Paper D9

X-Tan® an innovative organic tanning technology with superior sustainability

Dr. Dietrich Tegtmeyer, Chris Tysoe, Dr. Juergen Reiners
LANXESS Deutschland GmbH, 51369 Leverkusen , e-mail: dietrich.tegtmeyer@lanxess.com, christopher.tysoe@lanxess.com, juergen.reiners@lanxess.com

Abstract

A strong demand for wet white technology can be observed in the leather market. Currently, this process is based on either glutaraldehyde (GTA) or, to a less extend, tetra-hydroxymethyl-phosphonium sulphate (THPS). More recently, a pickle-free system was reported. However, all processes have known limitations. In this paper we present the introduction of the latest generation of organic tanning processes following a completely different chemical route that sets a new standard in the tanning technology.

In this novel process the tanning agent covalently bonds to the amino groups of collagen. Cross-links occur by the formation of urea bonds which are as hydrolytically stable as the collagen substrate itself. The resulting high quality leather has at least similar performance properties compared to that obtained by aldehyde tanning and can be used for all relevant applications; however, further advantages were identified: the leather is significantly whiter and other properties such as high tear strength and brilliant dyeing results can be achieved. Furthermore, the leather as well as by-products such as shavings are biodegradable, free of aldehyds and metals.

The easily controllable tanning process also consolidates several advantages in terms of sustainability: Any excess of product reacts with water under slightly alkaline process conditions (pH >7 to 9) leading to harmless compounds and thus the active tanning agent is not present in the effluent. Apart from that the new tanning procedure eliminates pickling so that the effluent contains considerably less sodium chloride. Process time and energy consumption are also reduced.

1. Introduction

Tanning from a scientific point of view is the permanent stabilization of the triple helix structure of collagen even after the removal of the majority of the water content. The industry differentiates between three main tanning principles, which all differ in respect to their stabilization mechanisms:

1. Metal salt tanning agents such as chrome salts which form complexes with carboxylic groups of the peptide chain inside the triple helix.
2. Vegetable tanning agents, which are ingredients extracted and concentrated from selected plant fruits and barks etc; they are mainly stabilizing the helix by hydrogen bond interactions between certain functional groups of the peptide.
3. Synthetic reactive tanning chemicals, which form a covalent chemical cross-linking reaction between functional groups of the helix. The most common system is based on GTA, which generates a network between the amino groups of the peptide chains.

All mechanisms have been studied in depth, and there are many even recent publications which give excellent process explanations[1]. When comparing the processes from an applicational and economical point of view, the chrome tannage is still the best performing technology for most types of articles. Even from an environmental viewpoint it is a favorable and safe tannage if operated correctly according to modern standards[2]. However, for some applications and articles metal free leather characteristics are technically required. For certain applications (e.g. dashboards, door panels in automotive use) the thermodimensional stability is an important issue where wet white tanned leather shows improved performance. Furthermore, the increasing demand for recyclability of leather has been a criterion for the selection of the wet white process in some cases. All in all, there are valid reasons why wet white tanning is an important market segment of its own.

2. System's chemistry

Until now all current wet white technologies had intrinsic limitations, especially with respect to environmental issues[3, 4] A recently published technology[5] shows the great interest of industry in innovative wet-white technology, although bulk performance data have not yet been published.

In this paper the latest generation of a wet white process is presented, which has already been verified in production and provides superior environmental and economical efficiency benefits for the tanner. This metal- and aldehyde-free tanning technology is based on polycarbamoylsulfonate (PCMS). In combination with special polymers and process auxiliaries it yields leather with all required properties. The new tanning agent is called X-Tan®, the resulting leather intermediate after tannage is called X-White due to its unique characteristics.

A basic tanning process based on polyfunctional carbamoylsulfonates was described by our company and others in the 1980´s and 90´s.[6,7,8] Due to the non-robustness of the tanning process and the insufficient shelf life of the liquid tanning agent the system proved to be non-practicable for introduction into tanneries.
The new, patented X-Tan® overcomes these limitations. X-Tan® is a whitish powder with very good storage stability. It is safe in handling due to its non-toxic and non-sensitizing classification and dissolves readily in water. The resulting process developed by a systematic and intensive research program provides a break through in the field of organic tanning.

A solution of X-Tan® in water is relatively stable in acidic to neutral medium. However, under weakly alkaline conditions (pH >7 to 9) which are recommended for the tanning process, it develops its reactivity. At lower to neutral pH X-Tan® can readily penetrate the entire cross section even in thick pelts and then by slightly increasing the alkalinity the tanning reaction is switched on. During the tanning there are two main reactions:

1. Once penetrated and activated X-Tan® reacts quickly with any available amine group of the collagen forming stable urea linkages (Fig 1). This desired reaction between the amino group of lysine in collagen results in a network stabilizing the triple helical structure of collagen. After complete reaction PCMS is covalently bound to the collagen which passes 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.

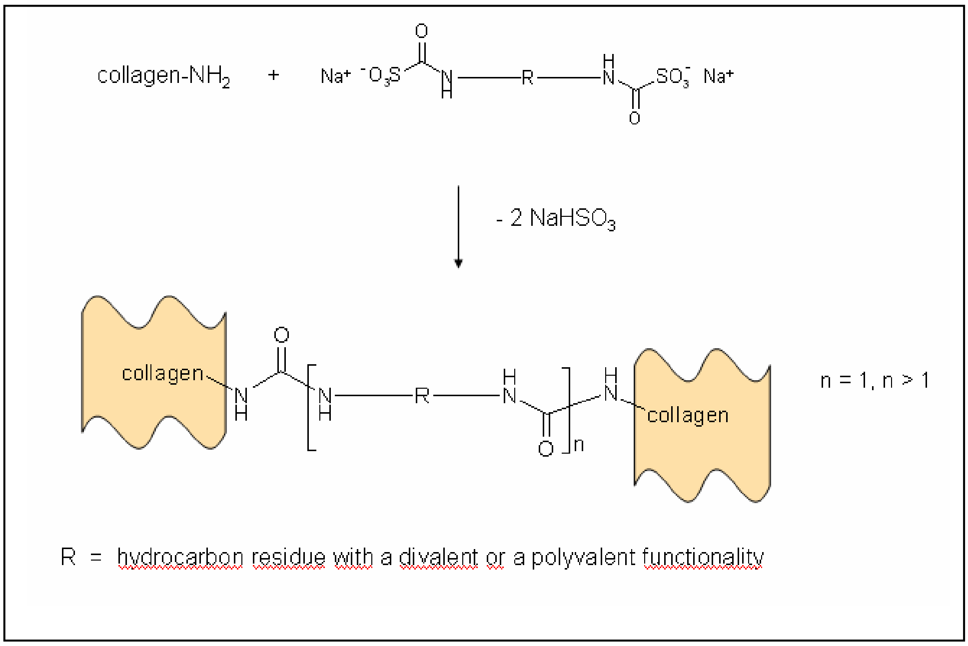

Figure 1: Simplified schematic view of reaction mechanism of polycarbamoylsulfonate (PCMS) with collagen

2. An alternative reaction to the cross linking is a hydrolysis reaction of PCMS with hydroxyl ions (OH^-). Here, PCMS, e.g. non exhausted X-Tan® in the float, is hydrolyzed by splitting off hydrogen carbonate (HCO_3^-) and bisulfite. This competitive reaction is negligible compared to the tanning reaction with amines due to its significantly lower speed (ca. 1.000 times). Thus, under the right reaction conditions in presence of collagen the first reaction (the tanning) is the predominant reaction route (at least as a first link to collagen).

In the pelt the situation might be different after the reaction of the first CMS-group with the collagen. Here, the degree of freedom for the next CMS-group to react with another amino-group of the collagen is restricted. This increases the likelihood of the hydrolysis reaction in the pelt which results in the formation of an amino group on the other side of the cross-linker. This amino group will immediately react with another carbamoylsulfonate (CMS) group forming a chain extension via a urea group. It is potentially possible that this side reaction might happen several times resulting in aliphatic polyurea chains of different length connected to one or two sites of the collagen; a possible reaction tree is shown in figure 2. Depending on the process conditions during tanning the most likely outcome of the tannage is a statistical mixture of polyurea chains of various length cross-linked in the collagen matrix; the result after tanning was studied and confirmed by an independent renowned institute[9] and is explained further below.

Similar hydrolysis reactions are happening in case of non-exhausted X-Tan® in the float. Due to its high reactivity in this pH-range the life time of free PCMS in the effluent is very short; the resulting hydrolysis products are either aliphatic amines, or after subsequent reaction with other PCMS molecules, longer aliphatic polyurea chains with amino end groups. Such hydrolysis products are non toxic and easily biodegradable and therefore no risk for workers and the environment. Similar reaction products occur in the case of complete hydrolysis of the leather.

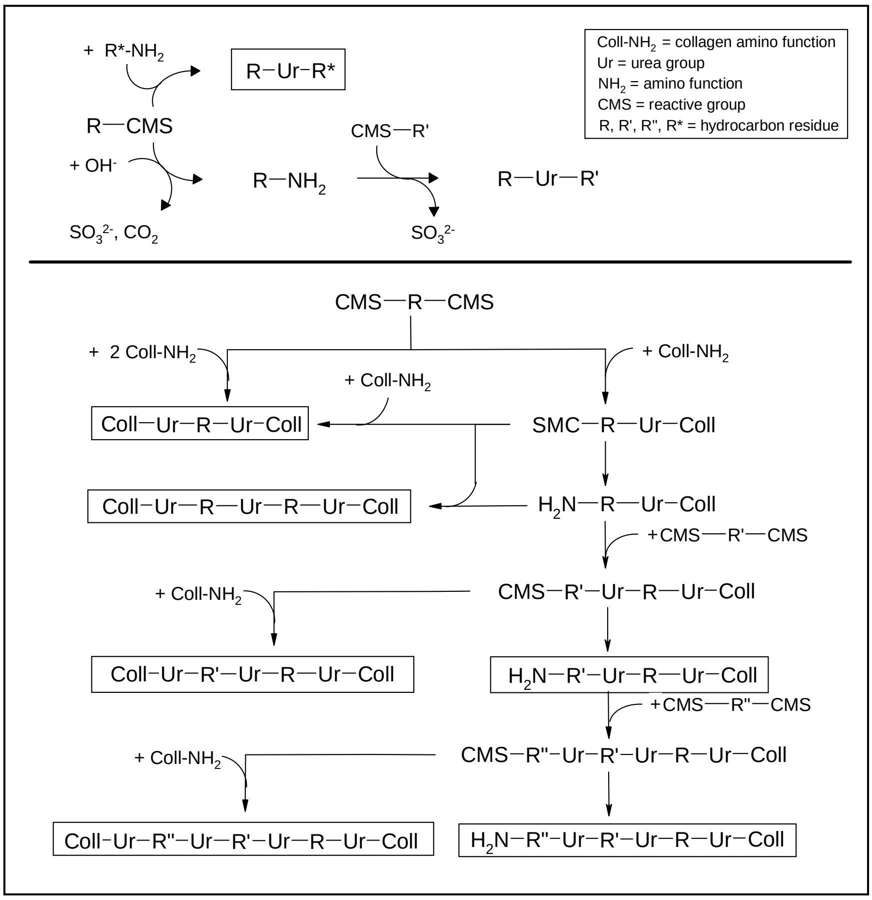

Figure 2: Above: Simplified schematic view of the two possible reactions of PCMS during the tanning step resulting in a statistical mixture of polyurea chains of various lengths, circled structures are most likely (below).

3. X-Tan® tannage: Proof of principle

Based on the analysis of the degree of cross-linking of X-White an independent research institute, that monitored its entire production processing from raw hide at their own facilities, confirmed that X-Tan® is a genuine tanning agent. Shrinkage temperature was measured in different leathers according to DIN EN ISO 3380 and recorded between 72.0 and 77.0°C after tannage and 84.0 to 85.5°C following retanning. Differential Scanning Calorimetry (DSC) measurements of different layers in the hide showed uniform values throughout the cut (73.5 to 80.0°C and 85.6 to 87.8°C respectively).

In order to elucidate more mechanism details separate tests based on hide powder were performed.[10]

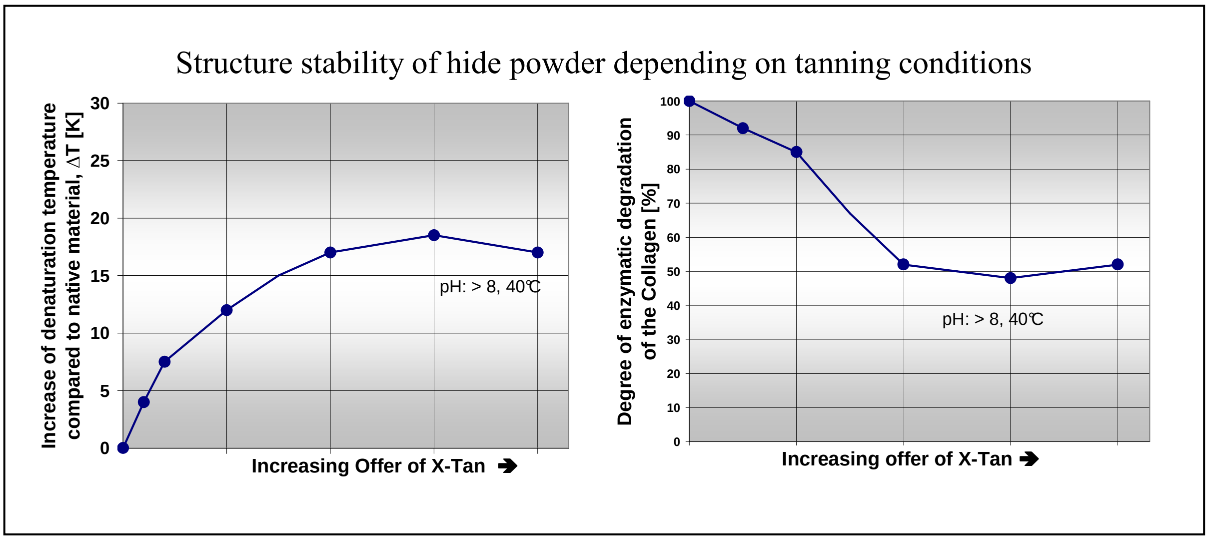

Figure 3: trials performed on hide powder[10]
Left: Increase of shrinkage temperature as a function of X-Tan® dosage.
Right: percentage of collagen enzymatically degraded (i.e. not cross-linked) as a function of the amount X-Tan®.

In a first experiment the increase of shrinkage temperature versus the amount of X-Tan® used was determined (fig 3). The addition of an equimolar amount of functional CMS-groups to amine groups in the collagen already resulted, under the right reaction conditions in the tanning step, in the optimum shrinkage temperature. The addition of further X-Tan® did not result in a further increase.

In a second experiment leather tanned with various amounts of X-Tan® was treated with a buffered solution of chymotrypsin for four hours. The degree of enzymatic degradation indirectly indicates how much of the collagen is cross-linked. In accordance with the results of the first experiment the equimolar addition of functional CMS-groups to amine groups in the collagen resulted in the optimum cross-linking. At this optimum use level of X-Tan®, despite the fact that only 50% of the collagen is cross linked, a very high shrinkage temperature is achieved.

Further experiments revealed that a significant proportion of lysine groups were left unreacted during the tannage. This and the other facts lead us to postulate an additional stabilization mechanism besides covalent cross-linking occurs:

> During tannage only a certain percentage of the CMS-groups is directly connected to the lysine groups of the collagen. The other CMS-groups are used to form polyurea chains according to the mechanism mentioned above. These polyurea chains can strongly interact via hydrogen bridges with the functional groups of the collagen. We believe that this stabilization is similar to the principle of vegetable tanning as mentioned in the introduction. If at least one end of the cross-linker is connected to the collagen, this stabilization is considered to be permanent under normal conditions.

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 satisfactory for shaving of X-White these groups are still free for further functionalization at a later stage of the retanning process. These free lysine groups increase the number of fixation sites of anionic chemicals such as dyes and syntans, which is proven by the good dye ability of the X-White.

4. Characteristics of the tanning process

Following the explanation of the chemistry, X-Tan® is added after bating (without the need for pickling) in order to allow thorough penetration within a relatively short period. By addition of an appropriate base the pH is increased to > pH 8 leading to a start ("switch on") of the cross linking reaction which rapidly follows the mechanism described above. During the cross-linking reaction sodium bisulfite is formed, causing a slow decrease of the pH to neutral. This is the signal that the tanned leather intermediate is ready for further treatment. The tanning reaction can easily be influenced further by raising or lowering of the temperature and can be interrupted by mild acidification ("switched off").

The shrinkage or denaturation temperature (T_S) reaches a level between 72 and 78°C depending on the amount of chemicals and the program followed. Higher shrinkage temperatures are possible; however, this level is sufficient for shaving. Samming and shaving were easily performed and showed good results on production scale machinery.

Depending on the leather article a retanning step with chrome tanning agents following X-Tan® tanning is also an option as 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-, aldehyde-, and organic chlorine-free shavings.

Analyzing the process from an environmental perspective several advantages can be identified. The most important difference to conventional wet white tanning is the elimination of the pickle process which leads to a 75% reduction of the total dissolved solids (TDS). Here, especially the chloride content could be reduced by more than 99.5% compared to a standard wet white process. Furthermore, internal benchmark studies have shown an approximately 10% reduction of all relevant production parameters from raw to wet white such as production time, energy consumption as well as the COD load of the tanning step.

Additionally, the shavings, the effluent and the wet white are free of any metal, aldehyde, AOX or other tanning agents which might have a positive impact to re-use these by-products of the leather production. Also the biodegradability of the leather and the shavings are improved; scientific studies have shown[11] approximately 50 % of the leather is biodegraded after just 56 days under special degradation conditions.

5. Technical X-Tan® leather properties

Analyzing X-Tan® leather characteristics standard physical testing results indicate that X-Tan® leather performs very similarly or even better than state of the art wet white processed leather. Due to the high quality of X-Tan® leather it gave excellent results for a wide variety of applications (e.g. automotive, shoe upper, furniture). Among others, the following test data have been produced to corroborate our interpretation:

Tear strength (according to DIN 53329A) has been recorded at 38 N, tensile strength (DIN 53328) 196 N, and elongation at break (DIN 53328) at 49% and thus should be well within specifications set by major automotive producers, the tear strength at 38 N is particularly noteworthy. Lastometer readings, especially relevant for shoe upper manufacturers, have been recorded at minimum 8.4mm distension at grain break. Stitch tear strength reached 75.4daN/cm.

Climate change tests (TL 52064 edition 12/2009 humid/Hot 20 cycles – performed by an independent research institute)[12] comparing thermo-dimensional stability of GTA and X-Tan® showed a similarly good performance for X-Tan®. This means that X-Tan® leather is also highly suitable for the special "dashboard" application where these conditions are critical and until now only satisfied by the state of the art wet white leather. Such performance is further evidence of the good tanning ability of X-Tan®.

Especially noteworthy is the white color and good dye ability. X-White is virtually white and thus forms the basis for brilliant shades so far not attainable with the state of the art so called wet "white" systems which tend to be yellow in color to varying degrees.

X-Tan® leather has been finished under production conditions and has passed the usual tests for finish adhesion (both wet and dry), flexing and rub fastness. Superior aesthetic properties were achieved via application of the appropriate retanning technology including special PCA softening polymers[13].

6. Conclusion

X-Tan® is the latest generation of organic tanning technology which leads to several valuable advantages compared to conventional wet white systems. The process is robust and controllable and leads to a shrinkage temperature throughout the entire cross section of being significantly higher than 70°C. (Which is the same claimed by the GTA process under the official same test conditions) The system has been thoroughly tested and the resulting leathers with excellent properties can be used for the vast variety of articles required. Generally, this innovative technology comprises superior properties in handling, leather performance and sustainability.

Handling:

- X-Tan® gives an excellent penetration, even in thick pelts.
- The X-Tan® tanning process is safe in handling and can be easily controlled ("switched on/off").
- X-White produced via a robust and easy process can be easily sammed and shaved.
- Process time can be decreased by ca. 10% compared to standard wet white process.

Leather performance:

- X-White is virtually white and is highly resistant to yellowing. Excellent dye ability can be achieved leading to brilliant colors.
- X-White show shrinkage temperatures significantly above 70°C and superior thermo-dimensional stability.
- High tear strength and aesthetic properties were achieved.

Sustainability:

- The X-Tan® process requires no pickling, resulting in a TDS reduction of the effluent by ca. 75 % and chloride reduction by ca. 99.5%.

- X-Tan® fully reacts resulting that neither the effluent nor the shavings contain aldehyde, AOX or unreacted tanning products, which could harm a biological treatment. This even opens the opportunity for the use of the shavings in many applications and leads to better recycling of a major by-product.
- The shavings and the final crust have been tested for biodegradability by a certified institute., ca. 50 % of the leather is biodegraded after 56 days.
- The process offers reduction in energy consumption.

7. References

1. G. Reich:.”Leather” in Ullmann’s Encyclopaedia of Industrial Chemistry, Wiley-VCH Verlag, Weinheim 2005
2. H.-P. Germann: B.M. DAS Memorial Lecture 2010: “Sustainable leather manufacture – Realistic objective or wishful thinking?”, LERIG Symposium CLRI, Chennai (India), Jan 29-30, 2010; Leather 212, 4/2010, p. 28-30.
3. LCA Study – A comparison of tanning technologies – report ref. ESVPO25 dated December 2003, prepared by Ecobilan in collaboration with British Leather Confederation (BLC)
4. G. Reich: „Ökologische Aspekte wichtiger Gerbverfahren“, Forschungsgemeinschaft Leder e.V., Germany
5. R. Gamarino, C. Reineking; “EasyWhite Tan leather: A new tanning evolution”, World Leather, Feb/March 2011, p. 17-23
6. B. Milligan; P.R.Buechler: “The use of dicarbamoylsulfonates as tanning agents”, JALCA (1982), vol. 77, p. 70 – 83
7. P.D. Hoagland; P.R. Buechler: “Mechanism of reaction of isocyanate-bisulfite adducts with primary amines”, JALCA (1983), vol. 78(8), p. 223-227.
8. H. Traeubel: “A new approach to tanning – an unconventional attempt”, JALCA (2005), vol. 100, p.304-316
9. FILK (Research Institute for Leather and Plastics), report 1111000, tanning trials with X-Tan® and corresponding analytic to determine the cross linking degree
10. FILK (Research Institute for Leather and Plastics), report 110685, Gerbtechnologische Untersuchungen mit Hautpulver
11. Hydrotox Institute, Report: Biodegradability in the CO_2-evolution test according to ISO 14852; April 2011
12. FILK (Research Institute for Leather and Plastics), report 110695, Investigation of area shrinkage of X-Tan leather versus GDA tanned leather
13. C. Tysoe; J. Reiners: “Leather Softening Technology”, (March 2009), http://www.lanxessleather.com/lea/en/service/news/lanxessnews/technical-articles/content/index_02598.php

8. Acknowledgements

Special thanks to LANXESS colleagues, who are not named as authors, as well as partners from the leather industry:
Dr. Harro Traeubel for his extensive and well documented R&D work
Scottish Leather Group Ltd. and Rino Mastrotto Group for the co-operation during scale up trials