



The first part of this paper, entitled the prospects and limitations of organic tanning was published in August/September 2006. This discussed the properties of free-of-chrome leathers when compared with chrome tanned, with special regard to automobile leathers. In this second part, the essential details for manufacturing wet white leathers based on glutaraldehyde are presented.

Automobile leather manufacture

Part 2: Practical considerations for the production of wet white

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Glutaraldehyde has become the major pre-tanning agent within metal-free leather production. When compared with alternative pre-tanning systems, glutaraldehyde avoids many toxicological problems, and produces good leathers with excellent lightfastness, and good resistance to heat. Experience shows that the essential points for the production of good quality wet white—and fulfilling the numerous requirements of car manufacturers—can be met by attention to the following details.

Preliminary beamhouse operations:

Soaking and liming are carried out as in the production of wet blue.

Deliming

Deliming must be complete so that the glutaraldehyde can penetrate easily through the whole skin section. The use of totally ammonium-free deliming agents involves serious difficulties in deliming in depth, but agents based on ammonium salts cause a yellowing of leathers pre-tanned with glutaraldehyde. Their use, therefore, must be limited when producing pastel shades. It must also be taken into account that bating agents often contain a certain quantity of ammonium salts in their blends. Skins should therefore be thoroughly washed at the end of deliming and bating to remove all traces of ammonium salts.

Pickle

The pickling process has a great influence on the penetration of glutaraldehyde through the leather section. The pH value must be lower than 3.0 throughout the whole section to enable an even distribution.

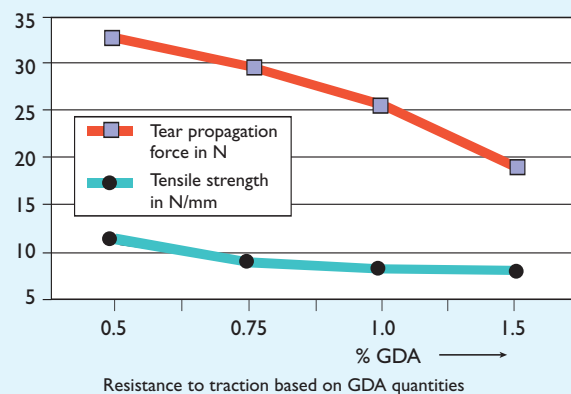
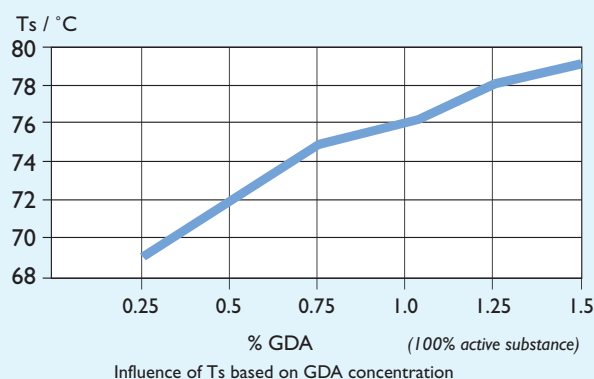
Pre-tanning with glutaraldehyde

The pre-tanning stage plays a fundamental role in the production of metal-free leather. The parameters influencing the process include: ➤

THE CONCENTRATION OF THE PRE-TANNING AGENT

An offer of 0.5% glutaraldehyde at 100% active ingredient produces a leather with a shrinkage temperature (T_s) of approximately 72°C. This is suitable to guarantee correct shaving. A higher offer of glutaraldehyde would provide a certain increase of T_s , but then the tensile strength and tear strength

Panel 1:





PRACTICAL CONSIDERATIONS FOR THE PRODUCTION OF WET WHITE

would decrease as shown in *Panel 1*.

In addition, there would be an increase in leather yellowing, causing problems when processing leathers for dyeing in light shades.

THE pH AT THE END OF PRE-TANNING

The reactivity of glutaraldehyde with the pelt increases with rising pH. Accordingly, the shrinkage temperature of the leather produced increases until the maximum level of pH 4.2 is reached. In practice, the pre-tanning begins at a pH lower than 3.0 to allow the aldehyde to penetrate through the section. The pH is then gradually raised up to a maximum level of pH 4.0 - 4.2. Higher pH values only intensify any leather yellowing without further increasing the hydrothermal stability.

THE USE OF MODIFIED GLUTARALDEHYDE

Glutaraldehyde can be modified by reaction with alcohols. The result is a masked product that is less reactive than non-modified glutaraldehyde. In addition, the modified glutaraldehyde can be blended with a polymer containing carboxyl groups. These groups block the amino groups of collagen, so that the modified aldehyde becomes even less reactive¹. This reduced astringency guarantees a more homogeneous penetration through the section, resulting in a finer smoother grain and lighter-coloured wet white.

THE LENGTH OF PRE-TANNING

The time required depends upon the leather thickness. Complete penetration of the pre-tanning agent will be longer for

full thickness leathers than for split pelts. In general, for perfect penetration and an optimal tanning effect, leathers must stay in the pre-tanning bath overnight after basification, with the drums set on automatic turn. If the length of the process is shortened, the leathers are of inferior quality.

CONTROLLING THE BASIFICATION PROCESS

In general, basification starts 90 minutes after the addition of glutaraldehyde. The pH is then gradually raised (*it is essential to avoid sudden changes*) so that the aldehyde can react with the leather slowly and without overloading the grain. If the pH is raised too rapidly this would affect the ease of penetration, cause coarse grain, and in some cases would even make the leather weak.

Often the float is first basified using salts that are mildly alkaline, such as sodium formate then followed with very slow additions of sodium bicarbonate. A neutralising auxiliary syntan with a milder action than these traditional basifying agents can be an alternative.

THE INFLUENCE OF SYNTANS IN THE PRE-TANNING PROCESS

Syntans improve wet white samming and shaving. Their effect is to prevent leathers sticking to the shaving machine cylinder, so that they can be shaved more easily.

The use of dihydroxydiphenilsulfone-based, lightfast syntans is particularly recommended. In the past small amounts of syntan in pre-tanning were used, which were just enough to guarantee easier pressing and shaving, but now it is normal to use larger amounts.

Panel 2:

Raw material: green-salted bovine hides.
Splitting thickness : 2.4-2.5 mm
Percentages referred to split weight

Phase	+	%	Product	°C	Dil.	Time minutes	pH and other controls
Pickling		40	Water	20			
		x	Salts			10	d=6.5°Bè
	+	0.5	HCOOH 85%		1:5	20	
	+	1.2	H ₂ SO ₄ 96%		1:10	120	pH 2.8-2.9 through section
Pre-tannage	+	2.5	GDA modified 25%		1:3	30	
	+	0.5	Synthetic fatliq. 70% stable to electrolyte		1:4	90	
	+	1.5	Neutralised syntan			20	
	+	3.5	Syntan solid to light			60	
	+	1.0	CH ₃ COONa			30	
	+	0.5	NaHCO ₃		1:10	60	pH 4.0-4.2
Temperature to 30°C	+	0.1	TCMTB		1:5	30	Automatically turn 3 min each hour through the night. In the morning run 10 min, pH 4.0-4.2
Draining off		150	Water	25			
		0.5	NaHSO ₃			30	
Discharge hides							

Rest 12 hours, samm, shave 1.0 - 1.1mm.

- Ts is approx. 72°C.
- The treatment with bisulfite is useful to eliminate excess glutaraldehyde from the grain, which could reduce elasticity.



Panel 3: The influence of vegetable tanning materials on leather properties

Type of natural tan	Resistance to traction (N/mm) (IUP 6)	Break lengthening (%) (IUP 6)	Tear propagation (N) (DIN 53329/A)	Burst charge (kg) (IUP 9)
Tara	13	50	27	22
Mimosa	9	42	19	20
Mirabolans	14	52	23	17
Sumac	10	41	21	14

The best results are obtained by using 3-5% of syntan. At this level of offer the changes in leather thickness between shaving and the finished leather become more predictable, and there is a lower variation between the thickness of the wet white shaving and the finished leather.

This means that:

- the shaving operation does not compromise the papillary layer
- the leather does not swell in the main tanning phase
- the wet white leather is firmer, especially in the belly parts
- the main tanning phase can be lighter

A guideline formulation that takes these parameters into account for the production of a wet white pre-tannage is given as *Panel 2*.

The main tanning/retanning process

This stage represents the real tanning process, where the shrinkage temperature of the leather is increased from approximately 70°C to 80-82°C. In general, various types of tanning substances are used at the same time including vegetable tannins, syntans, and polymers of different chemical nature.

The formulation depends on the kind of article desired. The use of glutaraldehyde in this phase can also bring a number of advantages such as:

- it allows a reduction in the amount of chemicals that are normally used
- it improves the penetration of retanning products and fatliquors applied

As a result leathers will be softer and more constant in production. Leathers also dry better on wet toggling; this is important, as sometimes this stage is not carried out under the best conditions of temperature and humidity.

The parallel use of vegetable tannins suggests that the process should begin using a short float, low temperature, and with dispersing syntans to assist the penetration. At the completion of this stage—carried out at a slow speed and for sufficient time to guarantee perfect penetration—the float is diluted at a temperature of 40°C, and the vegetable tanning agents are fixed by mild acidification.

A stronger acidification is required before the main fatliquor. It is noted that leathers treated as described have a very low isoelectric point. The anionic charge must therefore be reduced to achieve a good fixation of dyestuffs (*if necessary for top dyeing*) and of fatliquors.

Panel 4: Mechanical parameters based on the different types of tans. Leather in crust mm 1.1-1.2

Parameters	10% Tan	15% Tan	25% Tan
Resistance to traction (Method IUP 6)	14 N/mm	11 N/mm	8,0 N/mm
Break lengthening (Method IUP 6)	52%	38%	35%
Tear propagation (DIN 53329/A)	29 N	18 N	15 N
Grain resistance to burst (grain break charge) (Method IUP 9)	21 Kg	17 Kg	9 Kg

The type of natural vegetable tannin agent used has a great influence in terms of the quality, and on the mechanical/physical properties of the leathers produced. These important differences are given in *Panel 3* where, under similar processing conditions, different tanning products have been used.

Leathers processed with tara showed the best results for softness, surface touch and depth of colour at equal offers of dyestuff. Compared with the other tannins, tara also offers superior values for tensile strength, tear propagation and grain resistance to bursting, and elongation at break².

The use of exaggerated quantities of natural tannins causes, in general, a marked reduction of the mechanical/physical properties³. This is illustrated in *Panel 4*.

It is important to remember that the use of tara or other natural tannins contributes towards the reduction of any presence of formaldehyde in leathers. The parallel use of retanning and fatliquoring acrylic polymers, with their high capacity to fix to leathers, in combination with sulfited fish oils, enables good fogging performances. A guideline formulation is given as *Panel 5*. ►

Panel 7:

Alternatives to glutaraldehyde for pre-tannage

Among other aldehydes, glyoxal has many limitations, and formaldehyde, although giving fairly good results, cannot be used due to toxicological reasons. Isocyanates and epoxy resins that produce covalent bonds. Similarly aldehydes are used seldomly¹⁵.

However, oxazolidine A or I (4,4- dimethyl-1,3-oxazolidine), oxazolidine E or II, and Tetrakis hydroxymethyl phosphonium sulfate (THPS) are possible. Oxazolidine A is very reactive and provides a shrinking temperature of approx. 85°C, dependent upon the pH at the end of pre-tanning. Oxazolidine E is less reactive, and gives a shrinkage temperature of approx. 83°C at pH 7.5-8.0.¹⁵

Leathers treated with oxazolidine E in combination with vegetable tannins, differ from those pre-tanned with oxazolidine A, being softer and lighter-coloured. THPS provides a shrinkage temperature of approx. 75°C at pH 4.5-5.0. But both oxazolidine and THPS hydrolyses at pH > 7.0 and form formaldehyde.



PRACTICAL CONSIDERATIONS FOR THE PRODUCTION OF WET WHITE

Evaluation of the final leather

An example of test performance gained by applying this wet end technique is given as *Panel 6* (excludes values that might relate to finishing techniques.) In addition, *Panel 6* shows the values demanded by some car manufacturers for each parameter, and the relevant method of analysis. 

Bibliography

- 1] Wolf, G., Breth, M., Carle, J. Igl, G., JALCA, 96, 111, 2001.
- 2] Sammarco, U., CPMC, 70, 5, 205, 1999.
- 3] Sammarco, U., CPMC, 70, 5, 205, 1999.
- 4] Das Gupta, S., JSLTC, 61, 97, 1977.

Panel 5:

Main Tannage Formulation for Wet White Bovine Hides: Automotive Leather, Shaving thickness: 1.0-1.1 mm

Phase	+	%	Chemicals	°C	Dil. ratio	Time, min.	pH, Controls
Washing		150	Water	30			
		0.2	HCOOH 85%		1:5	30	
Draining off							
Neutralisation		150	Water	35			
		0.2	HCOOH 85%		1:5	20	
	+	1.5	GDA 25%		1:3		
		0.5	Synthetic fatliquoring agent, 70%		1:4	60	
	+	2.0	Neutral syntan			15	
	+	1.5	HCOONa			20	
	+	0.5	NaHCO ₃		1:10	40	4.7
Draining off							
Washing		150	Water	35		10	
Draining off							
Tannage-dyeing		50	Water	30			
		2.0	Synthetic fatliquoring agent, 70%		1:4	20	
	+	5.0	Acrylic- fatliquoring resin		1:3	20	
	+	2.0	Synthetic fatliquoring agent, 70%		1:4	20	
	+	5.0	Lightfast syntan				
		5.0	Tara				
	x		Dyestuff			30	
	+	5.0	Lightfast syntan				
		5.0	Tara			180	through dyeing
	+	80	Water	50		5	
	+	2.0	Natural sulfited oil, 80%		1:4	40	
	+	0.8	HCOOH 85%		1:4	20	
	+	0.8	HCOOH 85%		1:4	40	
Draining off							
Washing		200	Water	40		10	
Draining off							
Main fatliquor		100	Water	45			
		8.0	Synthetic fatliquoring agent, 70%				
		2.0	Natural sulphated oil, 80%		1:4	60	
	+	0.5	HCOOH 85%		1:4	20	
	+	1.0	HCOOH 85%			30	3.2-3.3
Draining off							
1° Degreasing		150	Water	35			
		0.3	Degreasing agent		1:3	15	
Draining off							
2° Degreasing		150	Water	35			
		0.3	Degreasing agent		1:3	15	

Cold washing, setting out, wet toggling, conditioning, staking, finishing


Panel 6: Mechanical, Chemical, Physical characteristics of metal-free leather in crust

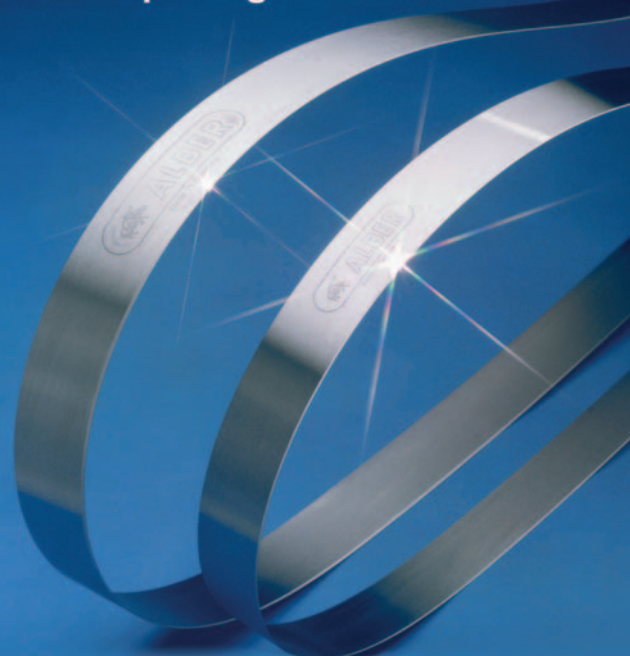
Parameter		Requested value	Method	Detected value
Thickness		1.1-1.4 mm	IUP 4	1.2
Appearing density		0.6-0.8 g/m ³	IUP 5	0.7
Fat contents		7-12%	DIN EN ISO 4048	10.6
pH value		> = 3.5	IUP 11	4.1
Chromium oxide		< 0.1	IUP 8	<0.1
Resistance to break		> = 130 N	IUP 8	167
Break lengthening		35-60%	IUP 6	52
German sewing		> = 60 N	DIN 53331	66
Tear propagation		> = 25 N	DIN 53329/A	29
Impermeability 1 ml of distilled water		OK		
Permeability to vapour		> = 2.0 mg/cm ² h	IUP 15	2.2
Resistance to heat	144th to 100°C	> = 4 s.g.	PV 3941	5
	4th to 120°C	> = 4 s.g.		5
PCP		0	CENTS 14494	Absent
Contraction	96 h, 70°C, 70% u.r.	< = 5%	PV 1200	5
	168 h, 120°C	< = 5%		5
Emissions		< = 100 microgC/g	PV 3341	< = 100 micr. gC/g
Fogging		< = 5 mg	PV 3015	4.5
Odour		< = 3	PV 3900	2
Formaldehyde		< = 10 mg/Kg	PV 3925	3 mg/Kg


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