

Tanning with ECOTAN PAP Gallic Extract in Combination with KEUSOL SP EQ Cationic Ester for the Production of High Performance Leathers

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Abstract

A new metal free tanning system was developed by using ECOTAN PAP, a modified hybrid extract from Gallnuts, Chestnut and Tara.

ECOTAN PAP has self-tanning properties with a shrinkage temperature of over 80°C, a very light colour and strong light / heat fastness.

The tannage with ECOTAN PAP was shown very anionic properties. Therefore, during tannage, it was recommended to add KEUSOL SP EQ, a cationic ester, in order to modify the reactivity of the system and, thus, changing the final leather charge to amphoteric. A very high level of exhaustion of retanning agents, dyes and fatliquors was obtained, as well as low COD and high biodegradability of the final effluent.

The system was associated to traditional vegetable tanning, a process which was carried out in different operative ways, such as recycling of pretanning and of main tanning liquors. A mass balance of the tanning material was performed and the discharged liquor tanning content was monitored throughout several batches. The final pretanning and / or tanning liquor was recycled to the following batch to make “colouring” and exhaust the unfixed tannins prior to discharge.

By varying the retanning / fatliquoring processes it was possible to obtain all types of leathers. The system worked well both on bovine and small skins.

A study on the effluent of the system was carried out, including a biodegradability test in a pilot tannery’s effluent plant.

Keywords: retanning, chrome, cationic.

1. Introduction

In the leather industry, the awareness of environmental problems has increased considerably and, during recent years, the care for the environment has become a global concern. In fact, regulatory pressure obliges tanners to make continuous improvements to the processing operations and consumers are willing to know whether hazardous substances are present in leather and leather articles. Furthermore, today’s market requirements in terms of process and finished products:

- are free from chrome salts and other metals;
- have a formaldehyde content of less than 3ppm;
- use no aldehyde;
- have high heat and light resistance;
- demonstrate high tensile/tear strength;
- comply with the Manufacturing of Restricted Substances List (MRSLS) and the Zero Discharge of Hazardous Chemicals (ZDHC) programme;
- contain a low percentage of chlorides and sulphates;
- show low COD values;
- are soft, tight and lightweight;
- take dyes well;
- can easily be scaled up in production and are as simple as possible to manufacture;
- cost as little as possible.

Having thought about different solutions to meet these expectations, it came to mind the marvellous and most ancient system of tannage, which is “Natural Vegetable Tannage”. Therefore the scope of the project is to develop a system in which selected tanning agents play a key role in permitting to reach not only the beauty of vegetable tanned leather but also the high performance values requested by the OEMs. An important part of the research focuses on the ecological impact of the process by deeply analysing spent liquors,

mass balance, recycling systems and biodegradability, in order to assure the sustainability of the process.

1. Material and Methods

Silvateam achieved its goals by using **ECOTAN PAP**, a natural dispersed gallic / ellagic tannin characterised by high fastness properties (Figure 1).

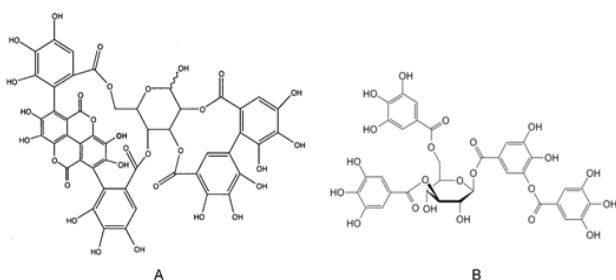


Figure 1 Chemical structure of Ellagic Tannin (A) and Gallic Tannin (B).

ECOTAN PAP was obtained by extracting tannins from various natural raw materials, such as fruits, pods and wood. The concentrated extract was then dispersed and hydrolysed to reduce its astringency and improve penetration (Figure 2).



Figure 2 ECOTAN PAP Production Process.

ECOTAN PAP has self-tanning properties on pickled pelt and it shows the following features:

- 100% soluble;
- Almost white colour (light beige);
- Good light fastness;
- Good heat fastness;
- Excellent penetration;
- Medium softness;
- 12-15% powder required for **Wet white** pretannage → Shrinkage temperature 68-70°C;

- 35-40% powder required for **Full Tannage** → Shrinkage temperature 75-80°C;
- Leather like appearance of both wet white and full tannage;
- Easy to wet back;
- Good dewatering on sammying;
- High increase in thickness;
- Easy shaving;
- Sensitive to iron ions (black colouration);
- High anionic charge (uniform dye shades but difficult to fix).

The analytical values of the product in powder form, obtained through spray drying, are listed in Figure 3.

Parameters	Values	Method
Appearance	Light brown powder	
Tannins (T)	66.4 %	ISO 14088:2012
Non Tannins (nT)	29.0 %	ISO 14088:2012
Insolubles	0.0 %	ISO 14088:2012
Water	4.6 %	ISO 14088:2012
T/nT Ratio	2.29	ISO 14088:2012
pH (10% sol.)	3.65	TAN/04
Ashes on Dry Matter at 650°C	20.9 %	TAN/06
Free Formaldehyde	< 5 ppm	ISO 17226-1
Sulphates (SO ₄) ²⁻	< 0.30 %	EPA 375.4

Figure 3 Analytical values of ECOTAN PAP.

This tanning material was assessed within two different processes:

- a) Pretannage with **ECOTAN PAP**;
- b) Full tannage with **ECOTAN PAP**.

a) Pretannage with ECOTAN PAP

12-15% of **ECOTAN PAP** on limed weight was necessary to stabilise a bovine hide, obtaining a shrinkage temperature of 68-70°C. The hides were full and flat with a light brown colour (Figure 4) which became ivory white after drying (Figure 5).



Figure 4 Pretanned ECOTAN PAP hide.



Figure 5 ECOTAN PAP natural crust.

This stabilised hide was sammed and shaved using standard chrome tannery machines. The dewatering was excellent as well as the shaving. Being very sensitive to iron, **ECOTAN PAP** leathers may show black iron spots, which can subsequently be removed during washing with sequestering agents. Unlike conventional aldehyde pretannage, **ECOTAN PAP** conferred a tanned leather look after drying and it wetted back very easily.

After shaving, through retannages, it was possible to obtain a very wide range of articles.

b) Full tannage with ECOTAN PAP

Leathers were alternatively fully tanned with **ECOTAN PAP** using rapid or semi-rapid tanning system. Around 35-40% material was required on limed weight, without any pretannage. Once tanned, the leather can be shaved, dyed and fatliquored without retanning. The leathers obtained with ECOTAN PAP were pleasant, full and round.

Low COD level by floats recycling

At the end of wet white pretannage and main tannage, floats were high in COD values due to unfixed tannins. Therefore they were recycled to pretan the following batch. This operation helped fixing almost all residual tannins, highly reducing the amount of unfixed tannins. After this “colouring” the liquid was drained to the effluent treatment plant with very low COD values, and a new float was prepared for the main pretannage / tannage (Figure 6).

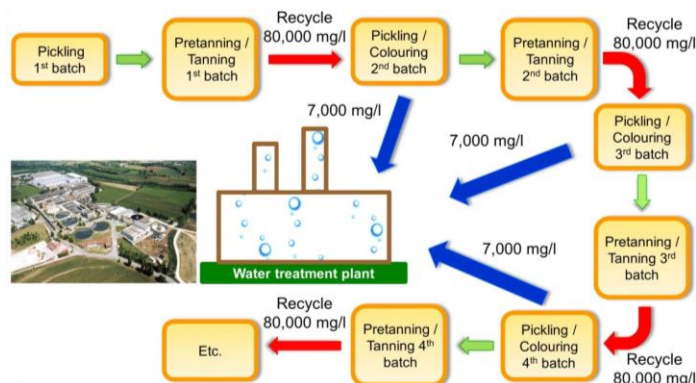


Figure 6 Pretannage / tannage with **KEUSOL SP EQ** and floats recycling with their COD values.

KEUSOL SP EQ: the cationic charger

In order to increase reactivity and fixation of the anionic chemicals, **KEUSOL SP EQ**, a cationic ester, was used to incorporate cationic charges and increase the isoelectric point of the leather (Figure 7).

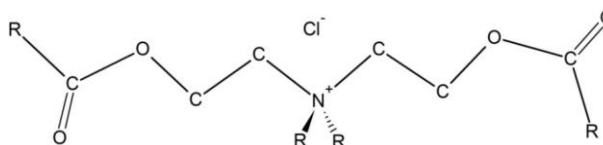


Figure 7 Basic structure of **KEUSOL SP EQ**.

The collagen structure, which was made of a well-balanced set of cationic and anionic groups (Figure 8), suffered from the strong anionic charges of the various tanning materials, dyes and fatliquors. The addition of **KEUSOL SP EQ** fostered a cationic charges gain which brought back the anionic / cationic groups ratio to a more balanced level (Figure 9). Figure 10 reports the stage in which the different products were applied along the process.

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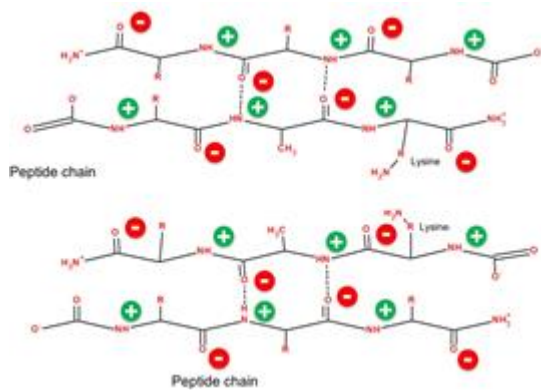


Figure 8 Collagen polypeptide chains.

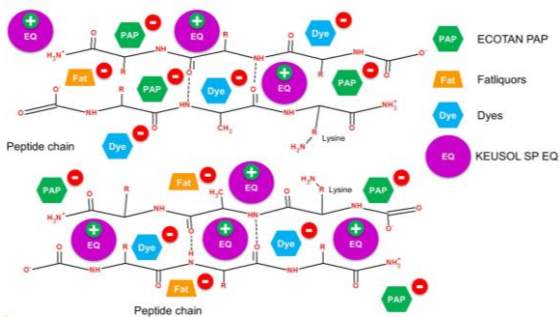


Figure 9 Chrome free tanned leather.

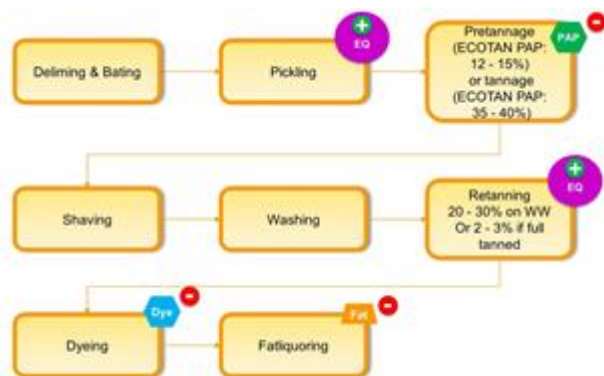


Figure 10 ECOTAN PAP + KEUSOL SP EQ process.

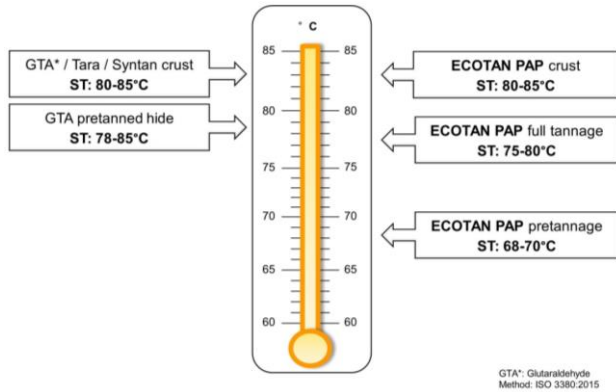
2. Results and Discussion

The various leathers tanned with **ECOTAN PAP** in combination with **KEUSOL SP EQ** were evaluated and compared with conventional Glutaraldehyde / Tara / Syntan leathers in terms of shrinkage temperature, dye fixation, tannins exhaustion, physical and biodegradability properties, obtaining very successful results. Furthermore, thanks to this innovative metal free tanning technology, it was possible to obtain a wide range of leathers by varying the retanning and fatliquoring stages.

Shrinkage temperature

Shrinkage temperatures obtained using **ECOTAN PAP** within tannage were between 68 and 85 °C (Figure 11).

Figure 11 Shrinkage temperature comparison between different pretanning and tanning



processes.

Dye fixation

By the incorporation of **KEUSOL SP EQ** further to the improvement of the exhaustion of tanning materials, dyes and fatliquors there was a considerable positive effect on dye shades (Figure 12).



Figure 12 Influence of KEUSOL SP EQ on dyeing.

Exhaustion of tannins by recycling the pretannage float

Spent liquors of **ECOTAN PAP** pretannage and tannage were recycled in the pretannage of following batches, obtaining a further exhaustion of up to 88% and bringing the total uptake of tannins to 98% of the original tanning spent liquor (Figure 13).



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Characteristics	Normal Pretannage Float with ECOTAN PAP	Pretannage Float after Recovery in "Colouring"	Reduction
Density	11.4 Bé	8.4 Bé	
% Tannins	2.4%	0.3%	-88%
% of non tannins	9.8%	8.1%	
T/nT ratio	0.24	0.04	
Ash on dry matter	66.7%	92.7%	
COD value (ppm)	74,800 ppm	7,000 ppm	-72%

Figure 13 Spent liquors of ECOTAN PAP pretannage and tannage were recycled for a pretannage of consecutive batch.

Physical properties of the leathers

ECOTAN PAP + KEUSOL SP EQ crust physical properties such as tensile strength were in line with conventional Glutaraldehyde / Tara / Syntan system. Tear values were slightly higher (Figure 14).

Parameters	ECOTAN PAP + KEUSOL SP EQ Crust	Conventional Glutaraldehyde / Tara / Syntan Crust	Method
Tensile strength (N)	62.0	62.2	ISO 3376:2011
Tear strength (N)	212	177	ISO 3377:2011
Grain looseness (1-5)	4.5	4.5	
Light fastness (Grey scale)	4.0-4.5	3.5-4.0	Xenon lamp, 72h
Heat fastness (Grey scale)	4.5	3.5	120°C, 24h
Softness (Softmeter)	3.2	3.6	ISO 17235:2002
Fogging (Gravimetric)	2.8mg	2.8mg	DIN 75 201-B

Figure 14 ECOTAN PAP + KEUSOL SP EQ crust physical properties.

Biodegradability of pretanning / tanning effluents

Biodegradability tests were carried out on the spent liquors during pretanning and after colouring. The test was performed in a pilot biological treatment plant with a retention time of 65 days using activated biological sludge from a tannery water treatment plant (Figure 15).

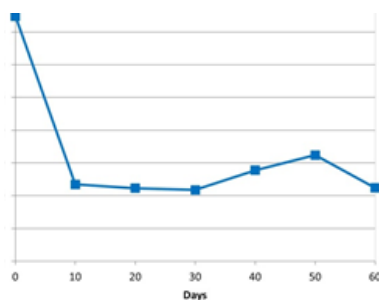


Figure 15 Spent liquor of ECOTAN PAP pretanning (A)

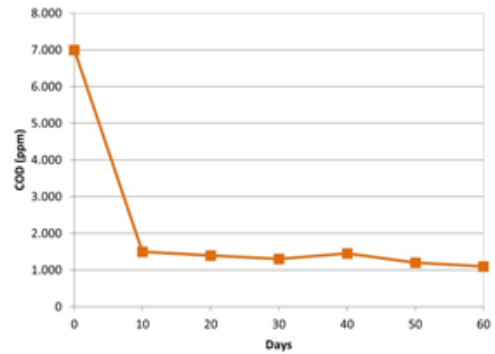


Figure 15 Spent liquor of ECOTAN PAP after colouring (B).

The test shows that spent liquor from pretannage is 70% biodegradable while the same liquor after colouring is 85% biodegradable.

Possible leather range

By varying the retannage and fatliquoring a very wide range of articles can be obtained, such as leather for automotive, furniture and shoe upper (Figure 16).



Figure 16 ECOTAN PAP + KEUSOL SP EQ leathers permit to obtain a huge range of articles.

3. Conclusion

The aim of this study was to assess an innovative metal free tanning system with the following key characteristics:

- Glutaraldehyde and / or metals free pretanned / tanned leathers;
- Simple process, similar to traditional vegetable tanning systems;
- Excellent light and heat fastness properties using **ECOTAN PAP** compared to other FOC techniques;
- Softness, dyebility and strength properties improvement thanks to the use of **KEUSOL SP EQ**;
- Very light leather colour obtained by the combination of **ECOTAN PAP** and **KEUSOL SP EQ**;
- Very high floats exhaustion thanks to the recycle of the final liquor of **ECOTAN PAP** tannage in the precolouring of following batches;
- Very high performing leathers as a result of **ECOTAN PAP + KEUSOL SP EQ** tannage.

4. Acknowledgements

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