



X-Tan - new leather qualities by sustainable organic tanning

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This paper describes an innovative organic tanning system suitable for a wide range of leather articles. The system is not based on metal salts or aldehydes and produces a very white and stable intermediate. This can be transformed into new types of leather with superior dyeing results and improved physical properties. As the pickle step is no longer necessary and any potential excess tanning agent hydrolyzes to toxicologically uncritical products, both the effluent and the resulting shavings present tangible advantages to the tanner. The system represents added value in terms of sustainability.

Tanning is the crucial step during the transformation process of raw hide into leather. Traditionally, there are three major tanning systems; chrome, vegetable and aldehyde based. Each of these possesses its own individual characteristics, with both advantages and disadvantages. Comparing these processes from an application and economical point of view, chrome is the tannage of choice for most articles. Even from an environmental viewpoint it is favourable and safe if operated correctly according to modern standards.

However, for certain applications and articles, metal-free leather characteristics are required. For example, with dashboards for automotive use, the thermo-dimensional

stability is an important requirement. Here, glutaraldehyde based wet white leather shows better performance. Also, the recyclability of leather has become a criterion for the increased selection of wet white tanning.

During the past years, several attempts have been made to overcome the limitations of the current wet white tanning. Unfortunately, until now, all technologies presented so far have intrinsic issues, especially with respect to the environment and to the quality of the resulting leather. However, during the development of this novel organic tanning system, we overcame such limitations without giving up the advantages of the state-of-the-art systems. Our new system, named X-Tan, follows the subsequent guiding principles:



- Utilises tanning chemicals that are not classified as toxic or sensitising in order to protect tannery workers. Furthermore, chemicals used must not be hazardous to the environment and must easily degrade into toxicologically uncritical substances.
- Ensures an easy and robust process that allows adjustments to customers' needs and offers potential savings in time, water and energy.
- Significantly improves sustainability by extensively reducing the salt load in the effluent and solving the shaving disposal issue.
- Produces a true intermediate that is transport and storage-stable and that allows a very wide range of leathers to be produced.
- Is commercially viable, especially when compared to the existing wet white systems.
- Allows the production of final leather articles with improved features in terms of dyeability and biodegradability.

The chemistry

X-Tan is a metal- and organic chlorine-free tanning technology, based on polycarbamoylsulfonate (PCMS). This is a whitish powder with very good storage stability. It is non-lumpy, easy to dose and readily soluble even in cold water. Classification of the product is toxicologically uncritical, i.e. it is not classified as toxic, sensitising nor toxic to the environment.

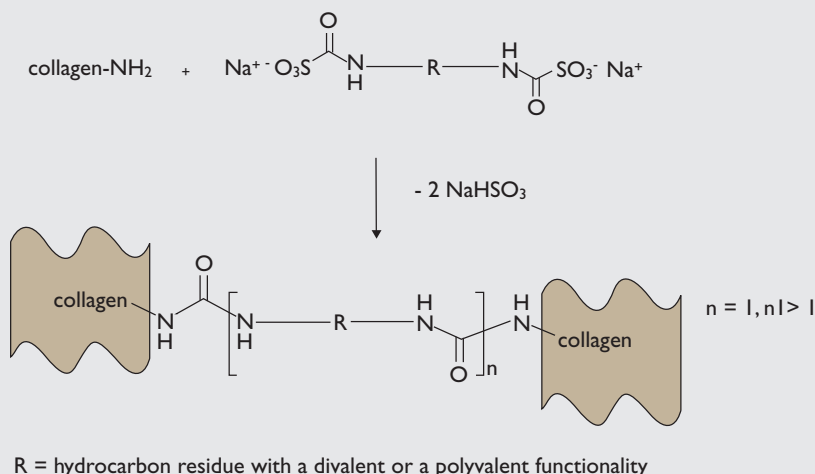
PCMS consists of reactive centres [carbamoylsulfonate (CMS) groups] that are connected by an aliphatic backbone. These CMS groups preferably react with free amines to form a urea group. During the course of this reaction one molecule of sodium bisulphite is released for each reaction of a CMS-group as shown in *Panel 1*.

The reaction by itself is easily steered by controlling the pH. No reaction occurs in an acidic-to-neutral pH range. Here the amine groups are protonated and a full penetration of X-Tan through the entire cross section, even in thick pelts, can be easily attained. However, under slightly alkaline conditions it develops its reactivity.

By increasing the alkalinity above pH 8 the tanning reaction is virtually "switched on" and PCMS reacts very fast with the lysine groups of the peptide chain. The covalent cross-links formed by this irreversible reaction pass the usual stability tests for hydrolysis. Even under very harsh conditions there is no chemical decomposition of the urea bonds as long as the collagen material itself is not hydrolyzed.

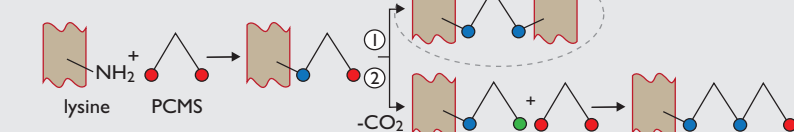
A fundamental difference to all other wet white systems is that an alternative reaction pathway occurs under the same alkaline conditions in the absence of a readily available amino group. Here, the CMS-group hydrolyzes with water and transforms into an amine group; carbon dioxide and bisulphite are split off. This amine group can then react with other available PCMS molecules resulting in a chain extension. Therefore, the two

Panel 1: Simplified schematic view of the basic cross-linking reaction of X-Tan with collagen.

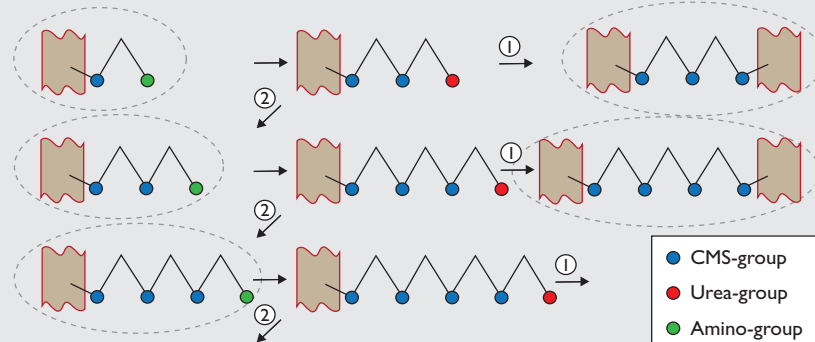


Panel 2: Simplified schematic view of the two possible reactions of PCMS and the chain elongation process resulting in a statistical mixture of various lengths.

1st section



2nd section



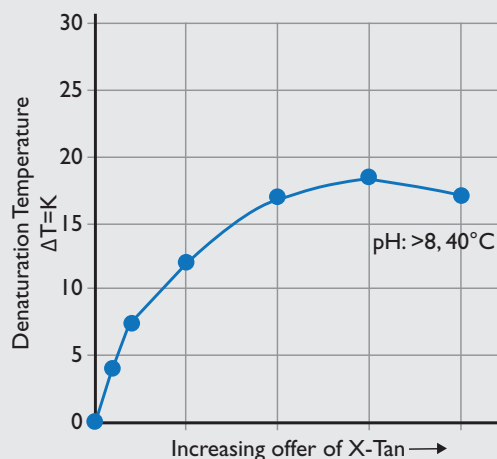
PCMS molecules are linked together by a urea group as illustrated in *Panel 2 (1st section of Panel)*.

As the speed of this hydrolysis reaction is around 1,000 times slower than the reaction with amines, the cross-linking is the predominant reaction in the presence of lysine groups. Nevertheless, the hydrolysis reaction is important for two reasons:

- 1) Any potential excess of PCMS in the float will be neutralized to either aliphatic amines, or after subsequent reaction with other PCMS molecules, longer aliphatic polyurea compounds. Such hydrolysis products are non-toxic and easily biodegradable, and therefore, they do not present a risk for those handling the product or the environment. This means no active tanning agent and no harmful substances will be present in the leather, the shavings or the



Panel 3: Structure elucidation of X-Tan cross linking: Increase of shrinkage temperature as a function of X-Tan dosage



effluent. Due to these reasons X-Tan significantly contributes to a more sustainable tanning process and higher leather quality.

- The connection of the first reactive group of PCMS with the collagen significantly reduces the degree of freedom for the remaining CMS groups at the other end of the same molecule. In case no lysine group is readily available the hydrolysis reaction followed by chain extension becomes the predominant reaction for this group. Depending on the availability of PCMS, and the lysine group distribution in the pelt, this reaction might repeat one or more times. This results in longer or shorter aliphatic polyurea chains as illustrated in *Panel 2* (2nd section of *Panel*). The most likely outcome of the tannage is a statistical mixture of oligomeric chains of various lengths. The urea groups of the cross-links further contribute to the stabilisation of the triple helix by hydrogen bonding with the peptide – a principle similar to that of vegetable tanning.

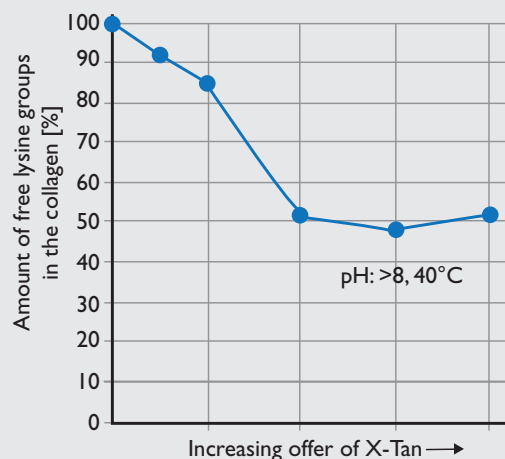
This added stabilisation effect, covalent cross-linking plus hydrogen bonding of the urea groups, and the proposed reaction mechanism based on a statistical mixture of cross links of various lengths were corroborated in numerous experiments.

In a first experiment based on hide powder the increase of shrinkage temperature versus addition of X-Tan was measured. The addition of an equimolar amount of the CMS-groups to the amine groups of the collagen resulted in the optimum shrinkage temperature. Further addition of X-Tan did not result in any further increase and these findings are shown in *Panel 3*.

In a second experiment the amount of cross-linking of the collagen versus addition of X-Tan was studied. This, combined with information about the amount of lysine groups left unreacted during tannage, resulted in the graph shown as *Panel 4*.

The lysine groups get increasingly cross-linked with the further addition of X-Tan. After a maximum is reached further addition of X-Tan did not result in a higher extend of cross-linking. In accordance with the first experiment the equimolar amount of

Panel 4: Structure elucidation of X-Tan cross linking: Percentage of free lysine groups as a function of the amount of X-Tan.



CMS-groups to amine groups in the collagen resulted in the optimum cross-linking. At this level of application of X-Tan, despite the fact that only 50% of the lysine groups are cross-linked, a high shrinkage temperature is achieved.

The high amount of non-cross-linked lysine groups in the collagen actually distinguishes this process from other wet-white processes and gives further advantages. While shrinkage temperatures are more than adequate for shaving, these groups are still free for further functionalisation at a later stage of the retanning process. Similar to chrome-tanned wet blue these lysine groups are still free as fixation sites of anionic chemicals, such as dyes and syntans, proven by the good dyeability of the wet white.

The process

The tanning process commences after the deliming and bating steps. Ammonia-free deliming and bating agents are used followed by a thorough wash. Subsequently, X-Tan is directly added to the float, and unlike conventional wet white systems, no pickling process with acid and salt is necessary.

At this approximately neutral pH no tanning reaction takes place. Thorough penetration, even of thick, unsplit pelts, is achieved within a relatively short period of time. By addition of an appropriate base, the pH is gently increased in a simple stepwise fashion. Moving the pH above 8 triggers the start of the cross-linking reaction described above and the tanning is virtually “switched on”.

During the cross-linking reaction, as depicted in *Panel 1*, sodium bisulphite is formed. This leads to a localised slight decrease in the pH which slows down further reactions. Thus, for a complete tannage the pH has to be adjusted.

After a few hours the tanning process is finished. By fine-tuning pH and temperature the process can be adjusted to customers' needs. Production trials have already confirmed good tanning results and revealed the process to be easy and robust. Samming and shaving have been confirmed by the tanners to be easy and with good results.

The relationships between pH and time when using the X-Tan process can be compared with conventional wet white systems, and these are given in *Panel 5*.



Several major advantages have been identified:

- The X-Tan process remains above pH6. Thus, the isoelectric point of the leather is not crossed and the structure of the triple helices remains intact. This results in a significantly improved tear resistance (*Panel 7*).
- No pickle step is required. Due to the good penetration of X-Tan at neutral pH, no addition of salt and acid is required. This results in a reduction of the total dissolved solids (TDS) by 75%, therefore, the quality of the effluent is significantly improved. In particular, the critical chloride content was reduced by more than 99.5%. Furthermore, the COD was decreased due to reduced collagen hydrolysis in the less acidic conditions. These environmental advantages are illustrated in *Panel 6*.
- The process is significantly shorter. Due to the absence of any pickle process and only minor neutralisation a significant saving of process time can be generated.

The shrinkage temperature has been measured to be between 72 and 78°C depending on the process conditions. Higher shrinkage temperatures have also been achieved, but this level is sufficient for shaving. On a production scale sampling and shaving were easy and good results were achieved.

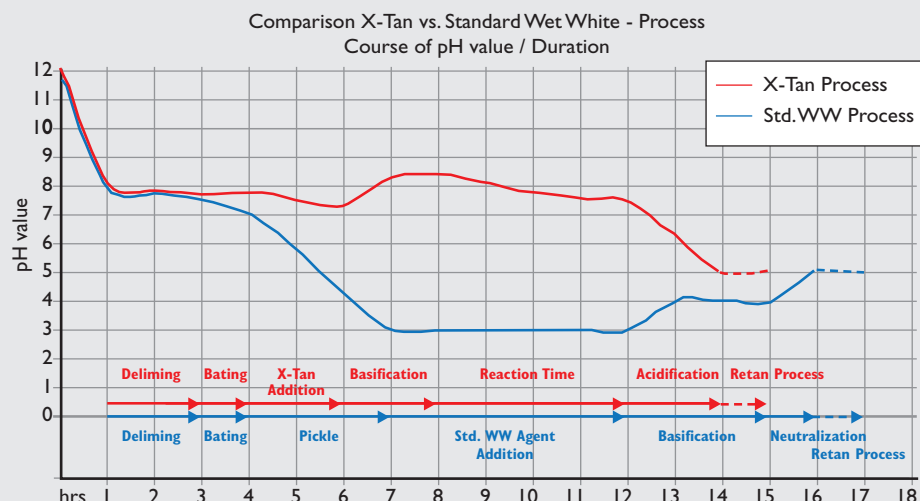
In further studies the wet white itself has been analysed. The immediately visible difference compared to conventional wet white systems is its virtual whiteness (resulting in the name X-White). This gives a good opportunity to create a whitish crust and to comply with current trends of lighter leather colours. The whiteness comes with superior light fastness, and no yellowing or other degradation of the crust has been reported.

Furthermore, the wet white is significantly more temperature stable. This is a significant advantage as current wet white materials cannot be stored or shipped for extended periods. Both of these effects can be chemically explained by the irreversible tanning reaction of PCMS.

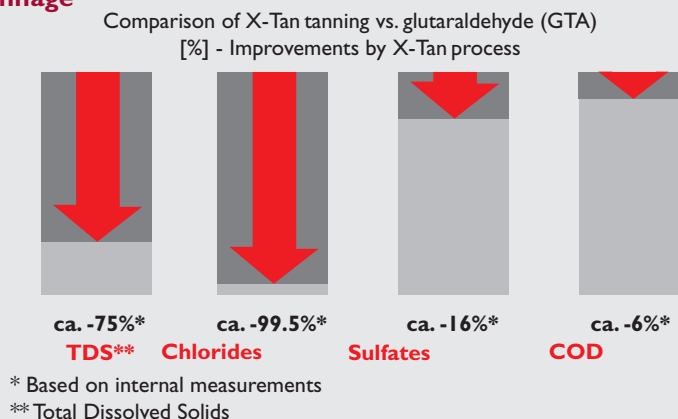
Further characteristics are a pleasant smell and a reported easy re-wet ability in situations where the storage conditions were inadequate and accidental drying out the leather had occurred.

Depending on the leather article a retanning step with chrome tanning agents following X-Tan tanning is also an option. This is because the carboxylic groups in the collagen are still accessible to form complexes with the chrome salt. This would enable a tannery to produce chrome type articles while having the benefit of chrome- and organic chlorine-free shavings.

Panel 5: Schematic comparison of X-Tan vs. conventional wet white tannage process (pH vs. time).



Panel 6: Effluent benchmark of the X-Tan process with standard GTA tannage



The leather characteristics

X-Tan has been proven to be very versatile so leathers for all kinds of applications have been produced on a small scale as well as in bulk loads. X-White, and crust leathers made from the tannage, exhibit their own properties, and in general it can be stated:

- The leather quality can be described as consisting of a very fine grain with very good aesthetic properties. The final leathers can be made far whiter than those made of conventional wet white substrates.
- Standard physical testing as given in *Panel 7*. These reveal that X-Tan leathers performs similarly or superior to those produced by conventional wet white tanning. Special emphasis should be put on tear strength and thermo-dimensional stability. Due to the absence of the pickle step there is less hydrolysis and fewer disturbances (charging and discharging). Both effects may result in the high tear strength potential.
- The results for climate change test showed comparable performance for X-Tan compared to standard wet white. This means that X-Tan can be used for the special "dashboard" application, a condition which up to now has only been achieved by the state of the art wet white leather.
- Especially noteworthy is the superior dyeability of X-Tan leather. Due to the complete absence of a strong self-colour of



Panel 7: Physical properties of standard X-Tan crusts

Criteria	Method	Requirement	Result
Tear strength	EN ISO 3377-I	≥25N	38N
Stich tear strength	DIN 53331	≥50N	75.4N
Tensile strength	EN ISO 3376	≥130N	196N
Elongation at break	EN ISO 3376	35-60%	49%
Distension at grain break	DIN 53325	>7.0mm	8.4mm
Climate change test	TL52064/ 20cycles	shrinkage: <6%	shrinkage: 5.6%

When finished under production conditions these leathers have passed the standard test requirements for finish adhesion (both wet and dry), flexing, and rub fastness.

the intermediate it is possible to generate a very whitish crust. No yellowing has been detected, and the characteristic colour of the crust is shown in *Panel 8*. This makes X-Tan highly suited for articles that follow the trend towards lighter colours.

- The significant amount of non-cross-linked lysine groups lead to an excellent exhaustion of the dye bath. Together with the virtually white tannage this leads to brilliant shades so far not attainable with state-of-the-art wet whites, and examples are shown in *Panel 9*. The dyeing is reported to be uniform on the grain surface and evenly penetrated through the cross-section. Flesh and grain show similar colours.
- The shavings and the final crust are biodegradable. Investigations have shown that, due to the toxicologically uncritical degradation products, X-Tan shows better biodegradability than conventional wet white crusts. Roughly 50% of the material was biodegraded during the first 56 days.

Conclusion

X-Tan fulfils all of the objectives set in the original development phase. Protection of the workforce is achieved by utilising substances known to be toxicologically uncritical for man and environment. In terms of sustainability there are huge advantages. The salt load on the environment from the pickling process almost disappears, and no unreacted tanning agent is present in the leather, shavings or remains in the effluent.

The tanning process is easy, robust, adjustable for customers' needs, and has been proven in practice. Savings in energy and time can be realised. Also, in the wet-white condition it is a stable intermediate that can, for the first time, be stored and transported.

The colour of the wet-white is virtual white and it is stable to conditions of light and temperature. Furthermore, white crusts and very brilliant colours previously unattainable can now be achieved. The physical test requirements for many applications are also comparable or even better than state-of-the-art wet white. The resulting leather can be used for a wide range of leather articles.

The technical aspects can be summarised as follows:

HANDLING:

- Based only on substances that are toxicologically uncritical for man and environment.
- Gives excellent penetration, even in thick pelts.
- The process is easy, robust and can be adjusted and controlled ("switched on/off") to customers' needs.
- Samming and shaving can easily be performed.

Panel 8: Typical colour of crust leather manufactured from X-Tan® wet white



- Process time and energy consumption offer a saving potential of minimum 10%.

SUSTAINABILITY:

- Material fully reacts during tanning, so leather, shavings and effluent are free of unreacted tanning agents. This provides an opportunity for the use of the shavings in many applications and leads to better recycling of a major by-product.
- The process does not require pickling. This results in a TDS reduction of the effluent by around 75 % and chloride reduction by around 99.5%.

LEATHER PERFORMANCE:

- Virtually white, the leather is highly resistant to yellowing. It shows a very good light fastness and allows production of a whitish crust.
- Proven as being very temperature stable, this results in a truly storable and transportable intermediate that will significantly facilitate production for multinational companies.
- Reported good re-wet ability in the event of the leather accidentally drying out.
- Brilliant shades have been achieved with uniformly dyed grain surfaces.
- Uniform penetration of dyes throughout the cross-section, and similar shades grain to flesh.
- Very good aesthetic and physical properties. In particular, high tear strength and very good thermo-dimensional stability.
- The shavings and the final crust have been tested for biodegradability and around 50% of the leather is biodegraded after 56 days. ☺

Panel 9: Examples of brilliant dyeing achieved with X-Tan

