New Challenges in Chrome-free Leathers: Development of Wet-bright Process

by

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Abstract

The aim of the present work was to develop a new tanning process (wet-bright) that produces perfectly white leather meeting all of the requirements for many kinds of articles, such as automotive, garment and shoe upper. This new process gives leather that is free of chromium, aldehydes, aldehyde precursors and organic solvents. It is the application of a new system based on a product designated Tanfor T™ from the manufacturer Kemira ChemSolutions. When compared to existing traditional wet leather processes, there are economic and environmental advantages resulting from the use of this new system. Also, the mineral character of the new product system offers leathers with high dye affinity; thus enabling very bright colors in all leather applications. We believe this leather offers such perfect dyeing properties because of the brilliant whiteness of the wet-bright intermediate substrate.

Introduction

About 85% of the world's leather is chrome tanned. Chrome tanning has a strong impact on the environment due to its potential to pollute wastewater and the difficulty to eliminate the solid wastes that contains chrome. A great variety of work has been carried out in order to minimize these impacts, such as; recycling of pickle-tanning floats, management of solid waste containing chrome, and using processes with high-exhaustion floats, etc.[1-4]

To reduce the negative environmental impact of the chrome tannage, wet-white tanning is increasingly used. As reported by G. Wolf *et al.*, wet-white in the strict sense of the term is taken to be completely free of heavy metals and aluminum salts.[5] Wet-white leathers mostly consist of aldehyde-based products, oxazolidine and/or phosphonium compounds.[6,7] This implies using products which could be harmful to human health. However, the term wet-white may also be applied to leathers that are free of chrome but which may be tanned with aluminum, titanium or zirconium salts.[8] In the present work, we present a new process with the aim of obtaining leather free of chromium, aldehydes, aldehyde precursors and organic solvents.

This new system applies the product Tanfor T™ (from Kemira). The product and its processes are based on a mineral tanning using compounds from aluminum, silicon and natural polycarboxylic acids. It was launched at the 2012 Tanning Tech in Bologna, Italy. It is formulated from environmentally friendly components that are used in water treatment, consumer household products and are partially biodegradable.[9]

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MATERIALS AND METHODS

This study was conducted in two stages:

- 1st stage. To establish the tanning mechanism of the new system.
- 2nd stage. To study the viability of the new system for use as a universal tanning system meeting all of the requirements for shoes, automotive and garments.

Material

The tests were carried out by using pickled hides at pH 3.2. Two types of tannage were compared: chrome tanning (Table I) and the new system using Tanfor T™ (Table II).

Tanfor T™ , it is designed as a two-component system:

i) Tanfor T™ -A is the tanning agent based on aluminum-silicon compounds. It is stable only in a certain pH range. At pH values above their stability range, the mineral salts will precipitate. At low pH, they are fully soluble, giving water clear solutions without signs of turbidity. Just below the maximum pH value of the stability range, a transition range is found where colloidal aggregates are formed. It is the colloidal aggregation state that is relevant for mineral tanning.[10]

ii) Tanfor T™-B is a self-basifying agent, self-buffering basic component of the Tanfor T™ tanning system, with a very high content of tanning active material.

The wet-bright intermediate that is obtained with Tanfor T™ is very cationic, which is a good and ideal substrate for anionic post tanning formulations.

Methodology

In order to determine the quality of the leathers and compare both systems, we carried out the physical tests set up by the IULTCS, which allowed us to assess the ability of the leathers to withstand the wear and tear of automotive upholstery, garment and shoe upper. The wet-end formulations used for each of the articles are shown in Table III, IV and V.

The following official methods were used to this end:

- IUP 6 Measurement of tensile strength and percentage elongation (in accordance with EN ISO 3376).
- IUP 8 Measurement of tear load (in accordance with EN ISO 3377-2).
- IUP 9 Measurement of distension and strength of grain by the ball burst test (in accordance with EN ISO 3379).
- IUP 16 Measurement of shrinkage temperature up to 100ºC (in accordance with EN ISO 3380).
- IUP 46 Measurement of fogging characteristics (in accordance with EN ISO 17071).
- IUF 402 Color fastness of leather to light: Xenon Lamp (in accordance with EN ISO 105-B02).
- IUF 450 Color fastness to cycles of to-and-fro rubbing (in accordance with EN ISO 11640).

TABLE I
Wet-Blue tanning formulation (on pickled hides).

Tanning	Wet-Blue	
Water	50%	T = 25ºC
NaCl	5%	rotate - 10’ ºBé=8.0 pH = 3.1
Chrome salt 33º Schorlenmeyer	2%	rotate – 60’
Chrome salt 66º Schorlenmeyer	5.5%	rotate – 2 h
MgO	0.3%	rotate – 6 h Overnight pH = 3.8
Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and retannage, dyeing, fatliquoring.		

TABLE II
Wet-Bright tanning formulation (on pickled hides).

Tanning	Wet-Blue	
Water	50%	T = 25ºC
NaCl	5%	rotate - 10’ ºBé=7 pH = 3.3
Tanfor T-A	4%	rotate – 3 h
Tanfor T-B	2%	rotate – 2 h
Tanfor T-B	2%	rotate – 2 h Overnight pH = 4.4
Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and retannage, dyeing, fatliquoring.		

TABLE III
Wet-end formulation for automotive.

Phase	ºC	%	Product	Time	Remarks
Washing	30	200	Water	10’	
					Drain
Neutralising	30	200	Water		
		0.4	Sodium formiate		
		0.9	Sodium bicarbonate	120’	pH=5.0
Retanning		10	Basyntan DLXN	30’	
		5	Tara	30’	
		2	Relugan RE	40’	
		10	Basyntan DLXN	30’	
		5	Tara	30’	
Dyeing		1	Beige A	240’	
				Aut night	Through cut
		1	Formic acid (1:10)	60’	pH=3.8
					Drain
Washing	50	200	Water	15’	
					Drain
Fatliquoring	50	200	Water		
		4	Lipsol MSG		
		8	Lipoderm licker A1	60’	
		1.5	Formic acid (1:10)	30’	pH=3.2
					Drain
Washing	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, drying, conditioning, staking and milling

TABLE IV
Wet-end formulation for shoe-uppers.

Phase	ºC	%	Product	Time	Remarks
Washing	35	200	Water		
		0.4	Acetic acid (1:5)	20’	
					Drain
Neutralising	35	150	Water		
		1.5	Sodium formiate	20’	
		1.0	Sodium bicarbonate		
		2	Sellasol NG liq.	120’	pH=5.2
Retanning		3	Relugan RE	40’	
		8	Mimosa		
		3	Basyntan D		
		2.5	Brown HG	120’	Through cut
					Drain
Washing	50	200	Water	20’	
					Drain
Dyeing	50	100	Water		
		0.7	Brown HG (1:5)	20’	
		0.8	Formic acid (1:10)	10’	pH=3.5
		0.3	Brown HG (1:5)	20’	Drain
Fatliquoring	50	100	Water		
		3	Trupon KIII		
		1.5	Truponol IMP		
		1	Trupon PB	60’	
		1.5	Formic acid (1:10)	30’	pH= 3.3
					Drain
Washing	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, vacuum drying, air drying, conditioning and staking

TABLE V
Wet-end formulation for garment.

Phase	ºC	%	Product	Time	Remarks
Washing	35	200	Water		
		0.5	Eusapon OD	20’	
					Drain
Retanning	35	200	Water		
		4	Tannesco HN gran.	60’	
		1.5	Sodium formiate	60’	pH= 4.2
					Drain
Neutralising	35	150	Water		
		1	Sodium formiate	20’	
		1.7	Sodium bicarbonate	2 x 15’	
				60’	pH= 6.2
					Drain
Dyeing	35	70	Water		
		2	Coralon OT		
		3	Blue ACL	60’	Through cut
Fatliquoring	55	130	Water		
		4	Derminol OS1		
		4	Trupon DB 80		
		1	Truponol IMP	60’	
		3	Relugan RE	45’	
		2	Formic acid (1:10)	2 x 15’	
				30’	pH= 3.7
					Drain
Washing	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, drying, conditioning, staking, wheeling, milling and straining

Also, the systems' potential to pollute wastewaters was assessed by analyzing the following parameters: Electrical Conductivity (µ/cm), Suspended solids (mg/L), COD (mg/L), N Kjeldahl (mg/L), Chromium (mg/L).

RESULTS AND DISCUSSION

The first step of this study established the tanning mechanism of the new system and the best conditions to apply Tanfor T™. Since it is a mineral system, application principles like those for chromium were used. Similar to salts of chromium (III) and other mineral compounds, the aluminum-silicon compounds that are the active tanning compound of Tanfor T™ are stable only in a certain pH range. At values above their stability range, the mineral salts will precipitate. At low pH, they are fully soluble, giving water clear solutions without signs of turbidity. Just below the maximum pH value of the stability range, a transition range is found where colloidal aggregates are formed. Colloidal aggregates are stable and will not precipitate, but are larger than the single molecule from which they are formed. It is this colloidal aggregation state that is relevant for the mineral tanning attribute of this system.

In order to formulate an effective tanning system around these aluminum-silicon compounds, Tanfor T™ was developed as a 2-component system. Tanfor T™-A was formulated such that the float pH was around 3.5 when starting from a pickle pH 3.2. At pH 3.5, the hydrodynamic radius of the colloidal aggregates was found to be very small, well below the desired colloidal dimensions. These small particles did not react with collagen; but allowed for a fast and an unhindered penetration through the cross section.

Tanfor T™ -B was formulated such that a pH equal to or higher than 4.2 was reached as an overnight value. At this pH, the aluminum-silicon compounds bind to the collagen matrix. Also, the aluminum-silicon compounds will aggregate which creates bridges between the collagen fibers. After dosing Tanfor T™ -B, the pH in the hide will increase more slowly than in the float. This slowed the locking reaction, which allowed the aluminum compounds of Tanfor T™ -B to also penetrate deeply into the collagen matrix, without excessive reaction on the surface or loss of material in the float.

Once the optimal working conditions were established, the aim of the second stage of this study was to assess whether the leathers made this new Tanfor T™ system had a variety of performance advantage over chrome-tanned leather.

Figure 1 and Figure 2 show the physical tests carried out on the tanned leathers.

As can be seen in both graphs, wet-bright leathers gave similar results like those for wet-blue. Wet-bright leathers showed slightly lower values in both tear load (IUP 8) and in shrinkage temperature (IUP 16) as compared with those obtained for wet-blue leather. But; wet-bright leathers gave a low value in Fogging test (IUP 46). This test measures the amount of volatile compounds, which has been released when high temperatures are achieved. Specifically, wet-bright leather gave a reduction of 8% versus wet-blue.

Another characteristic of wet-bright is that it did not deliberately contain chromium. Table VI shows the comparison of pollution in wastewaters between the processes due to wet-blue and wet-bright.

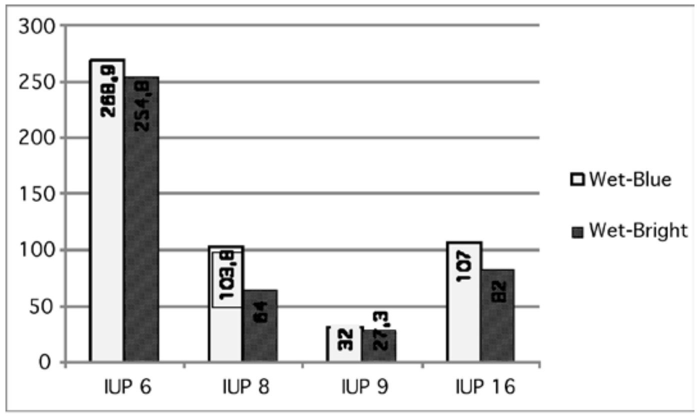

Figure 1. Physical tests.

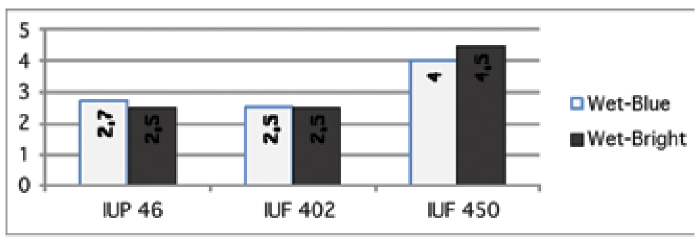

Figure 2. Physical tests.

TABLE VI
Comparison of pollution in wastewaters.

Test	Wet-Blue	Wet-Bright
Conductivity (µS /cm)	85966	101596
Suspended solids (mg/L)	1173	452
COD (mg/L)	9300	3800
N – Kjeldahl (mg/L)	470	165
Chromium (mg/L)	3219.0	No detectable

Chrome tanning is one of the most polluting processes in leather industry mostly due to the presence of chromium in the resulting wastewaters. Again wet-bright showed the following advantages versus wet-blue. Specifically, wet-bright reduced COD by 60%, reduced suspended solids by 61% and reduced nitrogen by 65%. And most important, wastewater did not contain chromium.

Once the tanning mechanism of the new system was established, we studied the viability of the new system as a universal tanning system meeting all of the requirements for shoes, automotive, and garments.

Figure 3 and Figure 4 show the physical tests carried out on the crust leathers (i.e. after the post-tanning processes).

As can be seen in both graphs, wet-bright leathers again gave results like those obtained for wet-blue. Only minor retanning and fatliquoring adjustments were required compared to wet-blue. Thus, we believe that wet-bright processes and their leather qualify as a universal tanning system meeting all of the requirements for shoes, automotive and garments.

Table VII shows the comparison of pollution parameters in wastewaters between the post-tanned wet-blue and the post-tanned wet-bright.

As can be seen in Table VII, wet-bright showed again an advantage over wet-blue. Specifically, wet-bright reduced COD by 40% versus wet-blue, reduced suspended solids by 32%, and reduced nitrogen by 31% in the automotive leathers. A reduction of 53% in COD, a reduction of 17% in suspended solids and a reduction of 18% in nitrogen was obtained in wet-bright shoe upper leathers compared to wet-blue. And wet-bright reduced COD by 7% in versus wet-blue, reduced suspended solids by 33%, and reduced nitrogen by 12% in garment leathers.

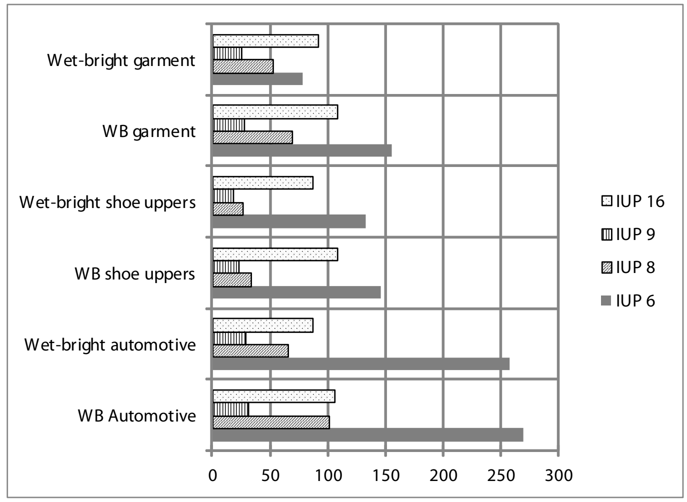

Figure 3. Physical tests after post-tanning processes.

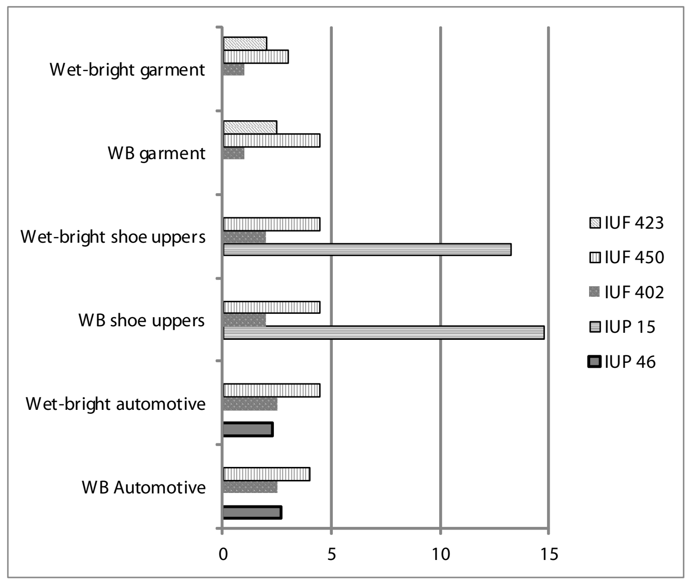

Figure 4. Physical tests after post-tanning processes.

TABLE VII
Comparison of pollution in wastewaters in post-tanning processes for each article.

TEST	WB Automotive	Wet-bright Automotive	WB Shoes	Wet-bright Shoes	WB Garment	Wet-bright Garment
Conductivity (µS /cm)	15183	17667	17970	20150	19400	20640
Suspended solids (mg/L)	3371	2291	761	356	976	648
COD (mg/L)	15450	9150	12100	10000	9500	8800
N – Kjeldahl (mg/L)	320	220	640	520	250	220
Chromium (mg/L)	102.5	No detectable	154.9	No detectable	203.9	42.5

And most important, wastewaters from the wet-bright leathers did not contain chromium. The chromium detected in wet-bright garment was due to the content of chromium salts in the post-tanning process. If this product were replaced by acrylic resins and syntans, the chromium in wastewater would not be detectable.

CONCLUSIONS

The new tanning process based on the aluminum-silicon compounds of Tanfor T™ produced perfectly white leathers meeting all of the requirements for automotive upholstery. The whiteness and strong cationic character of the intermediate substrate allowed for very bright colors. The leathers obtained with this process were free of chromium, aldehyde precursors and organic solvents. Only minor adjustments in retanning and fatliquoring were required compared to wet-blue. We believe that wet-bright qualifies as a universal tanning system because it produced leather meeting all of the current requirements for shoes, automotive and garments. Moreover, wet-bright leather did not contain chromium or heavy metals, and thus complies with Directive 2000/53/EC on End-of Life Vehicles. The new Tanfor T™ tanning system is environmentally friendly because it reduced COD by 60%, reduced, suspended solids by 61%, and reduced nitrogen by 65% compared with chromium tanning processes. Also important were reductions in COD, in suspended solids and in nitrogen after post tanning operations by using the wet-bright process compared with chrome tanning. And most important, wastewater from this new system contained no chromium.

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