SUSTAINABILITY IN PROCESS INNOVATION: DEVELOPMENT OF A GREEN TANNING PROCESS SUPPORTED BY LCA METHODOLOGY

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ABSTRACT

As a response to the growing concerns about a variety of environmental issues expressed by public opinion and political bodies, the leather industry needs to support its market by environmental criteria as a guarantee of quality. For this reason, assessment tools as Life Cycle Assessment (LCA) methodology, which allow a more thorough knowledge of the products to the enterprises and can help to guide the environmental policies, are recommended (e.g. EC Directive on Ecologic Labels). The LCA methodology, described in details by the ISO 14000 series, allows the assessment of the environmental impacts due to products, processes, or services, by the identification of the inputs (e.g. energy and material consumption) and outputs (e.g. waste and pollutant production) streams exchanged by the process with the environment (i.e. from raw materials procurement to waste streams disposal). The application of LCA as tool for integration of sustainability aspects in process design and development is gaining wider acceptance and methodological development. In this study, the life cycle modeling was used to support the development of a novel tanning process based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose). The experimental activity performed to investigate the technical feasibility of the innovative tanning cycle was supported by the modelling of the process using the LCA methodology in order to assess the environmental performance of the leather production cycle. Therefore, an LCA analysis was performed in order to compare the glucose-tannage process with the traditional one from an environmental point of view.

INTRODUCTION

As a response to the growing concerns about a variety of environmental issues expressed by public opinion and political bodies, the leather industry needs to support its market by environmental criteria as a guarantee of quality. Since sustainability is a global concept, this inevitably calls for a system-wide analysis. A system perspective is at the core of the Life Cycle Assessment (LCA) approach, which can provide valuable support in the sustainability evaluations, as demonstrated by the numerous environmental policies at European level (e.g. EC Directive on Ecologic Labels), based on the life cycle concept. The LCA methodology, described in details by the ISO 14000 series, allows the assessment of the environmental impacts due to products, processes, or services, by the identification of the input (e.g. energy and material consumption) and output (e.g. waste and pollutant production) streams exchanged by the process with the environment (i.e. from raw materials procurement to waste streams disposal). During the early years of LCA, the methodology was mostly applied to products but recent literature suggests that it also has potential as an analysis and design tool for chemical processes.[1,2] LCA could be used in several contexts. These include use in process design for comparison and selection of options;[3] in business planning for identifying weak links in a processing chain or in comparing processes with those of business competitor; at the research and development phase of a process,[4] in guiding process evolution[5].

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Besides, during the evolution of the methodology, a number of related applications emerged, including its use as basis to communicate the overall environmental performance of the products to stakeholders. Specific standards are available for LCA-based environmental labels and declarations. The International Standards Organization (ISO) has classified the existing environmental labels into three typologies—types I, II, and III—and has specified the preferential principles and procedures for each one of them (ISO 14021, ISO 14024, and ISO 14025). An Environmental Product Declaration (EPD), also referred to as type III environmental declaration, is a standardized (ISO 14025) and LCA-based tool to communicate the environmental performance of a product[6]. There are a number of requirements for how the LCA should be performed to be used as basis for an EPD. They are concerned on detailed specifications on how to model the product system in the LCA, what to include, what data to use, which environmental indicators to report, etc. These requirements are developed for different product groups by the industry and are referred to as Product Category Rules (PCRs). The aim of the PCRs is to achieve comparability in results between different producers of the same product. And as such, the PCRs are valuable and useful as basis for any type of LCA to be used in external communication of results. Recently, the PCR for the assessment of the environmental performance of "Finished bovine leather" are established.

In this study, the life cycle modeling was used to support the development of an innovative tanning process based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose). From the pilot scale experimental tests, the novel process by using glucose as tanning agent appears feasible leather processing, from the technical point of view, to produce high quality bovine upper leather. Results have shown that the finished glucose-tanned leather were comparable to the conventional chrome-tanned in terms of mechanical and technical properties.

Life cycle modeling was used to support the development the novel tanning process by assess the environmental performance associated to the whole production cycle. Therefore, the LCA methodology was applied in order to compare the novel process with the traditional one from an environmental point of view. The LCA study was performed in according to the Product Category Rules defined for the EPD system.

Methods

This study was performed using a methodological framework based on the International Organization for Standardization (ISO) recommendations (UNI EN ISO 14040 and 14044). According to the ISO 14044, LCA methodology consists of four phases: goal and scope definition, inventory analysis, impact assessment and interpretation. In the goal and scope definition are defined the objectives of the study, the functional unit (i.e. the reference unit to which the inputs and outputs are related), the boundaries of the system (i.e. the extension of the study), and the impact assessment methodologies. The inventory analysis involves data collection for all the activities in the studied system: raw materials (including energy carriers), products, and solid waste and emissions. This step includes calculation of the amount of resource use and pollutant emission of the system in relation to the functional unit. The impact assessment phase assigns the inventory results to impact categories and quantifies the system potential contribution to different environmental impacts.

Process Description

The semi-industrial scale tanning runs were conducted in a stainless steel drum (1.2 m diameter, 0.8 m length) by using heavy calf hides (8-12 kg) after the pickling stage (pH 2.6). In each run, the hides were divided into two sides: one side was conventionally tanned with chrome; the other side was tanned according to the innovative recipes (see Tables I and II). After tannage, the two halves followed a retannage/dyeing-fatliquoring cycle to obtain crust leathers currently used by the tannery to produce upper leathers.

Table III reports the results of the physical and mechanical tests of the crust leathers obtained. The results of the assessment of the technical properties of the innovative crust leathers, in comparison with the conventionally chrome tanned leather, are reported in Table IV. A conventional scale of grades ranging from 1 (worst performance) to 5 (best performance) has been used. The novel crust leathers comply very well with the mechanical standards required for high quality bovine upper leather.

Goal Definition and Functional Unit

The main objective of this LCA was to compare the environmental potential impacts of two tanning processes. The traditional chrome-tanned leather was compared to novel leather production based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose). The scope is to include all-important activities of the leather processing, i.e. covering raw materials acquisition and materials production.

Based on Product Category Rules of the international EPD System, the functional unit was set equal to the production of 1 m^2 of "finished bovine leather", intended as a finished product of the tanning sector and ready to become an input as a semi finished good for further transformation in various manufacturing sector. The leather can be used as a semi finished good for different kinds of final products (for example furniture, clothing, footwear etc.). Since the application of finished bovine leather in final consumer products varies substantially, no specific function has been defined for the product. Therefore, the use phase was not included in the analysis and a cradle-to-gate system was considered. Figure 1 shows the phases included in the analysis. According to the PCRs, the system boundaries include the main flow related to the leather processing: agriculture, cattle raising, slaughtering and tanning. As noted above, since no specific function has been defined for finished leather, the use phase and the waste treatment phase are omitted. The construction of facilities, including the machinery, electrical installation etc., were excluded from the system and only the operation stages were taken into account in the analysis.

Inventory Analysis

The environmental load was calculated in relation to the functional unit, and the inventory results are evaluated and distributed into the life cycle stages. The aggregated data collected for modeling the systems were derived from the experimental tests performed to explore the technical feasibility of the novel tanning cycle. The needed equipment and electricity quantities were calculated in relation to treatment time of the hides in the various stages of the process. Inventory data for the background system (production of chemicals, electricity, lorry transport, etc.) were based on average technology data from the Ecoinvent 2.2. Database.

As most industrial processes yield more than one product, it is necessary to allocate the burdens caused by these processes (resource consumption and emission) to all the products. As defined in PCRs, in this study a mass allocation procedure to rawhide of the impact of agriculture, cattle raising and slaughtering was applied. For example, in the slaughtering phase the allocation factor for raw hides is 7% (i.e. only 7% of the environmental burdens produced upstream of the skinning operation are allocated to hides).

Impact Assessment Method

The study was carried out by using SimaPro 7.3 software (Pré Consultants). To conduct an LCIA (Life Cycle Impact Assessment), it is necessary to select an impact assessment methodology, which regroups the different characterization models for each impact category. These characterization models allow the calculation of characterization factors, which express the measured substance's strength relative to a reference substance.

Among the different methods available in the software, the ReCiPe endpoint and midpoint (hierarchist version) methods were used. An endpoint method was used for the impact assessment in order to achieve maximal agreement with the comparative and management-oriented objectives of the study. Endpoint indicators describe the integrated damage of the components from the inventory, in contrast to midpoint indicators that address effects only. For global warming, a typical midpoint indicator would be the effect of radiative forcing (global warming potential), whereas the endpoint approach would assess the human and environmental damage based on radioactive effects. Use of endpoint indicators facilitates the interpretation of the results and allows integration of environmental burdens to a single score indicator (the midpoint characterization factors are multiplied

TABLE I
Recipe of the semi-industrial scale tanning runs with chrome (the dosages are reported as wt.% on the fleshed hide weight).

Pickle float	50%	
Chromium sulfate (26/33)	4.5%	30 min
Antibacterial	0.2%	1hr
Sodium acetate	0.6%	1 hr
Basic Chromium sulfate (26/33)	4.5%	4 hr
MgO basifying agent	1.0%	9 hr
Overnight		
Drain		
Horse up		48 hr
Pressing and shaving		

TABLE II
Recipe of the semi-industrial scale tanning runs with glucose (the dosages are reported as wt.% on the fleshed hide weight).

Pickle float	50%	
Sodium formiate	1.5%	
Liquid glucose (43°Bé)	10%	2 hr
Liquid glucose (43°Bé)	15%	8 hr
Hydroxysulphonic syntan	2%	2 hr
Overnight		
Drain		
Horse up		48 hr
Pressing and shaving		

with a damage factor to obtain the endpoint characterization values). ReCiPe uses three main damage categories: human health, ecosystems and resources. Human health includes climate change, ozone depletion, human toxicity, photochemical oxidant formation, particulate matter formation, and ionising radiation (expressed in disability adjusted life years, DALY). Ecosystems include climate change, terrestrial acidification, freshwater and marine eutrophication, terrestrial, freshwater and marine ecotoxicity, agricultural and urban land occupation, and natural land transformation (expressed in species·yr). Resources include metal depletion and fossil depletion, expressed in $.

RESULTS AND DISCUSSION

The results of the life cycle assessment of the traditional leather production (chrome-tanned) at endpoint level are reported in Figure 2. Regarding the three damage categories (human health, ecosystems and resources), the graphic highlights the environmental impact of the tannery compared with the others activities related to the leather production (agricultural phase, cattle raising, slaughterhouse are included in the *raw hides* block). The contribution to Ecosystems damage category is remarkably higher for the activities associated with the calf hides production in relation with the agricultural stage and cattle raising. The agriculture-related emissions are caused mainly by fertilizer use and production. The use of fertilizers causes N_2O emissions, which contribute to Climate change category included in Ecosystems damage category, and nitrate emissions in water, which contribute to Eutrophication and Human Toxicity categories. Also the emission of methane from the cattle raising causes the main impacts and contributes largely to Climate Change and Photochemical oxidant formation categories. This result is especially notable taking into account the fact that only 7% of the impacts generated in these phases have been allocated to leather production.

TABLE III

Physical tests results of the crust leather.

	Shrinkage temperature (°C) UNI EN ISO 3380 method	Tearing load (N) UNI EN ISO 3377/2 method	Grain distension (mm) UNI 11308 method
Traditional leather production	94	151.3	9.6
Novel leather production	92	154.4	9.4
		UNI 10594 guidelines: 30÷80[1]	UNI 10594 guidelines: ≥ 7

[1] depending on use

TABLE IV

Technical properties of the crust leather.

	Traditional leather	Novel leather
Color homogeneity	4	4
Color yield	4/5	3/4
Roundness	4	3
Fullness	4	3
Wrinkle	4	4
Hand	4	3
Grain quality	4	4

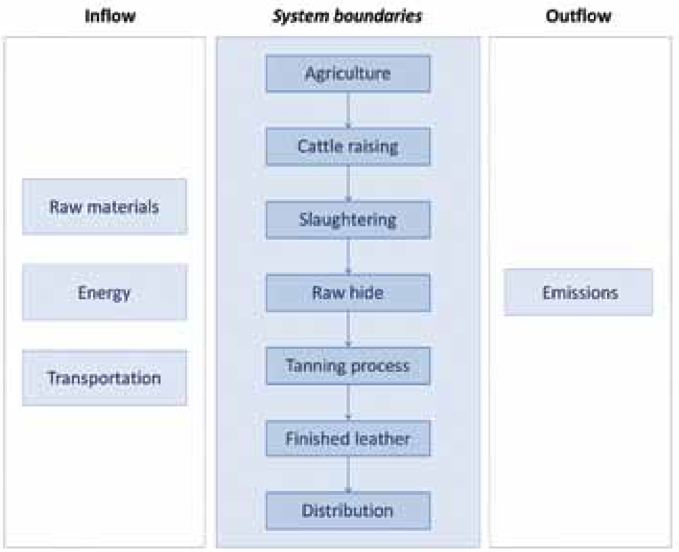

Figure 1. Life cycle flow diagram of the studied system.

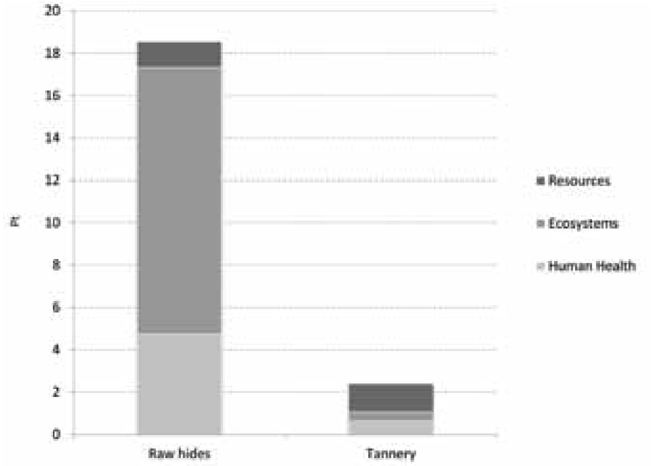

Figure 2. Results of the life cycle assessment of the chrome tanned leather at endpoint level.

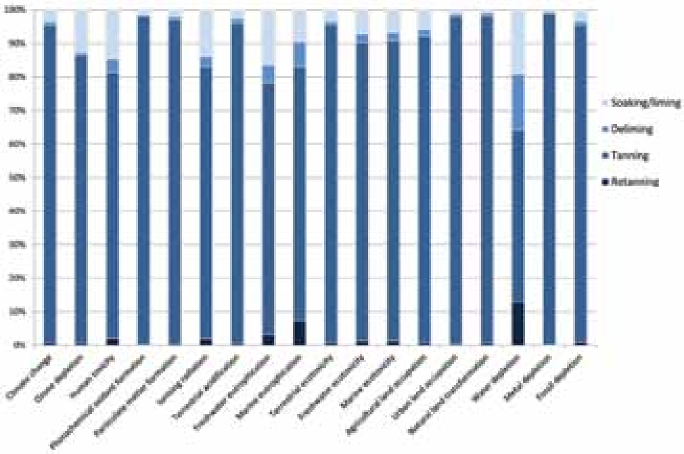

Figure 3. Contribution of subsystems of the chrome-tannage cycle to each impact category.

TABLE V
Midpoint results per impact categories.

Impact Category	Unit	Traditional leather production	Novel leather production
Climate change	kg CO_2 eq	$1.93 \cdot 10^{2}$	$1.75 \cdot 10^{2}$
Ozone depletion	kg CFC-11 eq	$1.63 \cdot 10^{-5}$	$1.37 \cdot 10^{-5}$
Human toxicity	kg 1.4-DB eq	3.33	1.39
Photochemical oxidant formation	kg NMVOC	$3.26 \cdot 10^{-1}$	$1.89 \cdot 10^{-1}$
Particulate matter formation	kg PM10 eq	$3.45 \cdot 10^{-1}$	$3.07 \cdot 10^{-1}$
Ionising radiation	kg U235 eq	2.72	1.21
Terrestrial acidification	kg SO_2 eq	2.25	2.16
Freshwater eutrophication	kg P eq	$5.63 \cdot 10^{-3}$	$4.05 \cdot 10^{-3}$
Marine eutrophication	kg N eq	2.64	2.63
Terrestrial ecotoxicity	kg 1.4-DB eq	$3.26 \cdot 10^{-3}$	$6.35 \cdot 10^{-4}$
Freshwater ecotoxicity	kg 1.4-DB eq	$8.92 \cdot 10^{-2}$	$2.28 \cdot 10^{-2}$
Marine ecotoxicity	kg 1.4-DB eq	$9.64 \cdot 10^{-2}$	$2.38 \cdot 10^{-2}$
Agricultural land occupation	m2a	$2.25 \cdot 10^{2}$	$2.24 \cdot 10^{2}$
Urban land occupation	m2a	$2.07 \cdot 10^{-1}$	$1.26 \cdot 10^{-2}$
Natural land transformation	m2	$6.61 \cdot 10^{-3}$	$6.38 \cdot 10^{-4}$
Water depletion	m3	$2.59 \cdot 10^{-1}$	$1.59 \cdot 10^{-1}$
Metal depletion	kg Fe eq	5.61	$1.86 \cdot 10^{-1}$
Fossil depletion	kg oil eq	$1.41 \cdot 10^{1}$	7.89

TABLE VI
Disadvantage factors per impact categories.

Impact Category	Unit	Traditional leather production	Novel leather production
Climate change	kg CO_2 eq	1.10	1.00
Ozone depletion	kg CFC-11 eq	1.19	1.00
Human toxicity	kg 1.4-DB eq	2.40	1.00
Photochemical oxidant formation	kg NMVOC	1.73	1.00
Particulate matter formation	kg PM10 eq	1.12	1.00
Ionising radiation	kg U235 eq	2.25	1.00
Terrestrial acidification	kg SO_2 eq	1.04	1.00
Freshwater eutrophication	kg P eq	1.39	1.00
Marine eutrophication	kg N eq	1.00	1.00
Terrestrial ecotoxicity	kg 1.4-DB eq	5.13	1.00
Freshwater ecotoxicity	kg 1.4-DB eq	3.91	1.00
Marine ecotoxicity	kg 1.4-DB eq	4.06	1.00
Agricultural land occupation	m2a	1.00	1.00
Urban land occupation	m2a	16.41	1.00
Natural land transformation	m2	10.37	1.00
Water depletion	m3	1.63	1.00
Metal depletion	kg Fe eq	30.20	1.00
Fossil depletion	kg oil eq	1.78	1.00

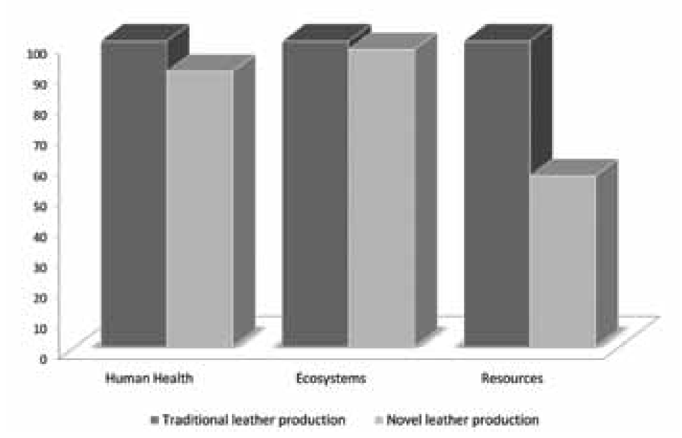

Figure 4. Comparison of the environmental impacts associated with the two tanning process at endpoint level.

Figure 3 shows the results of a contribution analysis performed to reveal the most important contributing stages for the chrome-tanning cycle. As it can be seen, the tannage phase accounts for most of the whole environmental impact. This result is related to chromium content of the wastes (solid wastes and wastewaters) and also its manufacturing process. Therefore, the substitution of chromium salts with tanning agents having a lower environmental burden in relation with its use (pollutants content of the exhaust bath) and its production can remarkable reduces the impacts of the tannery.

Table V lists the parameter values obtained from the life cycle impact assessment of the two tanning processes, which are used to calculate the disadvantage factors reported in Table VI.

The disadvantage factors are calculated by dividing the higher value by the lower value, in order to highlight how many times a process causes more environmental burdens compared to the other one[7].

The results show that the potential environmental loads for traditional tanning process are higher than the burdens associated to glucose-tanned leather production. As noted above (see Figure 3), the main contribution to environmental impact of hides processing is related to use of chromium salts, therefore the use of glucose instead chromium sulphate reduces the loads of the tannery. This result indicates that the environmental advantage in the novel leather cycle outweigh the costs to the environment in the form of greenhouse gas emissions, particle emissions, use of limited resources, etc. in the traditional chrome-tanned leather production, although the cultivation activities and manufacturing process associated to glucose production were considered. These phases contribute mainly to categories included in the Ecosystem category damage. So the potential effects on ecosystem are very similar for the two-system production, as shows in Figure 4. On the other hand, it must be taken into account that the potential damage on ecosystems is strongly affected by the agricultural phase.

CONCLUSIONS

A comparison of the environmental performance of two leather manufacturing processes was carried out. An innovative tanning process based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose) was compared to the traditional chrome-tanned leather production by using the LCA methodology. From the pilot scale experimental tests, innovative process by using glucose as tanning agent appears a feasible leather processing, from the technical point of view, to produce high quality bovine upper leather. Results have shown that the finished glucose-tanned leather is comparable to the conventional chrome-tanned in terms of mechanical and technical properties. Life cycle modeling was used to support the development the novel tanning process by assess the environmental performance associated to the whole production cycle in view of the application of this new tanning process at industrial scale.

The results of the impact assessment of the chrome tanned leather underline that the main potential impact is associated with the rawhides production in relation with the agricultural stage and cattle raising rather than with the tanning phases. The contribution analysis of the stages reveals that the main contribution to environmental impact of hides processing is related to use of chromium salts. The use of glucose instead chromium sulphate reduces remarkably the environmental loads of the tannery, as highlighted from the results of the comparative analysis at midpoint and endpoint level. Then the outcomes obtained indicate that the novel leather production is a promising alternative to the traditional process to overcome the ever-increasing environmental constraints.

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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.

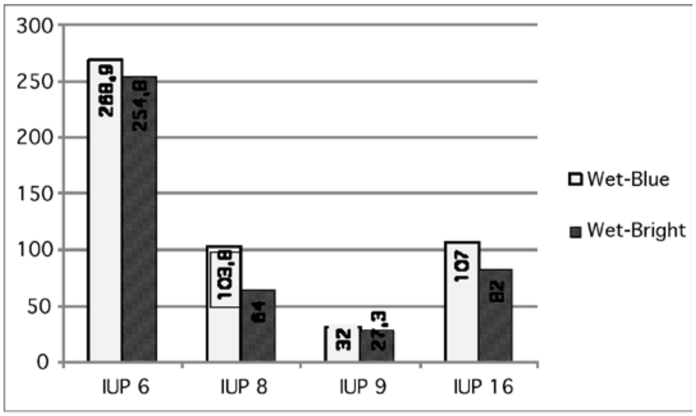

Figure 1. Physical tests.

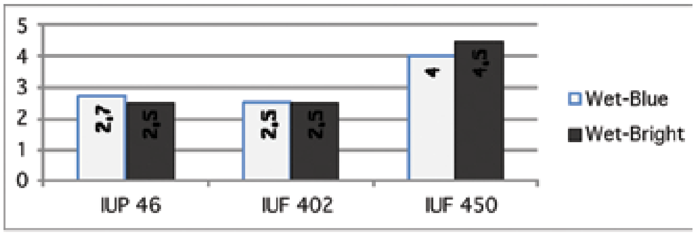

Figure 2. Physical tests.

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.

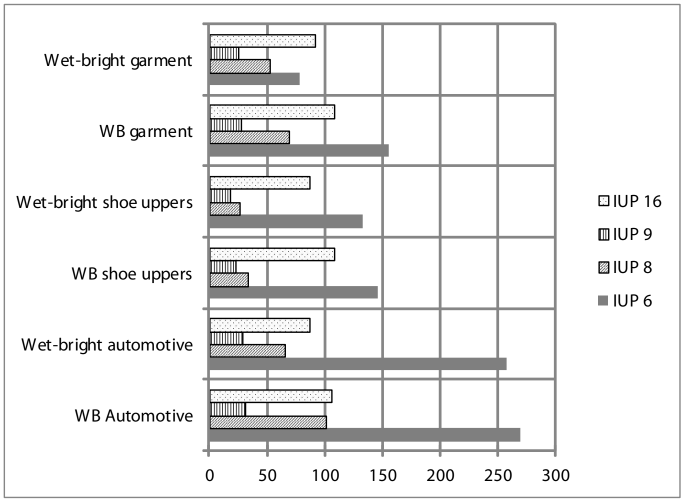

Figure 3. Physical tests after post-tanning processes.

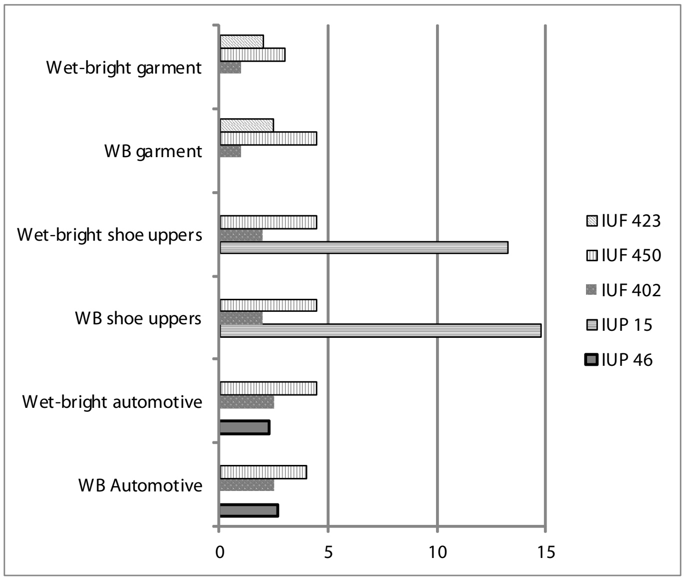

Figure 4. Physical tests after post-tanning processes.

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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