, a chromium-free leather can be produced as a skin-friendly material with no potentially sensitising properties.

The technology is versatile and it allows the tanner to produce a full range of articles. The technology is widely used on limed split hides, and the tannage of full substance hides is taking place. In addition, these leathers in the crust condition show that both high heat resistance and waterproofing are possible without the use of chromium compounds. ☉

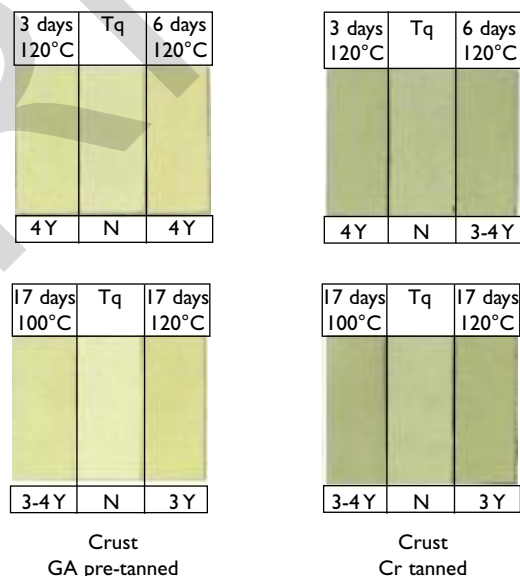
References

1. Wolf, G., Breth, M., Carle, J., Igl, G., *J Am Leather Chem As*, 2001 (96), 111.

Panel 11: Heat resistance of wet white vs. wet blue



Panel 12: Heat resistance of chromium-free vs. chromium tanned crust leather



Panel 13: Comparison of heat resistance at various processing steps for chromium tanning and glutaraldehyde tanning

