INNOVA-LEATHER - INNOVATIVE TECHNOLOGIES FOR LEATHER SECTOR

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Leather industry has to cope nowadays with major environmental problems because of the polluting processes (a World Bank report has placed the leather industry in the ninth place when considering the environmental impact). Therefore, increasing the environmental efficiency in the leather sector is the major aim of leather, auxiliary materials and equipment manufacturers. The development of new tanning agents and new technologies is required to cope with the increasingly higher environmental pressure on the current tanning materials and processes such as tanning with chromium salts. This paper presents the main results obtained in the framework of INNOVA PROJECT. The original contribution of this project in solving the above problems has involved the use of solid titanium wastes (cuttings) resulting from the process of obtaining highly pure titanium (ingots) in the preparation of new tanning compounds intended to increase the environmental efficiency of the leather sector. Also, is within the above line, aiming to obtain wet-white leather by an organic tanning process in order to reduce chromium in tannery effluent. Other main objective of the project is valorization of wet white leather waste as raw material for obtaining new biodegradable auxiliaries with application in agriculture, cosmetics, industry.

Keywords: tanning agents, wet white, FOC leather, waste valorization, cosmetics, soil remediation, sustainable development

INTRODUCTION

Chrome tanning is the most common type of tanning in the world. Chrome tanned leathers are characterised by top handling quality, high hydro-thermal stability and excellent user properties. Chrome waste from leather processing poses a significant disposal problem. It occurs in three forms: liquid waste, solid tanned waste and sludge. In most countries, regulations governing chrome discharge from tanneries are stringent. Today, all tanneries must thoroughly check their waste streams. Chrome discharge into those streams is one of the components that has to be strictly controlled.

Conventional chroming process generally involves in pickling, chroming and basifying, and there are several defects existing in the process (Sykes, 1981; Germann, 1995): i) 8-10% salt and 1.0-1.2% sulfuric acid were used in pickling, which results in higher contents of chlorides, sulfates and chemical oxygen demand (COD) in the effluent; ii) The uptake of chromium in conventional chroming is lower (70-80%), a considerable amount of chromium left in the effluent may result in environmental problems (Ludvik, 1997); iii) A great deal of chrome containing solid wastes such as splittings and shavings are produced, which is certainly difficult to be degraded and harmful on the environment if discharged directly.

Much criticism has been directed towards the use of chromium salts in leather tanning, but it has to be borne in mind that chromium can occur in different oxidation states and its compounds behave differently. Most chromium(VI) compounds are highly

toxic and classified as MAK III A 2 carcinogens, but chromium(III) is an important trace element in man and animals. Chrome is mentioned in list 2 of the Annex to Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Tannery wastes containing chromium are not included in the European Hazardous Waste List on the basis that the wastes do not possess the characteristics necessary for classification as a hazardous waste (COTANCE, 2002).

The Main Objective of the project was to **develop a new "clean", eco-friendly tanning technology, alternative to chrome tanning (wet blue)** and **valorization of leather wastes** obtained through this system. This new system includes obtaining of new tanning agents **(*Knowledge/based Tanning Agents / KTA),*** of a new tanning system, and obtaining of new type of leather, so called **"wet white"**.

S&T Objectives of the project were:

(*) **synthesis the new tanning agents (*Knowledge/based Tanning Agents / KTA)**;

(*) development of **new eco-technologies** for leather pretanning/ tanning;

(*) development of new type of leather, so called **"wet white"**;

(*) development of **new conversion procedures of "wet/white" leather wastes** into **by-products with increased added value**;

(*) **transformation / functionalization of different peptides** (obtained from "wet/white" leather wastes) by coupling/reticulating chemical reactions, into raw materials for obtaining new, biodegradable auxiliary materials destined for various applications: industrial, agriculture, cosmetics etc.;

(*) development of **new biodegradable auxiliary materials**;

(*) **LCA - Life Cycle Assessment Studies** for the new developed processes.

RESULTS AND DISCUSSION

The main results obtained in the project are:

Tanning Agents KTA-M Based on Ti and Al

Exploring the valorisation of solid Titanium metallurgic end wastes, as a low cost raw material has yielded new tanning agents for the replacement of Cr(III) tanning salts, a hitherto unthinkable or non technically feasible mission. In turn, as demonstrated here it is plausible to: increase of eco-efficiency in the leather manufacturing sector by making use of solid wastes, which cannot be recycled in the industry that generated them:

i) total or partial replacement of chromium salts in the tanning process with cheap to produce and easy to apply in rapid full substance bovine leather manufacture, that, in turn required minimum process rationalisation or modification; moreover, the new mineral tanning agents are free of restricted or regulated metals Cr, Pb, Cd, Hg and Ni;

ii) increase in articles diversity (Crudu *et al.*, 2014).

Figure 1. Tanning agents KTA-M

Tanning System KTA-S Based on Resorcinol and Oxazolidine

Combinations of oxazolidines with resorcinol can replace chrome tanning without sacrificing the physical and thermal properties of the tanned leather. Finally, with the use of oxazolidine, a more effective salt-free pickling process can be achieved and the environmental impact within leather manufacturing can be further reduced.

Since there was no chromium existed in the splittings and shavings, the wastes could be treated and reused more easily (Deselnicu *et al.*, 2012).

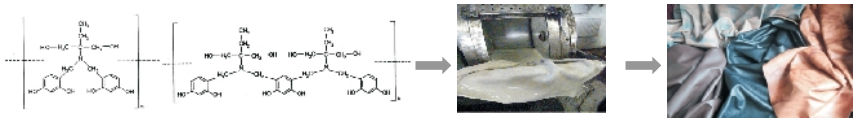

Figure 2. Tanning system KTA-S

Obtaining of New FOC (Free of Chrome) Leather Assortments: Bovine Upper Leather, Bovine Upholstery Leather, Clothing Leather

Chrome-free leather tanning system has many **demonstrable advantages**:

* no chromium in the effluents;
* solid leather wastes which can be recycled into value-added products (fertilizers and / or chemical auxiliaries used in leather industry and other industries, cosmetics);
* solid wastes (sludge resulted from purifying waste waters) without chromium;
* no risk of Cr(VI) – (causes cancer) formation from Cr (III);
* excellent shrinking behaviour;
* brilliant dyeing, especially for fashion items;
* heavy metal free leathers for allergic persons;
* improved sorting leathers for various destinations, as early as the pretaning stage;
* the possibility of storage and marketing of wet - white leathers;
* materials economy by sorting and assigning hides before tanning, to optimal sorts;
* reducing the depollution costs;
* more biodegradable leathers (Chirila *et al.*, 2014).

Valorization of Wet-White Leather Waste

Studies have been made for transferring the solid wet-white leather waste into raw materials which can be used for development of novel bio-composites (fertilizers and / or chemical auxiliaries used in leather industry and other industries, cosmetics) (Figures 3-5) (Albu *et al.*, 2014; Deselnicu, D. *et al.*, 2014; Zainescu *et al.*, 2014).

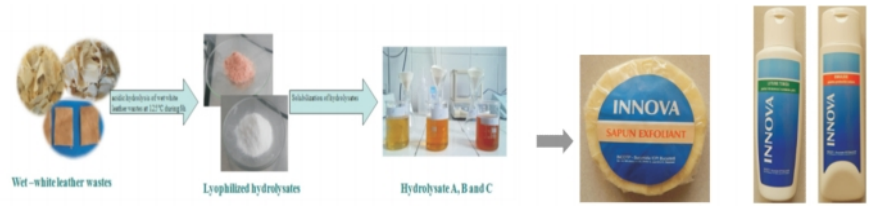

Figure 3. Obtaining of new cosmetics

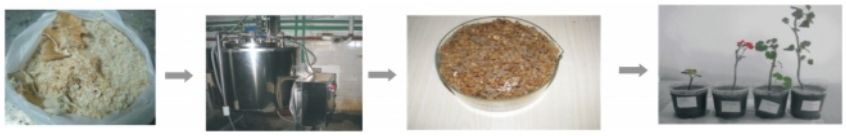

Figure 4. Obtaining the soil remediation product for agriculture

Figure 5. Obtaining Pigment paste for leather finishing and adhesive for footwear sector

LCA Study (Deselnicu, V. *et al.*, 2014)

Application of new tanning systems and transformation of the solid leather waste into **new value-added products** lead to remarkable life-cycle-improvements of the starting materials and close loops in terms of sustainable utilization of former wastes, i**ncreasing the eco-efficiency** and **economic efficiency** of leather sector. LCA comparative study between chrome tanning (Cr) and tanning leather with KTA-M system (FOC) revealed the results presented in Figures 6 and 7.

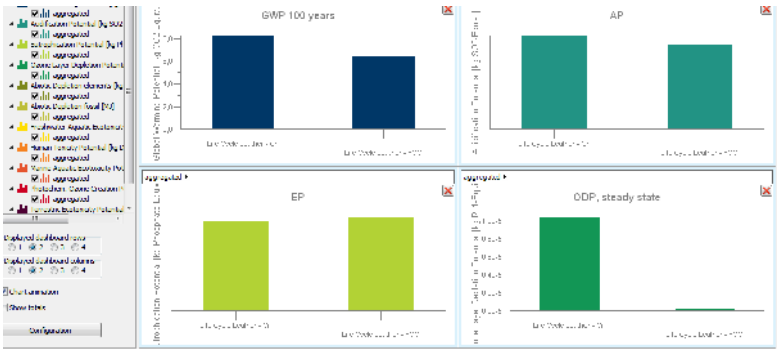

Figure 6. Global Warming Potential (GWP), Acidification Potential (AP), Eutrophication Potential (EP) and Ozone Depletion Potential (ODP)

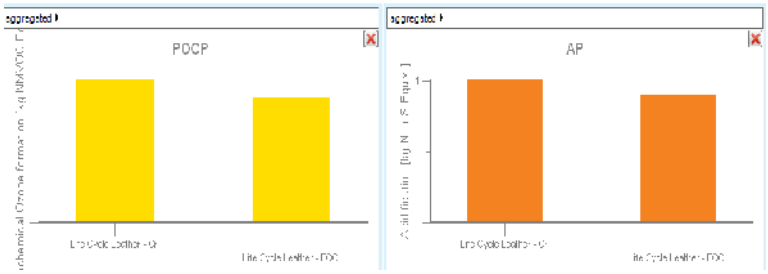

Figure 7. Photochemical Ozone Creation Potential (POCP), Acidification Potential (AP)

The Carbon footprint obtained for KTA-M -Ti-Al technology system was 9,7250 kg CO_2 equiv. and for chrome tanning system was 11,4848 kg CO_2 equiv.

The main conclusion of the study is that **the new KTA-M overall tanning technology developed in INNOVA LEATHER project generates a 15% lower environmental impact measured as Carbon footprint (Global Warming Potential indicator) than the classic Chrome tanning technology.** The other calculated impact category indicators have comparable values between the two technologies.

New Data Bases (Macovescu *et al.*, 2012)

Five new data bases were developed regarding: DB1 - *Environmental legislation database for the leather and footwear industry*, DB2 - *Clean technologies for leather manufacture*, DB3- *Specific analysis for leather*, DB4 - *Information about Romanian companies from leather- footwear sector* and DB5 - *Project results.*

Patents and Awards

The innovative solutions made the object of **5 patent applications** and were awarded with **7 Gold medals** and **3 special awards** at important international fairs.

Beneficiaries

The main beneficiaries of the project results are:

Direct Beneficiaries

1) INCDTP - Division ICPI by:

- The implementation of the project created a **scientific and technologic competence core** by **research – development** – **innovation** within INCDTP Division ICPI in the leather processing field at European standards, having as a result **the development of new products, technologies and services**, with high added value and market demand, as a basis for technological transfer in the industrial sector and production application;

2) Civil society by living in an environment less pollutant for a healthy life;

3) The leather industry in Romania (tanneries), mostly SMEs;

4) The Association of Leather and Fur Manufacturers in Romania and **The Owners Organization in the Leather Footwear Industry,** which are interested in the project realization and are directly capitalizing its results, thus contributing to the project implementation process.

Indirect Beneficiaries

1) Related industries: footwear, leather clothing confections, morocco goods, fashion;

2) The chemical industry in Romania/Europe, because, in the project, methods of sustainable use of wet white leather wastes will be elaborated, supporting thus the use of renewable resources other than oil;

3) Food industry (butcheries) from which result significant quantities of inedible wastes, which can be recovered by similar procedures, after adaptation (the elaboration of a new project is taken into account for recovering these wastes);

4) Cosmetics – by making new products with animal protein content;

5) Agricultural sector by applying the fertilizers obtained from wastes;

6) Education system - pupils, students, teaching staff, benefiting from the new information acquired by elaborating the project.

CONCLUSIONS

By application of new innovative tanning systems **significantly reduces the environmental impact** (generating solid wastes and effluents without chromium), **and people safety impact** (leather without chromium). The solid wastes without chromium can be valorized as **by-products with increased added value,** leading to favourable economic and environmental benefits by increasing their life cycle (as compared to *incineration* which is currently practiced in EU, and *disposal* which is currently practiced in Romania).

The Project's results contributes to the **development and validation of a sustainable production system** for the leather sector in Romania.

Acknowledgements

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