Production of bio-polymers from leather shavings – Reuse as retanning agents

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Abstract

Despite all tremendous efforts done until today in order to develop an organic tanning process able to meet the same standards as the chrome tanning and WB production, no universal system has still been developed with the same performance and wide spectrum of applications.
Assuming that the chrome tanning and WB production will still be in use over the next years, and bearing in mind that chrome shavings and other solid chrome containing wastes represent one of the major problems for disposal or recycling, TRUMPLER focused its efforts in order to reduce the environmental impact of this tanning procedure.
TRUMPLER is presenting an innovative process designed to reprocess and reuse shavings (from wet-blue or wet-white) in the production of a novel range of green chemicals with low carbon footprint for the retanning of leather.
Keywords: chrome shavings, green chemicals, recycling, carbon footprint.

1. Introduction

Chrome tanning still represents the main tanning system, and according to statistics chrome tanned leathers represents more than 90% of total world leather production. Solid wastes from WB (non use of splits, shavings and trimmings) represent per year around 600.000TN, chrome shavings being the major quantity with 75% of this total. [1]
Leather production will always generate solid tanned wastes but when talking about chrome containing solid wastes then the way how to manage these residuals becomes more complicated.
Until some few years ago, chrome shavings used to be starting material to be used in food industry, obtained according very old patents and processes [2]. Actually main options will be dispose in landfills or recycling in the production of leather board. Always an economical cost is involved.

Table 1 -Disposing Chrome Shavings. Approximate Costs In Spain

	Cr (III) In lixiviate	**per TN shavings**	**per 1000 sqft leather**
Cost of landfilling - As non dangerous - Class II	< 10 ppm	180 €	9,5 €
Cost of landfilling - As dangerous - Class III	<100 ppm	450 €	23,4 €
Cost of recycling per leather board		90 €	4,7 €

The total quantity of chrome shavings produced will be strongly dependent from the kind of article and the process used in the tannery. Average figures in indicate ranging from 51 Kg/per 1000sqft [3], [4], [5].

2. Proposal

It is a very old and simple idea, try to work with zero or minimum residuals and when necessary and possible try to re-use the material after recycling in the same system. With this idea and also because the main component of this chrome shavings is collagen, many works [5], [6], many proposals and also some patents [7], [8] have been printed and developed. The actual chemical process is not complicated and easily available and technologies are also well known. The only difficult point remains in finding the right equilibrium to develop an economically profitable process to produce consistent and top quality chemicals.
All the information we are printing and showing here is based actual practical experience from TRUMPLER. It corresponds to an industrial plant able to process 5 TN of chrome shavings per day and working full capacity after 2 years.
The chemical process used consists of an enzymatic digestion of the chrome shavings, followed by a subsequent filtering process in

order to separate pure-collagen hydrolyzed and chrome-containing collagen hydrolyzed. Chemicals obtained after this filtering step, could be treated and used in many different ways according the design of the processing plant.

In a tannery starting from Wet Blue leather, chrome shavings will represent the mains solid residual material and through a process as described before, it's possible to produce 31 Kg of dry and high concentrated chemicals per every 53 Kg of wet shavings.

Table 2 – Mass Balance - Production Of Retanning Chemicals

Chrome Shavings as Raw material			
SPANISH BOVINE WB (18-20sqft per side)	2,0-2,2 mm	4,5	Kg
SHAVING WB TO	1,4-1,6 mm	3,5	Kg
PRODUCE SHAVINGS - per side		1,0	Kg
PRODUCE SHAVINGS - on WB weight		22	%
PRODUCE SHAVINGS - on shaved WB weight		29	%
PRODUCE SHAVINGS per 1000 sqft		53	Kg
Obtained retanning chemicals on dry weight			
Dry Chrome-Protein derivatives - per 1000 sqft		11	Kg
Dry Protein hydrolyzed- per 1000 sqft		21	Kg
TOTAL Dry Retann. Agent - per 1000 sqft		31	Kg
TOTAL Dry Retann. Agent - per Kg Shaved WB		17	%

(These values could change significantly depending on the article and process)

This quantity of chemicals will represent an average of 17% of retanning agents when trying to re-use in the same tannery and that looks really too high a ratio to be realistic. Then it will be necessary to find strategies to use these chemicals in other ways, that could be selling to other tanneries, could be using hydrolyzed collagen in the fertilizer industry, or could be producing other derivatives to be used as tensides and fatliquors.

3. About Obtained Chemicals – Properties

The use of protein chemical derivatives, both for cosmetics, textile and leather applications, is really old. First chemicals and patent applications talking about recovering protein from chrome shavings and trimmings are as old as from before 2nd world war [9]. It is also important to point that some very well known and very traditional retanning agents are based on proteins from many different origins. But this different origin and treatment will also mean very different properties when applied to the leather, reactivity, fixation and stability will be really different.

All chemicals obtained by this procedure will be collagen derivatives, and most of them will show an amphoteric behavior, coupled with a characteristic isoelectric point as also shows leather. These properties confer to this chemicals strong reactivity with leather, independent of whether chrome or vegetable tanned.

All chemicals obtained by this procedure will be bio-polymers, coming from a controlled hydrolysis of the starting collagen. The final molecular weight of the obtained bio-polymer will also be critical, and choosing it correctly will impart very different properties in the leather application.

All chemicals obtained by this procedure will show many benefits from the environmental and ecotoxicological point of view. Will be formaldehyde free, will show excellent biodegradability and will show excellent bio-compatibility with human skin and mucosa. [10], [11].

Table 3 – Percentage Of Biodegradation

Closed bottle test 28 days – OCDE 301	
Standard Sodium Polyacrylate (pH 7)	46%
Bio-polymer based in collagen hydrolyzed	100%

The chemicals obtained from such a process could be used alone and directly in the leather manufacture, however it is better to modify them to certain degree in order to improve their properties and facilitate improved control of their reactivity towards the leather.

Hydrolyzed collagen can be modified and reacted in many different ways and depending from these reactions and from the starting MW, it is possible to produce retanning agents, wetting agents or fatliquors for leather.

4. Economical Evaluation

In this economical evaluation we will take into consideration the next hypothesis:
1.Tannery producing 70.000 sqft per day
2.Cost of disposing chrome shavings as non dangerous waste Class II – 180€/TN
3.Average cost of retanning agents used in the tannery: 1,50 €/Kg
4.New retanning agents obtained from Chrome Shavings: 1,00 €/Kg
Investment: Industrial plant able to process from 4TN to 5TN per day will need investment of around 1.000.000€
Workers: 3 workers in 2 shifts will be able to manage the production plant.

Table 4 - Economical Evaluation

Tannery with production per day of Starting from Spanish WB	***70.000***	***Sqft***	
FROM WB	2,0-2,2 mm	4,5 Kg	per side
SHAVING WB TO	1,4-1,6 mm	3,5 Kg	per side
PRODUCE SHAVINGS		1,0 Kg	per side
PRODUCE SHAVINGS per 1000 sqft		53	Kg
WB supply at 2,0-2,2 mm		16.579	Kg per day
SHAVED WB at 1,4-1,6 mm		12.895	Kg per day
PRODUCE SHAVINGS PER DAY		***3.684***	***Kg per day***
COST OF DISPOSAL PER DAY		663	€ per day
COST OF DISPOSAL PER YEAR	220	145.895	€ per year
CONSUME OF RETANNING AGENTS on WB	***12%***	***1.547***	***Kg per day***
COST OF RETANNING AGENTS per Kg	1,50 €	2.321	€ per day
COST OF RETANNING AGENTS per YEAR	220	510.632	€ per year
TOTAL Dry Retanning Agent Production		2.172	Kg per day
SURPLUS of production in Retanning agents		624	Kg per day
PRODUCTION COST RETANNING AGENT per	***1,00 €***	***1.105***	***€ per day***
SAVING IN CHEMICALS	0,50 €	774	€ per day
SAVING IN CHEMICALS PER YEAR	220	170.211	€ per year
TOTAL SAVINGS - CHEMICALS + DISPOSALS		***316.105***	***€ per year***

5. Carbon Footprint of bio-polymers from chrome shavings

Ten warmer years on records have all occurred since 1998 [12]. These data are related with the global warming of the earth. Warming of the climate system is unequivocal, and scientists are more than 90% certain that it is primarily caused by increasing concentrations of greenhouse gases produced by human activities such as the burning of fossil fuels, deforestation, gas flaring and cement production [13]. A particular attention is paid on CO2 being the countries with high levels of economic development the main responsible of these emissions.
To measure and quantify the greenhouse gases emissions, a new concept has been created: The carbon footprint (CF). There is no consensus on how to measure or quantify the CF, but one of the most general definitions is the next: the CF is a measure of the exclusive

total amount of carbon dioxide emissions that is directly and indirectly caused by an activity or is accumulated over the life stages of a product [14].
A simple and clear way to express the carbon footprint on finished leather is kg CO2 / m2 [12].

In order to reinforce the image of the leather goods and articles as natural and environmentally friendly, should be necessary to demonstrate that leather articles are linked with low values of product carbon footprint (PCF). According many papers [15], [16], chemicals used in the production and manufacture of leathers are the major responsible for the total PCF values on leather articles.

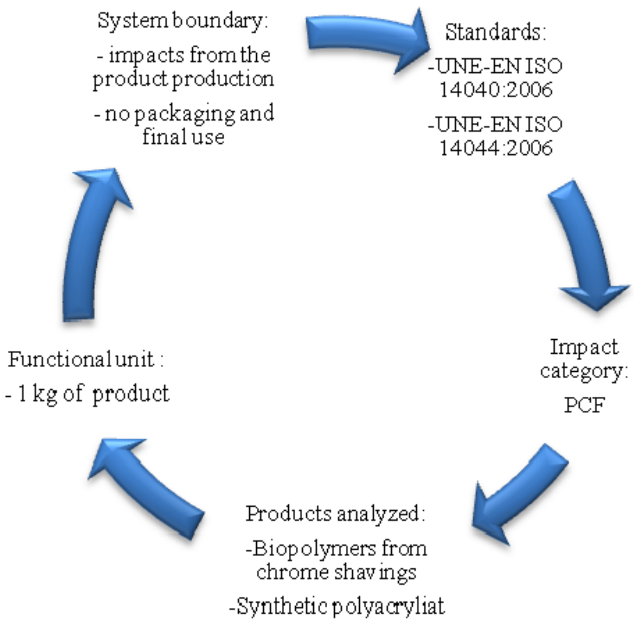
But when trying to calculate accurate PCF leather values, one major problem will be to get real (PCF) of all leather chemicals used in the leather production. Actually the chemical industry is starting to calculate and supply this information, but getting real and accurate figures will take still some time.

What is really clear is that leather chemicals can show really different PCF values depending on its nature, its production process and its final application process into the leather. That's why a correct selection of leather chemicals will allow the tanneries to produce leather articles with lower PCF.

The calculating of PCF has been conducted by using Life Cycle Assessment ISO 14040:2006, with some specifications of PAS 2050:2011. We don't take in consideration products used less than 1 % in the process and complementary information is obtained from the international database Ecoinvent.

Under this philosophy, Trumpler is presenting here a comparative study consisting on the calculation of PCF between the new range of retanning bio-polymers obtained from chrome shavings and a standard family of retanning agents, synthetic polymers.
To develop a life cycle assessment of a product should be determined a framework and methodology. The figure below shows the variables to be considered in life cycle of the products under study.

Figure 1. Concepts of Lyfe Cycle Assessment of a product



The figure below shows the inputs and outputs coming from the production operations. The impacts from the production operations of factory will vary depending on the inputs and outputs you have throughout the process. The phases of packaging, distribution, use and end of life have not been considered in this study.

Figure 2. General Inputs And Outputs Of The Production Operations

INPUT:

- POWER CONSUMPTION of equipment involved in the process (electricity and natural gas)
- Consumption of RAW MATERIAL and auxiliary materials. It has taken into account the impact that lead associated with its acquisition.
- WATER CONSUMPTION. From the general network in the processes of biopolymers, and softening treatment in the case of synthetic products.

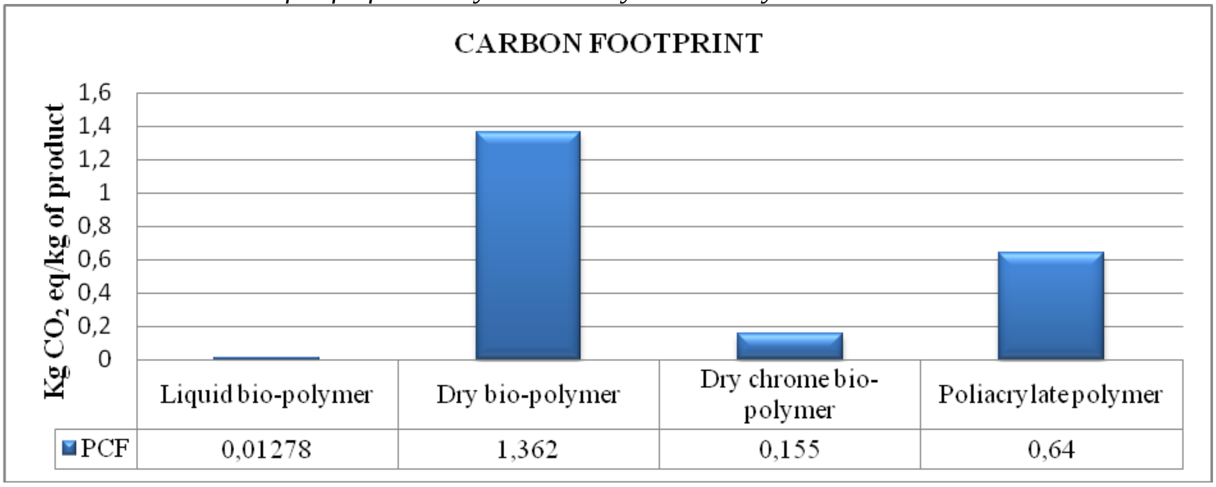
OUTPUT:

- AIR EMISSIONS: emission of steam.
- WATER: discharges do not occur since recirculated water or emitted as water vapor.
- SOLID WASTE: no solid waste in the processes studied

The result of the study shows that chemical synthesis process will not differ a lot between this two families and in any case a final drying step will be a major energy consumer and consequently PCF increaser. The main difference between synthetic polymers and bio-polymers is the starting raw material PCF.

The starting raw material of bio-polymers are the chrome shavings a waste that doesn't affect the PCF and in the case of synthetic polymers the raw material is the Acrylic Acid (actually it's PCF is under recalculation by major producers) that comes from the petrochemical industry.

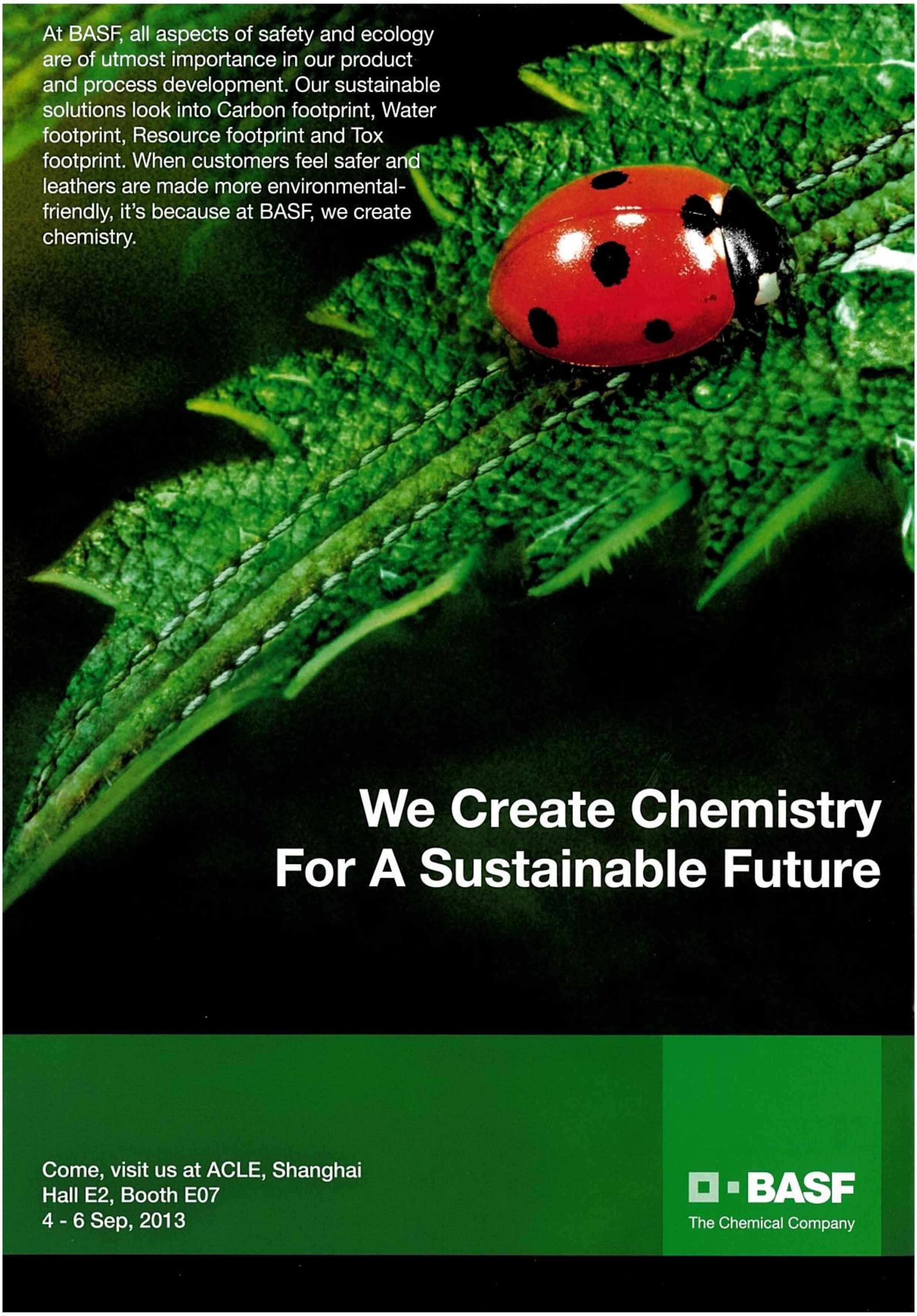
Table 5. Final Values Of Pcf Of Bio-Polymers And Synthetic Polymers



The liquid biopolymer product has the lowest carbon footprint impact (0.012 KgCO2/Kg) and liquid retanning polyacrylates show PCF values around 50 times higher (0.64-0.67 KgCO2/Kg) due the impact of raw material. The drying process is having a dramatic cost, in economical aspect and also in the PCF aspect (gas-energy). Could be seen how the drying process is increasing PCF from 0,012 KgCO2/Kg to 1,35 Kg CO2/Kg.
This PCF study shows that in terms of environmental impact the liquid biopolymers will always be a better alternative to the liquid synthetic polymers to be used as retanning agents that allows obtaining finished leather with low PCF.

6. Conclusions

The chrome tanning process and wet blue production is and will probably be the major one tanning process in use worldwide. Trumpler has done a great effort to develop an innovative technological process useful to reprocess and reuse chrome shavings in the production of leather chemicals.
As is well known, protein chemical derivatives are widely used as retanning agent. This new technology allows production of collagen hydrolyzed with a selected molecular weight suitable for the production of better performing leather chemicals. These chemicals also show excellent environmental and ecotoxicological performance (improved biodegradability, biocompatibility and formaldehyde free).
From the tannery point of view, this new technology should allow to fully eliminate chrome shavings, until now the major solid waste in the leather processing. And that will represent easier environmental management coupled with a direct economical cost saving. These savings come both, from no more chrome shavings disposal and from using new leather chemicals at more competitive prices.
Trumpler has been testing and demonstrating this technology during 2 years in a real production plant able to process 5 TN of chrome shavings per day and obtaining the corresponding chemicals for the retanning and fatliquoring of leather. These chemicals have been sold and used worldwide in many different leather applications.
Through the treatment of chrome shavings Trumpler is producing bio-polymers with a low PCF impact compared with other retanning agents obtained from a non renewable raw material. This is a an important aspect to take in consideration for the tanneries that in the future will need to produce finished leather with low PCF to meet market needs.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