



Iron tannage: an alternative chrome-free tanning system^(Legend 1)

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Due to ecotoxicological reasons and the growing need for recyclability, today's classical tanning systems are under a close review. While chrome tannage, particularly in the automotive industry, is under discussion for problems regarding legislation, recycling and waste management, other reagents such as aluminum salts and glutaraldehyde are toxic in their own right.

Tannage using vegetable extracts and synthetic tanning agents works well for a limited set of articles, such as belt, bag and sole leathers. However, for lightweight leathers, such as garment and upholstery, it is generally more expensive and aesthetically not always acceptable.

A new tanning process

From a tanner's point of view, there are few motivations to change from the versatile, simple and low cost chrome tannage. Other tanning systems are usually first choice for only a small number of special leather articles.

Unfortunately, some downstream users such as the automotive industry, and shoe producers who have their own, different view on ecology, have taken the decision out of the hands of the tanners. Ignoring the overall ecological balance of leather, they demand a final article to fulfil their requirements. And the tanners have to follow suit, if they want to stay in business.

However, a new cost effective two-step tanning process has been developed which can overcome a great part of these problems.

Without using any problematic mineral salt or toxic reactive reagents, a leather intermediate with a shrinkage temperature greater than 80°C has been produced, which can be shaved like wet blue. Optimised retannage, including some newly developed synthetic retanning agents, delivers an automotive type crust leather which can compete with existing chrome-free systems for

aesthetics, fastness and mechanical properties.

Requirements of downstream users

The requirements of downstream users are influenced by two factors:

- legislation on recyclability
- absence of hazardous substances in the article.

In addition, the tannery itself might prefer a chrome-free tannage for easier disposal of leather waste, such as shavings. And with some articles, such as dashboard or sole leathers, chrome-free is not requested for the absence of chrome, but for the characteristics provided by this class of leather.

ALTERNATIVE SYSTEMS

The systems and products to transform raw hides into leather as alternatives to the standard basic chrome sulfate can be set down as:

Commercial alternatives:

- aluminium sulfate
- zirconium sulfate
- glutaraldehyde
- tetrahydroxymethyl phosphonium sulfate
- syntan, vegetable, and/or acrylic resin

Academic or outdated alternatives

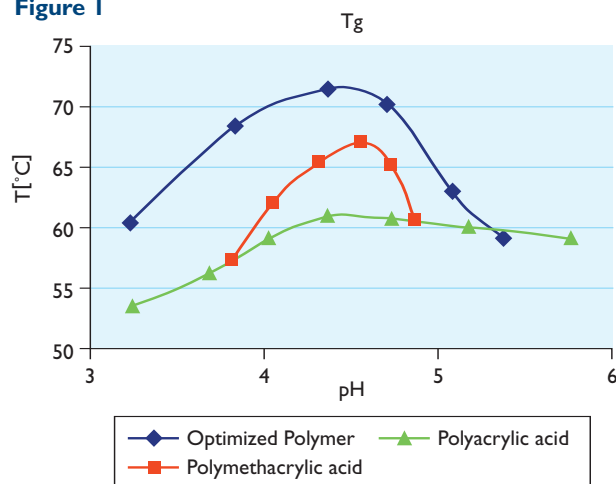
- formaldehyde
- isocyanates/polyurethane
- sugar aldehydes
- activated carboxylic acids

Apart from "chrome-free", descriptions that include "heavy metal free", "mineral free", "organic tannage" or "wet white

Above photo: Crust leathers from iron tannage: smooth and milled full grain, and split for automotive upholstery.



Figure 1



leathers” are often used. Regardless, all of them are somewhat misleading and do not fully identify the underlying problem.

For example, aluminium is not a heavy metal, but has ecological problems due to aquatotoxicity. Magnesium or calcium are certainly mineral forming metals, but are never considered a problem, not even in “organic tannages”. Glutaraldehyde or tetrahydroxymethyl phosphonium salts (THPS), being reactive organic molecules, have their own problems with acute or latent toxicity. So what tanners and downstream users are dreaming of is:

“A tanning process which does not use any toxicological problematic substance, nor produces ecological problematic residues in the processing wastes or final articles, and is as versatile and convenient as chrome tannage.”

Not surprisingly, nobody has come up with such a system. The closest is probably a tannage with glutaraldehyde, although there are several drawbacks, which can be seen from the following comparison:

THE IMPOSSIBLE DREAM

- chrome-free, wet white leather, with the thermo-dimensional stability of chrome leathers.
- shrinkage temperature of more than 100°C
- light fast and resistant to heat yellowing
- foolproof, reproducible, cheap process
- no problems with sammying, shaving, etc.
- versatile tannage for all types of articles

THE REAL BENCHMARK

- glutaraldehyde pretanned leathers with synthetic/vegetable retannage
- shrinkage temperature between 70-80°C
- medium lightfastness
- process much more sensitive
- sammying, shaving, etc., a more delicate operation
- more costly due to product intensive retannage.

These drawbacks are quite substantial, and there are only few advantages for compensation. The demands of the downstream users, however, can be fulfilled with this system. Tanners can live with it, even if it is not their first choice.

Specifications for a new system

The specifications derived from this situation towards a new system are seen as follows:

- no ecotoxicological problematic substances
 - chrome: Cr limitations for landfills, waste water;
 - aluminium salts: aquatotoxicity, waste water;
 - glutaraldehyde: toxicity;
 - phosphonium salts: teratogenic, mutagenic, toxic by inhalation;
- shrinkage temperature sufficiently high to make splitting and shaving non-problematic i.e. > 75°C.
- physical fastness properties and aesthetics competitive at least to glutaraldehyde leathers.
- process cost and handling comparative at least to a glutaraldehyde-based chrome-free system.
- not a replacement for chrome, but an improvement to state of the art chrome-free system.

A new approach

Most new approaches of the last two decades have been concentrated on organic tanning materials such as phosphonium salts or isocyanates, but have not resulted in a commercially successful system.

New developments using metal salts have somewhat been neglected, since their properties are all well known and documented, and nothing promising seemed to be in line. Only very recently, some institutional researchers have been reviving tanning methods with iron salts, addressing the properties and problems of iron tanned leathers described in the literature.

The iron tanning system

Pelt can be tanned with various iron salts with different levels of success. First patented in 1770 in Great Britain, Fe (III) is believed to be the “active” form. Shrinkage temperatures of 80 to 97°C can be achieved as described in literature (Heidemann or Stather.) Recent results with iron tannages are quite encouraging, indicating that many of the specifications required for a new system can be met. The outline process comprises the following stages:

Liming, deliming, and bating: - conventional system
Pickle: - pretreatment with special polymer-based carboxylic acid
Tannage: - basic iron (III) sulfate, solution with 13% Fe
Basification: - conventional chemicals
Retannage, dyeing: - process with special synthetic retanning agents and auxiliaries.

This procedure closely follows the process steps of the conventional chrome tannage, but the key to success is found in the products used during the pickle and retanning steps.

THE DETAIL OF IRON TANNAGE

It has been published that iron (III) has to be masked for use as an effective tanning agent. Most publications advocate a masking with different sorts of carboxylic acids, which have been reacted with iron salts prior to the addition to the tanning float. However, given the nature and solubility of those compounds, this can create both technical problems and high costs.

On the other hand, it has been known that pelts can be thermodynamically stabilised using polymeric carboxylic acids, as demonstrated in Figure 1.

This information has been transformed into a pickling process.





Figure 2: Raw material: Bovine limed pelt, 2.5 mm

	%	Product	°C	Time Min	Remark
Rinse		Water	35		
Deliming	100	Water	35		
	2.0	Ammonium sulfate			
	0.3	Sodium bisulfite		10	
	0.2	Degreasing agent			
Bating	1.1	Bating enzyme		90	pH: 9.1 drain
Rinse		Water	20		
Pretreatment,	20	Water	20		
Pickle	6.0	Sodium chloride		5	°Bé: >6
	0.3	Preserving agent			
	2.0	Low fogging fatliquor			
	2.5	Special masking agent		60	pH: 4.4
	1.0	Formic acid 85% 1:10		15	
	0.5	Sulfuric acid		60	pH: 3.4
Tannage	13.5	Basic iron (III) sulfate 45%		120	pH: 1.7; Penetration
Basification	100	Water			
	3.2	Slow Basification Product	480		pH: 3.5

Selected carboxylic compounds are used to mask the collagen “in situ”, so that a simple solution of basic iron (III) sulfate can be added to the pickled pelt at a normal pH without precipitation.

After a suitable time for penetration, basification is conducted using classical basification chemicals. A leather intermediate with shrinkage temperature above 80°C is obtained, that can be sammed and shaved as a classic wet blue. A typical compact iron tanning suitable for an automotive upholstery leather runs on the process given as *Figure 2*.

The uptake of the iron tanning salt shows quite impressive results as shown in *Figure 3* with a remaining iron content of less than 500ppm in the spent float at pH of 4.0.

LEATHER PROPERTIES

This intermediate is known as “wet tan” due to its light brown colouration, and is shown as *Figure 4*. It has superior lightfastness, and its performance during sammying and shaving is similar to wet blue.

The “wet tan” can be retanned using a variety of retanning, dyeing and fatliquoring products, but unless the right products are used the softness and sometimes the tear strength can be less than satisfactory. However, new synthetic tanning agents for neutralising and retannage appropriate for wet tan are available to avoid these matters. A compact retannage for automotive upholstery leather is shown in *Figure 5*.

In addition to providing good fullness and softness to the iron tanned crust leather, this new group of synthetic tanning agents shows excellent lightfastness and resistance to heat yellowing.

ENVIRONMENTAL EFFECTS

The overall amount of products used for tannage and

Figure 3

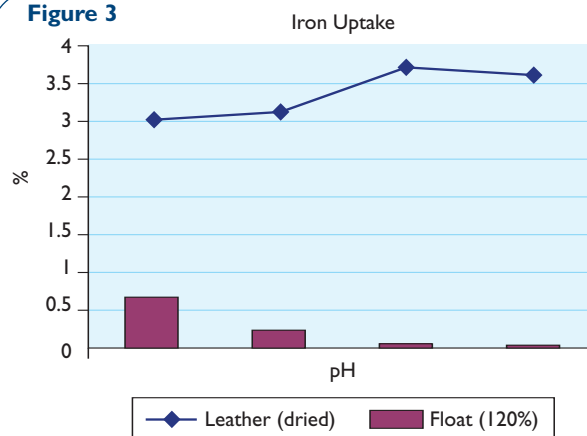


Figure 4



“Wet Tan” from split hides for automotive upholstery leather (with wet tan shavings). The leather shaves as wet blue without burning or sticking to the shaving roller.

retannage is typical for a chrome system. Accordingly, the organic load of the effluent is similar to chrome tanned leathers, and lower than chrome-free based on glutaraldehyde or pure sytan/vegetable tannins. This is shown in *Figure 6*.

Although it is impossible to obtain a really white crust, light shades of finished leathers can be achieved. The migration properties of all the auxiliaries are excellent, and an undyed crust shows fastness against migration into PVC of 5 and higher.

Brilliant shades can be obtained as well as various browns without any problem. For producing black articles, the reaction between iron and vegetable tanning extracts can be used to give really deep black, for example, 2% of dyestuff combined with 2% of tara. This is demonstrated in *Figure 7*, the wet rub fastness of 3-4 being due to the complex nature and fixation of the dye.

These crust leathers finished with classical automotive finishing systems, based on polyacrylate and polyurethane show high physical properties, and unimpaired finish quality.

THE HYDROLYTIC STABILITY

Tests associated with the hydrolytic stability of iron tannage have been performed. After 7 days at 70°C and 95% humidity, both crusts and finished leathers were firmer but still flexible. While chrome tanned leather survives this treatment almost without change, chrome-free leather based on glutaraldehyde and vegetable tannage will be completely destroyed.

The thermo-dimensional stability under dry conditions also compares favourably with chrome tanned leather. The performance, as a degree of shrinking after 1 hour at 150°C in relation to the amount of retanning materials offered on shaved weight, is shown as *Figure 8*.

Uses for iron tannages

The prime use for these new leathers is probably as a full grain

**Figure 5: Raw material: Bovine limed pelt, 2.5 mm**

	%	Product	°C	Time Min	Remark
Wash	200	Water	40	15	drain
Neutralization	100	Water	20		
	4.0	Special neutralizing syntan			
	4.0	Low fogging fatliquor A		60	pH 4.8 drain
Retannage	100	Water		20	
Fatliquoring	5.0	Low fogging fatliquor A			
Dyeing	4.0	Resin tanning agent		30	
	5.0	Special softening syntan			
	2.0	Dyestuff		60	
	100	Water	50	5	
Pickle	2.0	Low fogging fatliquor A 1:4			
	2.0	Fatliquor B 1:4		30	
	2.0	Lightfast classical syntan	60	pH 5.2	
Fixation	1.0	Formic acid 1:10		15	
	1.5	Formic acid 1:10		30	pH 3.7 drain
Rinse		Water	20	5	drain

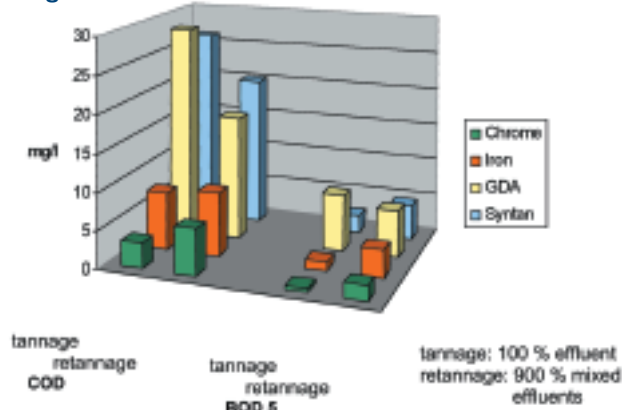
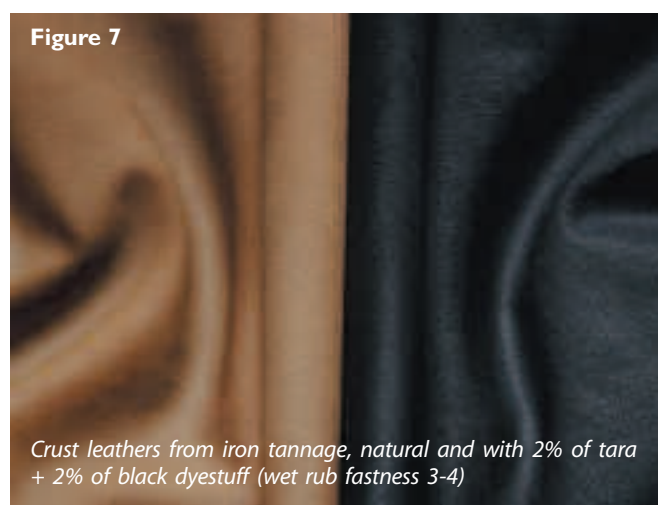
automotive upholstery leather. However, other uses may be of interest.

- There is the possibility of introducing leather (flesh) splits into the automotive sector after finishing using a reverse coating system (*Legend 2*). Trials have shown that iron tanned splits are very suitable for reverse coating due to their compactness and very short fibres after buffing. The physical and fastness properties of such leathers, especially finish adhesion and flexibility, are very satisfactory.
- The manufacture of chrome-free waterproof leathers. So far there are no products on the market that can overcome the hydrophobic tendencies of the classic chrome-free tanning process. Since "wet tan" is basically a mineral tanned intermediate, it can be transformed into a chrome-free waterproof crust if the waterproofing system does not need chrome for fixation.

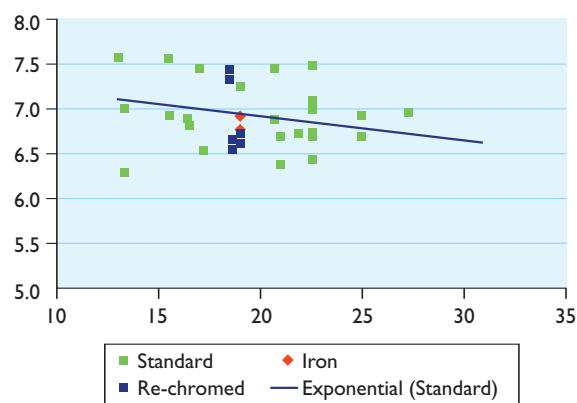
Using a recently developed waterproofing system (*Legend 3*), several different chrome-free waterproof leathers have been made. These include a 1.3mm sport shoe split suede, and a 3mm full grain leather for leather goods which resist water penetration in the Bally penetrometer for several hours, with water uptakes of less than 15 - 20 %. These are shown in *Figure 9*.

Other characteristics of iron tanned leathers

While most of the misconceptions about iron tanned leathers were refuted, some new aspects came up during the development

Figure 6**Figure 7**

Crust leathers from iron tannage, natural and with 2% of tara + 2% of black dyestuff (wet rub fastness 3-4)

Figure 8

that should be taken into account.

- The presence of ferric ions enhances the reactivity of double bonds. Due to this fact, fatliquors with a high iodine number, and especially fish oil based fatliquors, develop a stronger smell than usual and should be avoided.
- For the production of very soft leathers, a somewhat higher offer of fatliquor during the tanning process has proven useful. However, this might lead to higher fogging values.





Nevertheless, both of these problems can be overcome by optimised process conditions to achieve acceptable crust leathers.

Summary of properties

The properties of the iron tanned leathers can be summarised as follows:

WET TAN INTERMEDIATE (3.6% Fe):

- Shrinkage temperature 80 +/- 2°C; pH 3.7-3.9.
- Sammying and shaving behaviour similar to wet blue
- Light fastness 4-5, PVC migration fastness 5
- Resistance to biological attack comparable to wet blue

CRUST LEATHER:

- Tear strength satisfactory
- Hydrolytic stability (7-day, 70°C, 95%) - better than aldehydes, not as good as chrome

FINISHED LEATHER:

- flexes and rub resistance unimpaired
- finish adhesion more difficult
- embossing satisfactory

The overall costs are not as low as a chrome tanning system, but competitive with other chrome-free processes. The optimised iron tannage has the potential as an alternative to the existing chrome-free systems. However, as with any other systems of this type, it probably will never match all the properties of a classical chrome tannage. 🌀

Legend:

1. FERROTAN⁴
2. LEVACAST⁴
3. XERODERMTM P-AF + XERODERMTM S-AF

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References:

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3. Balasubramanian S. et al., *JALCA*, 1997, 218 - 224;