Paper D7

New type of titanium-based tannage

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Abstract

For thousands of years, leather has been tanned with vegetable extracts, which was fine, although generally the result was very thick and hard leather. Then, for the last hundreds of years more than 90% of the leather has been tanned with Chromium. Chromium has brought many advantages for the leather industry: it has allowed the production of thinner, softer and water resistant leather, fulfilling the needs of modern life for better footwear, garments and upholstery. Even though, Chromium has always produced very much concern regarding one of its forms called *Chrome VI,* which is known to be toxic. In general, tanners consider that after 100 years of experience they have this under control; however it still remains worrying.

This work focuses on a new titanium-based tanning system and shows the advantages it brings. SANOTAN leather is new chromium-free leather, tanned with titanium. Titanium seemed to be a good candidate for leather tanning because it proved to be bio-compatible, it has no toxic state, it has a long history of use in surgical instruments and brings no actual or potential drawback whatsoever to the leather industry.

SANOTAN leather brings many new features and benefits to the footwear and leather goods industries. In this way, the biocompatibility test carried out showed that SANOTAN leather did not produce irritation or allergy. SANOTAN leather showed more thermal comfort than chrome-tanned leather, offered a better adaptation and better breathability. Sweat evaporation through SANOTAN leather is easier than through conventional leather, thus obtaining more comfortable footwear. Also, Titanium-tanned leather shoes were perceived as 40% warmer than chromium-tanned leather shoes.

These studies led to the preparation and launching of the Ecoinnovation project TiLEATHER "Ecofriendly Leather Tanned with Titanium", whose main objective is to introduce SANOTAN leather into the European market. This project is partially supported by the Executive Agency for Competitiveness and Innovation (EACI) under the Eco-Innovation Programme.

1. Introduction

Chrome tanning presents certain environmental risks derived from the possible oxidation of chrome to its hexavalent state, which is carcinogenic according to the International Agency for Research on Cancer (IARC). For this reason, over recent years, the Footwear Technological Institute (INESCOP) has been working to find new tanning agents that could provide an alternative to chrome tanning, as is the case of titanium-tanned leather developed by Industrias del Curtido, S.A. (INCUSA).

Titanium was first considered as a possible tanning agent in 1930, as its properties allow it to react with collagen carboxyl groups present in leather. Titanium used as a tanning agent has been proven to produce leathers with a level of quality suitable for commercial use. What is more, it is a non toxic metal and gives additional advantages in that it is biocompatible, inert and avoids possible allergic reactions derived from contact with the skin. However, the leather industry has traditionally opted to

use other agents, such as chrome, aluminium or organic compounds, with their associated environmental impact. This was mainly due to several difficulties in using titanium throughout the entire tanning process.
INCUSA carried out research into the development of a novel eco-innovative tanning technology that allows the use of titanium as a tanning agent, while avoiding the drawbacks that had limited its use until now and, what is more, avoiding the use of titanium dioxide as tanning agent (as the manufacture of this substance can cause harmful effects on the environment).

The new titanium tanning technique is an alternative to those that have been known to date. This technique makes chrome retanning unnecesary; therefore, chrome is completely eliminated from tanning processes and thus this technique is more environmentally friendly.

As a result of the development of said technique, it was possible to obtain titanium-tanned leather registered by INCUSA under the trade name SANOTAN®. These leathers show multiple innovative properties that had never been attained with tanning agents other than chrome.

These studies led to the preparation and launching of the Ecoinnovation project TiLEATHER "Ecofriendly Leather Tanned with Titanium". This project is partially supported by the Executive Agency for Competitiveness and Innovation (EACI) under the Ecoinnovation Programme. The project is coordinated by INESCOP and relies on the participation of INCUSA, a leather manufacturer and owner of the trade mark SANOTAN®, as well as FLUCHOS footwear business in Spain and, EUROKA and MILLE in France. The main environmental objective of this Project is to introduce into the European market more ecofriendly leathers which better respect the environment during the production process, as well as reducing the environmental impact of leather at the end of its useful life.

This paper presents the results obtained so far in the framework of the TiLEATHER project.

2. Methodology

In previous works, the titanium tanning technique was developed on a laboratory scale and subsequently on a semi-industrial scale. At a further stage, already in the framework of the TiLEATHER project, SANOTAN® leather was produced on an industrial scale by setting up a production line for 1.200.000 $feet^2$/year. For this, studies were conducted with the aim of:

- Reducing chrome contamination in titanium tanned leather, since the new production line was to be integrated in the same facilities as the other chrome-tanning lines.
- Optimally investing in new equipment needed for the new titanium-tanning line.
- Improving the properties of SANOTAN® leather in order to meet the requirements of footwear manufacturers participating in the TiLEATHER project.

After having set up the new production line, the first cattle hides tanned with titanium on an industrial scale were obtained, and their properties as well as the wastewater derived from the tanning process were analysed. What is more, a further step was taken with the production of several shoe styles by the manufacturers participating in the project, with a view to checking the suitability of said leathers.

2.1. Obtaining titanium-tanned leather

The titanium tanning technique uses titanium sulphate (ammonium titanyl double sulphate $Ti(NH_4)_2(SO_4)_2H_2O$), masked with certain organic products as a tanning agent. Titanium combines with the skin collagen in the same way as chrome does. This combination does no longer produce the blue colouring that is characteristic of chrome-tanning (wet-blue), since titanium-tanned leather shows a yellowish shade, which allows tanners to obtain bright colours that can hardly be achieved with

chrome tanning. Figure 1 describes the interaction of titanium sulphate with the skin's collagen carboxyl groups.

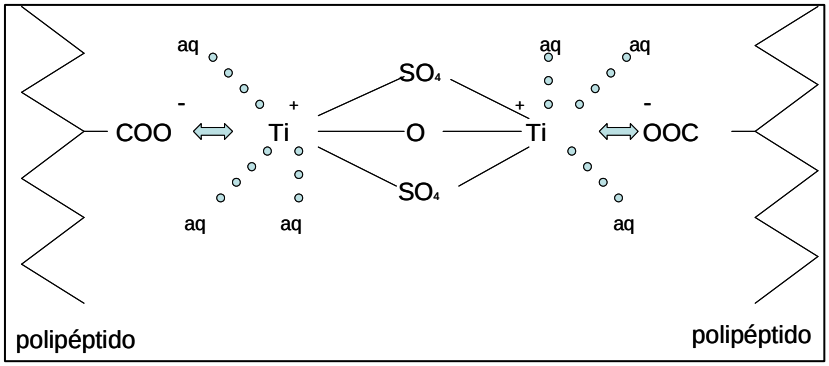


Figure 1. Interaction of collagen carboxyl groups with titanium

Once tanned with titanium, leather undergoes retanning, dyeing and fatliquoring with chrome-free vegetable extracts or synthetic products. These processes lend leather its characteristic comfort properties and desired high performance.

2.2. Leather properties

As well as verifying the good stability of leathers, it is also necessary to mechanically characterise them in order to check whether their physical resistance properties are optimal for use in footwear production. The tests carried out for the characterisation of SANOTAN® leather are the following:

- Tear strength: The leather's ability to withstand multidirectional strain is assessed. A leather test piece is clamped in a tensile testing machine that stretches it causing tearing up until complete breakage.

- Tensile strength: The leather's resistance against stretch-induced breakage is measured. A leather test piece is clamped in a tensile testing machine and the clamps are separated at a constant rate. The results is expressed as the maximum force need to break the test piece.

- Resistance to damage on lasting (Ball burst test): A rounded test piece of leather is firmly held on a lastometer and a mechanisms pushes a steel ball capped plug upwards until the first grain burst is produced.

- Water resistance: Water penetration and absorption in leather is determined by means of a dynamic test (penetrometer). It can be applied to whichever leather used for footwear uppers.

- Titanium and total chrome content: The determination is carried out by inductively coupled plasma emission spectrometry.

Table 1 shows the standards used in the tests carried out on leather:

2.3 Reduction of contamination in leather tanning

To test the environmental improvement derived from titanium-tanning, the fixation of tanning agents to the leather was evaluated by analysing the residual baths from titanium-tanning processes. In these residual baths, the following parameters were addressed: pH, conductivity, colour, QOD, BOD_5, fats and oils, chlorides and sulphates.

Table 1. Standards for physical tests on leather

TESTS ON LEATHER	STANDARD
Thickness	UNE-EN ISO 2589:2003
Tear strength	UNE-EN ISO 3377-2:2003
Tensile strength	UNE-EN ISO 3376:2003
Determination of distension and grain burst	UNE 59025:1983
Shrinkage temperature	UNE-EN ISO 3380:2003
Water resistance of flexible leather	UNE-EN ISO 5403:2003

2.4 Biodegradability of leather

One of the objectives of the TiLEATHER project is the introduction of more ecologically friendly leathers onto the European market, so it is important to test the reduction of the environmental impact of titanium-tanned leathers at the end of their lifecycle. For this the study on the biodegradability if SANOTAN leathers was set up with respect to the chrome-tanned leathers, and tests were carried out from which an estimation of the degree of biodegradability of leathers was obtained according to the tanning agent used. This allows comparisons to be made between both technologies with respect to the environmental impact of the waste they produce.

Due to a lack of methodology or specific standard for the determination of the biodegradability of tanned leathers, a method designed and optimised by INESCOP and the University Miguel Hernández of Elche (Alicante, Spain) was used. This method is based on a standard for assessing the aerobic biodegradation of polymers in the presence of municipal wastewater (ASTM D5209-92) using collagen as the reference standard substance and tannery wastewater as the inoculum for measuring biodegradability.

The tests were carried out on a prototype designed and built for this purpose in which the sample of leather dust gets in contact with the inoculum on bacterial culture, while maintaining constant agitation and temperature for a period of one month. The biodegradation of the samples is evaluated by indirect measurement of the CO_2 generated as a function of time and the degree of biodegradability is calculated based on the relationship between the theoretical maximum production and actual production of CO_2, based on the content of soluble organic carbon in each leather sample.

2.5 Suitability of leather for footwear production

To test the suitability of SANOTAN® leather for footwear production, different footwear prototypes with different material assembly methods were manufactured. The trails and tests carried out are described below:

- Visual inspection of footwear, not taking into account fashion aspects and following INESCOP's internal procedure specific for checking of finished shoes. A systematic evaluation is carried out on footwear factors which, beforehand, could affect durability, apparent comfort, physical appearance or the performance in use for the evaluated model.

- Weight determination. Weight is a factor that is directly related to energy spent when walking. Excessive weight increases energy consumption, fatigue as well as decreases comfort.

- Dimensional evaluation using an INESCOP's internal procedure specific for evaluating the fit. The adequate dimensions of the shoe are evaluated in relation to the type of shoe it is,

taking into account design characteristics and specific demands, if any. The main measurements of the shoes are compared with the limits established by each size.

- Flexibility evaluation, according to test prEN ISO 17707:2000. This property is related to force necessary to flex the shoes. A shoe that is too rigid offers an inadequate level of flexibility that can affect how the foot functions and produce an increase in muscular fatigue as well as a reduction in comfort.

- Evaluation of perspiration management. Perspiration is managed within the interior of the shoe through different ways; one part is absorbed by the components of the shoe and sock, while the other escapes the shoe through the materials. These two possibilities of evacuating humidity near the foot can be identified by the following properties:

  - Permeability and water vapour coefficient, tests according to the standard UNE-EN ISO 20344:2005 to measure the breathability of the upper (instep and lining). These properties are related to heat and humidity sensations in the foot. The lack of permeability can provoke the associated risk of fungal infections.

  - Water absorption/desorption. Test according to the standard UNE EN ISO 20344:2005, which indicates that capacity of insole and insock materials for capturing perspiration and eliminating it, thus avoiding its accumulation on the foot or its surroundings.

After checking the good appearance of the shoes, a study on comfort was carried out on one of the prototypes made with the aim of realising a functional assessment of SANOTAN leathers by means of wear trials. The tests were carried out by personnel trained by INESCOP, who also wore the footwear prototypes for a month during the working day. The subjective assessment of the comfort perception was obtained after the completion of a comfort assessment test by a panel of qualified, expert testers.

3. Results and discussion

3.1. Leather characterisation

Various SANOTAN® leathers obtained in industrial-scale tests were subjected to different quality tests according to international standards to test their applicability in footwear manufacture. Table 2 shows the leather characterisation results.

Table 2. SANOTAN® leather characterisation results.

PARAMETER	OBTAINED VALUES	RECOMMENDED VALUES ACCORDING TO STANDARDS
Thickness (mm)	2.0	>1.1
Tear strength (N)	170	>50
Tensile strength (N/mm^2)	15.8	>15
Grain burst (mm)	>10	>8
Shrinkage temperature (ºC)	85	>70
Water resistance (%) Absorption after 3 h Absorption after 6 h Penetration time (min)	 18 22 >360	 Absorption after 180 min ≤ 25%

On observing the obtained results, it can be concluded that SANOTAN® leather meet the required standards for footwear manufacture. It is to be noted that the shrinkage temperature, a critical parameter for footwear manufacture, exceeds the 75ºC obtained with other tanning formulae in which vegetable extracts and organic syntans are used.

3.2 Characterisation of SANOTAN® leather wastewater

Upon wastewater characterisation and comparison with conventional chrome-tanning wastewater, an improvement was noted thanks to the achievement of high exhaustion of product fixation during titanium tanning. Table 3 shows the results of the analyses carried out.

Table 3. Results of the characterisation of wastewater after titanium tanning

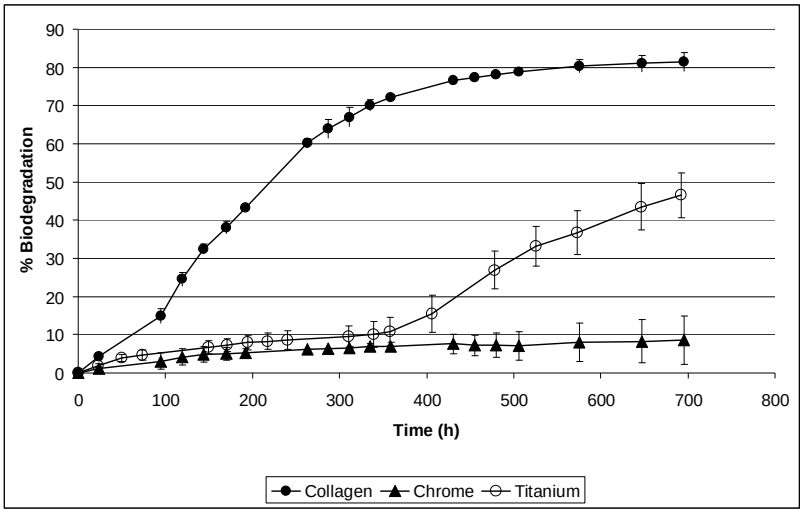
PARAMETER	NEW WASTEWATER	CONVENTIONAL WASTEWATER	SEWER SYSTEM REQUIREMENTS
pH	6.9	7.1	5.5 to 9.5
Conductivity(µs/cm)	4500	6000	2000
Colour	Imperceptible	Cloudy	Colourless
COD (mg/l O_2)	1450	1900	1500
BOD_5 (mg/l O_2)	560	700	1000
Fats and oils (mg/l)	3.5	9	10
Chlorides (mg/l)	1830	2200	2000
Sulphates (mg/l)	400	500	1000

The COD reduction is mainly due to savings in chemical products in the dyeing and fatliquoring stages.

3.3 Biodegradability test on SANOTAN® leather

In the biodegradability tests carried out, it was found (figure 2) that titanium-tanned leather showed a higher biodegradability degree than those conventionally tanned with chrome; therefore, the environmental impact of titanium-tanned leather at the end of its lifecycle is lower.

Figure 2. Biodegradation percents of titanium-tanned leather against chrome-tanned leather



3.5 SANOTAN® leather's suitability for footwear manufacture

Finally, SANOTAN® leather's suitability for footwear manufacture was verified with regard to different types of footwear. Figure 3 shows different footwear styles produced by project partners using SANOTAN® leather.

Figure 3. Some footwear styles produced with SANOTAN® leather.

Tests were carried out on nine pairs of shoes. Sizes were chosen in this way: two pairs in size 37, three pairs in size 38, and four pairs in size 39.

The length values obtained for the sizes under study were within the nominal value range. The increase in length between sizes (grading) was within the range of standard values (6.6 mm). The parameters verified in the visual inspection of the shoes, such as centring and straightness of seams, back height, toe-cap deformation resistance and absence of creases in the lining, among others, were satisfactory.

Table 4. Footwear assessment results

FEATURE	RESULT	REFERENCE VALUE
Weight [(1)] (g)	Size dependent	--
Flexibility (N)	9.5	<30
Permeability (upper+lining) [(2)] (mg/cm^2. h)	2.7	>2.0
Water vapour coefficient (upper+lining) [(2)] (mg/cm^2)	26.9	>30
Water absorption (insole+insock) (mg/cm^2)	245	>70
Water desorption (24h) (insole+insock) (%)	100	>80

[(1)] The weight of the footwear, for the different sizes, is within the usual range of values for this type of footwear. In the wear trials it was considered adequate.

[(2)] Only on SANOTAN upper leather, the permeability value reached 5.4 mg/cm^2.h and the water vapour coefficient obtained was 45.8 mg/cm^2, thus enhancing the footwear comfort.

During the wear trials (figure 4), one of the styles was assessed by a qualified tester panel made up of 6 experts: one expert wearing size 37, 2 experts wearing size 38 and 3 experts wearing size 39.

Figure 4. A member of the tester panel during a wear trial.

The main feedback gathered during controlled wear trials indicated that 100% of testers considered that the upper was soft and comfortable, and the weight and flexibility of the shoes were adequate.

4. Conclusions

The main conclusions drawn are summarised below:

- Titanium-tanned leathers pose an alternative already available on the European and international market.
- Titanium-tanned leather completely avoids the use of chrome.
- On avoiding chrome use, its possible effects on human skin, such as irritation or allergies, are also avoided.
- Water vapour permeability (breathability) of leather is high, without being excessively elastic. This feature makes the leather adapt to the foot shape without deforming, thus offering a comfortable feeling with the footwear made of such leather.
- Titanium tannage implies an environmental improvement in that:
    - Leather waste does not contain chrome.
    - Chrome contamination is avoided in tannery wastewater as well as in wastewater treatment sludge.
    - Titanium-tanned leather shows higher biodegradability than chrome-tanned leather.

5. References

[1] Anthony D. Covignton *"Modern tanning chemistry"*. Chemical Society Reviews 1997, p 111-126.

[2] De la Casa Lillo M.A., Díaz Tahoces A., Mazón Canales P., De Aza Moya P.N., Segarra Orero V., Martínez Sanchez M.A., Bertazzo M. *"Biodegradation of leather: establishment of a valuation method using aerobic microorganisms from tannery wastewater"*. XI National Congress of Materials. Zaragoza. June 2010.

6. Acknowledgements

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