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Evaluation of a new environment friendly tanning process

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ABSTRACT

The aim of the present work is to develop a new tanning process (that we call Wet Bright) that produces perfectly white leather and meets all the requirements for automotive leather. What is obtained through this new process is a leather free of chromium, aldehydes, aldehyde precursors and organic solvents. This new system consists of the application of Tanfor T™ system (from Kemira), which is safe for both humans and the environment and is not classified as hazardous. When compared to existing traditional processes, namely chrome tanned leather (Wet-Blue) and aldehyde tanned leather (Wet-White), there are economic and environmental advantages resulting from the use of this new system. In this vein, this new process results in significant COD reductions. More specifically, the new system is an environmentally-friendly process since it reduces COD by 60%, suspended solids by 61%, and nitrogen by 65% compared with chromium tannage. In addition, Wet-Bright leathers present a reduction of 43% in volatile compounds versus Wet-White and a reduction of 8% versus Wet-Blue. And most importantly, wastewaters from this new system do not contain chromium.

1. Introduction

Automotive leather, as a component of a vehicle, must comply with the European Union Legislation on End-of-Life Vehicle 2000/53/EC. Every year, motor vehicles that have reached the end of their useful lives create between eight and nine million tonnes of waste in the European Union. The European Commission adopted a Directive to tackle this problem. Among the different aspects that cover the Directive along the life cycle of a vehicle and the aspects related to treatment operations, we will focus on preventing the use of certain heavy metals such as cadmium, lead, mercury and chromium (Directive 2000/53/EC).

Indeed, 90 per cent of the world's leather is chrome tanned. Chrome tanning has a strong impact on the environment due to the pollution of wastewater and the difficulty to get rid of the solid waste containing chrome. A great variety of research has been carried out in order to explore how to minimize this impact, including work on: recycling of pickle-tanning floats (Thanikaivelan et al., 2004; Saravanabhavan et al., 2003), management of solid waste containing chrome (Muralidharan et al., 2001) and processes with high-exhaustion floats (Morera et al., 2007).

To reduce the negative environmental impact of chrome tannage, Wet-White tanning is increasingly used, especially in the automotive sector following the EU Legislation on End-of Life Vehicles and the market trends for chrome-free tanned leather, mentioned above.

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 aluminium salts (Wolf et al., 2001). Wet-White leathers mostly consist of aldehyde-based processes, oxazolidine and/or phosphonium compounds (Taylor et al., 2011; Jayakumar et al., 2011). This implies using products harmful to human health.

However, the term Wet-White may also be applied to leathers that are free of chrome but which may have been tanned with aluminium, titanium or zirconium salts (Ollé et al., 2011).

More recently, a system has been proposed in order to minimize the negative effects of such pollution, but without rejecting the use of chrome as a tanning material. This system is based on the use of compressed carbon dioxide as process additive. Compared to conventional process less chromium-III salt is used and the process time can be reduced to 2.5 h. While this system may effectively minimize the discharge of chrome (it results in a tanning process practically free of wastewater) what tends to get ignored is the use of chromium in the process (Renner et al., 2012).

Otherwise, two greener leather tanning processes have been studied to obtain chrome-free leathers. The first process is based on unnatural D-amino acids (D-AA)–aldehydes as a substitute of chromium salts. Although the developed process results in significant reduction in total solids content and improves better biodegradability of organic compound present in the effluent compared

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to chrome tanning, this system is using a hazardous substance (Krishnamoorthy et al., 2012).

The second process consists of using D-Lysine aldehyde complex as novel tanning agent for chrome-free tanning. However, this system also is using a hazardous substance (Krishnamoorthy et al., 2013).

In this paper, we present a new process with the aim of obtaining leather free of chromium, aldehydes, aldehyde precursors and organic solvents.

This new system consists in applying the Tanfor T™ system (from Kemira), which is safe for both humans and the environment and is not classified as hazardous. The process is based on a mineral tanning using compounds from aluminium, silicon, and natural polycarboxylic acids.

Tanfor T (product launched at the 2012 Tanning Tech in Bologna, Italy) is formulated from partially biodegradable environmentally-friendly components widely used in water treatment and consumer household products.

2. Material and methods

2.1. Material

The tests were carried out using pickled hides at pH 3.2. Three types of tannages were compared: i) chrome tannage, ii) Wet-White tannage, and iii) the new system using Tanfor T™ (Table 1).

The chemicals used in the operations were those normally used in the leather industry.

In order to carry out the chrome tanning, the hides are immersed in a saline dissolution at acidic pH. The presence of salt in the dissolution is necessary to prevent the hides from swelling because of the acidity resulting from the process and the chrome from penetrating the hides. The process takes place inside some cylindrical containers called drums. By rotating on their axis, the drums provide the necessary agitation for the chrome to be absorbed by the hides. The main component of the hide is a protein called collagen. Once the chrome has been absorbed by the hides, gets fixed to the collagen by an increase in the pH. This stabilizes the protein against putrefaction. It is considered that at this point the hide has become leather.

Polyaldehyde tannage system (Wet-White tannage) produces chrome free leather by cross linking the NH_2 groups of collagen with glutaraldehyde ($CHO-CH_2-CH_2-CH_2-CHO$). After as usual soaking, liming, deliming, bating and pickling operations the pickle pelts were tanned with polyaldehyde and other syntans. Polyaldehyde tanning is not capable to bring about a full tannage with a broad spectrum of properties of leather sellable on the market. That is the reason why a syntan is used. In addition, a full retannage has to be done to obtain similar properties to those obtained using chromium salts. The tanning process, as can be seen in Table 1, is similar to the chrome tanning process.

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

i) Tanfor T-A is the tanning agent based on aluminium–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 (van der Burgh, 2012).
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 substrate for anionic post tanning formulations.

Table 1
Tanning formulations.

Tanning (on pickled hides)[*],[a]		
Wet-Blue		
Water	50%	$T = 25$ °C
NaCl	5%	Rotate – 10 min °Bé = 8.0 pH = 3.1
Chrome salt 33 °Schorlenmeyer	2%	Rotate – 60 min
Chrome salt 66 °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, fatliquor		
Wet-White		
Water	50%	
NaCl	5%	Rotate – 10 min °Bé = 8.2 pH = 3.1
Aliphatic polyaldehydes	3.25%	Rotate – 3 h 30 min pH = 3.3
MgO	0.5%	Rotate – 2 h 30 min pH = 3.6
Synthetic tanning agent	7%	Rotate – 5 h overnight pH = 4.2
Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and retannage, dyeing, fatliquor		
Wet-Bright		
Water	50%	$T = 25$ °C
NaCl	5%	Rotate – 10 min °Bé = 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, fatliquor		

[*] Pickled leather is an intermediate product of a leather tanning industry. Pickled leather is acidified hides and skin for allowing the tanning agents to penetrate while wet blue leather is hides and skin treated with chrome tannage.
[a] The percentage of added products in each process is related to weight of pickled hides. That is, if we are working with 1000 kg of pickled hides, we add 500 kg of water per each process.

2.2. Methodology

In order to determine the quality of the leathers and compare the three systems, we carried out the physical tests set up by the IULTCS, which allowed us to assess the capacity of the leathers to withhold the wear and tear of automotive upholstery. To this end, the following official methods were used to this end:

IUP 6 Measurement of tensile strength and percentage elongation (in accordance with EN ISO 3376). To carry out this test a leather sample is fixed on the clamps of a dynamometer. Then the clamps are subsequently separated at a constant speed while the force exerted on the sample is measured with the load cell of the device. The elongation is calculated as the difference between the final and initial separation of the sample. This difference is expressed as a percentage of the initial separation.
IUP 8 Measurement of tear load (in accordance with EN ISO 3377-2). This method is used to determine the capacity of the leather to withhold multidirectional tensions. In order to perform this test the dynamometer is also used by fixing a leather sample with a slot and subsequently separating the clamps at constant speed, causing the leather to tear completely.
IUP 9 Measurement of distension and strength of grain by means of the ball burst test (in accordance with EN ISO 3379). This test assesses the performance of the leather in the upper side of the shoe by using a lastometer, a machine developed by SATRA. The leather is progressively deformed until the first