ECO-INNOVATIVE PRODUCTS AND TECHNOLOGIES BASED ON THE RECYCLING OF CERTAIN WASTES FROM TANNERIES AND NON-FERROUS METALS INDUSTRY FOR THE TRANSITION OF THE LEATHER INDUSTRY TO A CIRCULAR ECONOMY MODEL

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This paper presents experiments of recovery/recycling/reuse of as much tannery waste as possible to obtain new auxiliary materials with high added value and low eco-aggressiveness intended for leather processing. The paper also deals with conversion of waste difficult to manage (some of which is unrecyclable) from the non-ferrous metal industry into factors for increasing the eco-efficiency of the leather industry.

Keywords: Waste recovery-recycling-reuse, leather industry, non-ferrous metallurgy, circular economy

INTRODUCTION

Circular economy is one of the topical themes of the European environment policy, in the context of the increasing resource demand and the pressure it exerts on the environment (www, 2014).

The focus is on the transition from the linear economic model in which each product has a limited lifetime, to the circular economy, whose goal is to keep the added value in products for as long as possible and reduce waste to zero.

This concept of the modern world means shifting towards an economy based on reducing energy and raw materials, where the waste resulting from the multitude of activities has precise destinations from the design phase, through its integration in the cyclic spiral of reuse. In other words, waste occurring in a manufacturing process can constitute a raw material for other processes or even for the same technological process which produced it.

It is known that leather processing industry is currently facing serious environmental problems related to high consumption of water, use of chemicals with negative impact on people and the environment and, last but not least, due to the generation of large quantities of solid and liquid waste difficult to manage.

This paper presents experiments of using protein waste from the leather industry and metal waste from the titanium metallurgic industry to obtain new eco-friendly auxiliaries for the leather industry.

The processes of waste recycling and recovery do not follow the usual course for the other types of waste that can be reused as raw material (such as metal, glass, textiles, etc.) due to association of hide protein with a variety of other chemical species, some of which are eco-aggressive, which imposes additional costs of separation and co-recovery and also neutralization of aggressive effects.

This is why we need to establish technologies for extraction of collagen protein - the basic component of hides - in the form of short or solubilized fibers, aiming to achieve as high an yield and recovery (conversion) as possible (Paul *et al.*, 2013).

In this regard, we studied the recovery and superior exploitation of titanium waste resulting from the technological process of obtaining extra pure titanium (Crudu *et al.*, 2009a; Crudu, 2008; Crudu *et al.*, 2009b; Crudu *et al.*, 2008; Crudu *et al.*, 2013; Buzatu and Moldovan, 1994) and considered unrecyclable in the industry that produced it due to the high level of impurities.

MATERIALS AND EQUIPMENT

Raw materials and auxiliaries: solid titanium waste (filings-SC ZIROM SA Giurgiu Romania), limed and delimed bovine hide waste (trimmings-pilot-scale tannery INCDTP-ICPI Bucharest, Romania), technical auxiliaries used in leather processing, wet salted bovine hides, 20-25 kg (Constanta County, Romania), organic wet-white (Czech Republic), wet-blue (Romania, Netherlands).

Equipment: reaction vessel with stirring and temperature adjustment system (Caloris, Bucharest, Romania), experimental drum (DOSE MAT-Germany), device for shrinkage temperature determination (GIULIANI Italy), device for thermogravimetric analyses STA 449F1 Jupiter (Netzsch-Germany), DSC analyser 200F3 Maia (Netzsch-Germany), scanning electron microscope (SEM) equipped with Qanta 200 (FEI Netherlands) energy dispersive X-ray analysis system (EDAX) for qualitative, quantitative and elemental mapping.

EXPERIMENTS

Figure 1 shows the experimental model for obtaining the new innovative low eco-toxicity materials based on leather and titanium waste, intended for leather processing.

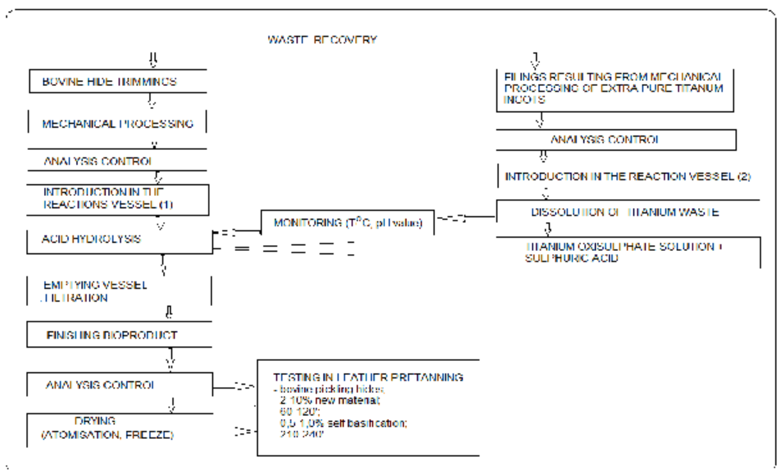

Figure 1. The experimental model for obtaining the new low eco-toxicity products

RESULTS AND DISCUSSIONS

The biomaterials obtained from leather waste and titanium waste were characterized and the results are presented below.

Table 1 presents the physical-chemical characteristics of new biomaterials.

Table 1. Physical-chemical characteristics of new biomaterials

No.	Characteristics	Determined values
1.	Dry substance, (%)	18-22
2.	Ash, (%)	3-5
3.	Total Nitrogen, (%)	7-8
4.	Protein substance, (%)	35-50
5.	Metal oxide, (%)	2.5-5.0
6.	pH, (unit. pH)	1.6-2.2

Table 2 presents values of shrinkage temperatures, reflecting hydrothermal resistance and therefore pretanning degree.

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No.	% Material amount	Shrinkage temperature °C
1.	1-2	65-68
2.	3-5	70-75
3.	6-10	78-85

Table 3 presents the physical-chemical characteristics of wet-white pretanning using the new biomaterial in comparison with wet-blue and other wet-white (polyaldehydes).

Table 3. Physical-chemical characteristics of wet-white pretanning using the new biomaterial in comparison with wet-blue and other wet-white (polyaldehydes)

No.	Characteristics	Determined values		
		Our Wet-white	Wet-blue	Wet-white (polyaldehydes)
1.	Dry substance, %	60-80	60-80	60-80
2.	Ash, %	2-8	9-12	0-1
3.	Total nitrogen, %	12-17	12-14	14-18
4.	Protein substance, %	82-91	75-85	85-93
5.	Metal oxides, %	4-6	5-8	-
6.	pH	3.5-3.7	3.7-3.9	4.2-4.6
7.	Shrinkage temperature, ^{o}C	70	98	68

Table 4 presents elementary composition of the our wet-white, wet-blue and wet-white (polyaldehydes) by EDAX.

Table 4. EDAX elementary composition of the our wet-white, wet-blue and wet-white (polyaldehydes)

No.	Element	Determined values		
		Our Wet-white, %	Wet-blue, %	Wet-white (polyaldehydes), %
1.	**C**	45.85	51.08	64.90
2.	**N**	11.12	12.26	9.71
3.	**O**	26.24	26.12	20.29
4.	**Na**	2.98	1.40	2.04
5.	**Mg**	1.29	0.27	0.07
6.	**Al**	0.21	0.06	0.08
7.	**Si**	0.00	0.10	0.11
8.	**S**	2.71	2.64	1.65
9.	**Cl**	4.51	2.11	1.61
10.	**Ca**	0.20	0.33	0.25
11.	**Ti**	4.89	0.07	0.00
12.	**Cr**	0.00	3.57	0.00

CONCLUSIONS

Romania is known to have a waste recycling degree of 3%, while the European Union recycles on average 36%, but even so, there is the potential for approximately 600 million tons of waste recovery at Community level.

This paper attempted to propose new relevant solutions in the direction of recovery-reuse-recycling of industrial waste generated by the leather industry and other industries.

As a result of experiments, the following conclusions can be drawn:

- Using simple methods of processing untanned hide waste and unrecyclable titanium cuttings, new relatively low-cost but high added-value pre/tanning agents may be obtained;
- Their use in total or partial replacement of chromium in the leather tanning operation induces a series of technical, economic, social advantages, as well as major implications in environmental protection, due to recovery and reuse of waste difficult to manage and to the reduction of the negative impact on the environment of the leather processing industry, as tanning effluents and waste from mechanical operations no longer contain chromium compounds and large amounts of salts;
- The new semi-processed wet-white leather obtained by pretanning using the proposed materials are comparable to those obtained at international scale, allowing further mechanical and physical-chemical processing without any problems, even providing a superior technological versatility due to structural stability and light color (almost white);
- Compared to wet-blue, the new wet-white leathers, even with a lower hydrothermal stability, have the advantage of a lower content of metal oxide and ash, but a higher content of protein substance, while the color is also an advantage, not to mention the lack of chromium compounds;
- The use of the new tanning agents in leather pre/tanning does not involve changes in logistics or technology;

- The encouraging results will prompt further research in streamlining technologies for developing and using the new products from the waste used in this paper, as well as from other waste from leather processing and from other industries.

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