Paper D11

Eco-friendly tanning agents for use in leather manufacture

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1. Introduction

Hitherto, the mineral tanning agents most frequently used throughout the world are salts of chromium (III) (ca. 85% of total world finished leather output), which remain unsurpassed in the qualities offered to leather; these, in turn, include high hydrothermal, thermal and light stability and versatility with regard to the variety of leather articles, which can be made from the intermediate, chromium(III)-tanned leather, «wet-blue» [1]. In general, chromium (III) tanning agents uptake under typical technological conditions is of the order of 60 - 80 % of the offered quantities (typical offer: 80-90 kg Cr-tanning salts/t of pelt weight), with 3-7 kg $Cr^{3+/}$t of raw hides /skins (2-7g Cr(III)/Lt of exhaust tanning liquor) discharged with the process effluent. Even though there is no legislation or norm that requires that chromium (III) should be absent from leathers, maximum allowable concentrations have been stipulated for the total chromium or chromium (III) content in leather digests or extracts, whereas an even stricter concurrent legislative requirement has been imposed for chromium (VI) absence (non detectable) in most finished leathers. In particular, Chromium (VI) and its salts are classified as known carcinogens not used for tanning and normally absent from chromium (III) tanning salts. However, apart from its potential presence in pigments, colouring additives and fixatives, commercial chromium tanned leathers can be tested positive for the presence of chromium (VI) in quantities exceeding the stipulated legal or normative limits. De-facto chromium (VI) does not exist in finished chrome-tanned leather, and apart from the frequently never told truth of test method inefficacy or non-appropriateness, intelligent tentative interpretations of the observed chromium (VI) formation agree that can be the product of oxidative conversion of chromium (III) under specific leather manufacturing or storage conditions e.g. high leather pH or use of specific fatliquoring agents. Along the same lines, several eco-certification schemes stipulate limits in Cr(III) content: (i) in aqueous extracts of leathers and leathers products with water, artificial sweat or in some cases in their digest and (ii) in the effluent after depuration (0,2-3 ppm) that are impossible to match, if leathers continue to be tanned or/and retanned with Chromium (III) tanning agents.

These practical and operational constraints have stimulated research efforts to find an alternative to chromium (III) tanning [2] for the production of **F**ree-**O**f-**C**hrome (FOC) and in some cases also Metal-Free leathers, whilst retaining the often expected by the consumer mineral character in leather articles, with some profound examples of succeeding in replacing fully chrome-tanning lines in Industrial upper leather production [3]. Accordingly, Al (III) [4,5], Zr (III), Ti (III & IV) [6], Fe –salts [7,8], their mixed salts [9], and most recently nano-silicates [10] and sodium waterglass [11] were tested as effective partial or total replacement mineral tanning agents for the production of a reversibly or irreversibly – most recently - tanned new intermediate semi-processed product and commodity: “wet-white” or “wet-stabilised” leather. Overall metal ion complexes have some affinity for protein, however, the mechanism of their binding to collagen – if taking place – is far from being resolved with several hypotheses and models often postulated and used, but seldom proven for this purpose. Moreover, when applying the criteria of adequate reactivity, colour, availability, cost and toxicity, and most recently LCIA, nearly all of the commercially available agents were rendered redundant as viable options. A good example is Aluminum salts that have long been associated with stabilising animal origin pelts and have the advantage of being abundant and cheap. However, Aluminum is only loosely bound and fixed to collagen, so that the reaction is readily reversed, when the leather is wetted and found in acidic environments; for this reason, this process is regarded as a pseudo-tannage and called tawing, rather than tanning. However, as shown by one of the co-authors in earlier studies [12] the effectiveness of a tanning molecule depends on its ability to provide high molecular weight cross-linked moieties within the collagen molecule and was possible to propose reactive Aluminum tanning agents preparations that match this requirement [13], which, on the other hand, were never taken up by the Industry, due to emerging renewed eco-toxicity considerations, but primarily as a result of the undoubtedly superior versatility, cost effectiveness and reliability of Cr(III)-tanning systems.

Within this framework of industrial needs high levels of excess Cr(III)-tanning products remain a potential threat and hazard to the environment or contribute significantly to the amount of recalcitrant pollutants. Consequently, there is mounting pressure on tanners to reduce levels of Cr(III)- tanning agents employed during leather manufacture and their discharge with the outflow of tannery ETPs.

Along these lines, new Ti (III)-based, Cr(III)-free, precursor tanning agents have been produced from metallurgic Industry end waste, aiming at the development of new tailored sustainable wet-white tanning chemistry that enables for the first time the in-situ generation of reactive Ti(IV)-tanning species, as a viable alternative to Cr(III), vegetable and syntan (pre)tanning agents. Hence, the principal axes of our synthetic approach, from product design phase to its industrial eventual application, have been: recovery and recycling of waste metals, simplicity and cost-effectiveness of the new tanning agent application, as well as closed loop processing, in order to protect the environment and improve the quality of life. Major challenges to match in our efforts remain commercial viability and consumer acceptability of the finished leather article.

The new tanning agents, in fact, will act as a prelude towards new eco-friendly leather manufacture, in which no potentially toxic, noxious and harmful chemicals have been used and discharged – currently and according to the Environmental Reports of the Tanning Sector 30-40 % of chemicals used during leather manufacture are characterised as potentially toxic or hazardous.

2. Materials and methods

Raw and auxiliary materials: Solid Titanium waste (filings); aluminum sulphate, (SR EN 878/2004); sodium citrate (STF 116/2000); sodium tartrate (STF 34/199); ammonium sulfate (STAS 450-1975) Magnesium oxide (STAS 4995-1980); sulphuric acid (95-97% -STAS 97-1980)

Bovine Pelts: For all tanning trials bovine pickled pelts of Romanian origin, with mean weights ranging from 20-25 kgs were used (pH ca. 3.0)

Ti –based agents synthesis: For the solubilisation of Titanium waste and in order to obtain tanning compounds was used a glass reaction vessel equipped with a VELP SCIENTIFIC mechanical stirrer. In-house design laboratory equipment with vacuum ILMVAC type was used for the filtration of Titanium solution resulted by dissolving wastes. The pH of the tanning bath was determined using a calibrated for this purpose WTW- INOLAB pH LEVEL 2 -digital pH-meter.

Metal content in Ti-end waste: Metals' content was determined using plasma emission spectroscopy device (ICP-SPECTRO) and an in-house protocol for this purpose.

Hydrothermal stability measurements of prototype leathers: Wet-white and control prototype leathers thermal analysis was carried out using (i) a Differential scanning calorimeter (204 F1 PHONIX-NETZSCH. To determine the curves of heat of enthalpy change as a function of the temperature a Perkin-Elmer DSC 7 calorimeter was used. Each sample was weighed (3-6 mg) and placed in an

Aluminum crucible. Thermal effects were measured against a similar empty crucible in the calorimeter at room temperature while nitrogen was purged, and heated in the temperature range 50-260^{o}C. On the other hand, shrinkage temperature measurements were recorded within the range 22-to-100°C at a heating rate of 2°C/min using the micro-hot-table technique with a CALORIS Micro Hot Table coupled with a LEICA Stereomicroscope. Finally, standard shrinkage temperature measurements were undertaken using a standard GIULANNI apparatus according to SR EN ISO 5397:1996.

Tanning Trials: Leather tanning trials were undertaken using pickled bovine pelts and a DOSEMAT laboratory-micro pilot DOSE MAT inox-drum. The tanning brine bath length varied from 200-400% on pickled weight and the initial float pH=3.1-to-3.2, before the administration of the tanning salts. The temperature of the tanning bath varied was ca. 25°C and the drum rotational speed was 15 rpm. At this point the Ti-Al tanning agent was added with offers ranging from 2-5% w/pickled weight. The pH measured five minutes after the addition of the tanning agents was reduced pH=2.2-2.3. The tanning bath had a characteristic purple colour and the section of the pelt was fully penetrated («through») after 10-25 min (visual control). Basification was initiated using commercial MgO products for this purpose (2-3% w/pickled weight offer). After 30-60 minutes - with an optional heat induction (heating of float from 25-to-35°C) – a cationic fatliquor was added (2-3% w/pickled weight offer) and the drum run to reaction completion over a period of 1-to-6 hours with the tanning bath fully de-coloured – end pH=3.4-3.7. Prototype wet white shrinkage temperatures ranged from 73-to-78°C.

Scanning Electron Microscopic Energy Dispersive Analytical Survey (SEM-EDAX): The examination of prototype leather samples tanned with the newly proposed tanning agents was performed with a scanning electronic microscope type TESLA. High resolution images of surface topography, with excellent depth of field are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 – 30 kV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm). High sensitivity to topographic features on the outermost surface (< 5 nm) is achieved when using a primary electron beam with an energy of < 1 kV. In addition to low energy secondary electrons, backscattered electrons and X-rays are generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information was obtained. The analysis of characteristic X-rays emitted from the sample gives more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 cubic micron. SEM, coupled with energy dispersive X-ray analysis, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis.

3. Results and Discussion

3.1 Synthesis of new mixed Ti-Al tanning agents from metallurgic end waste

Basic metal composition of the Titanium wastes (filings) used as raw materials for the production of the new Ti(III) tanning agents is given in Table 1.

Table 1: Heavy Metal composition of the Titanium wastes

Metal	Ti	Al	V	Fe
%	89 - 95	1- 6	0.1- 4	0.0001-0.0005

The Aluminum salt used was $Al_2(SO_4)_3 \cdot 18\ H_2O$ (15.3% Al_2O_3, 8.55% Al)

The schematic outline of the synthetic pathway designed and applied for the generation of the mixed new tanning agents based on Titanium and Aluminum is shown in Figure 1[14-17].

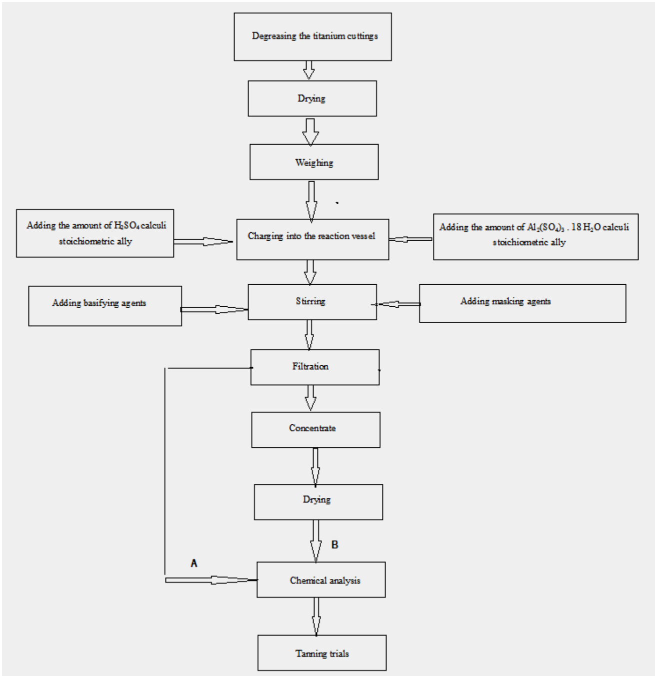


Figure 1. Chemical synthesis pathway for obtaining the new tanning agents based on Ti and Al

The results of chemical analysis carried for the novel tanning agents' solution are reported in Table 2.

Table 2: Chemical analysis of tanning agent solution

Parameter	
Density (g/cm^3)	1.25 – 1.45
pH	1.8 – 2.3
Total ash (g/dm^{-3})	75 – 140
Total metal oxides content (g/dm^{-3})	65-130

On the other hand, analyses carried out on dry Titanium-Aluminum tanning agent powders have given the results shown in Table 3.

Table 3: New Titanium-Aluminum tanning agents (powder form) metal content and pH

Parameter	
Total metal oxides, %	15 – 20
pH (1:10)	1.8 – 2.3

Moreover, ICP-MS analysis (plasma emission spectroscopy, ICP-type SPECTRO) of one of the newly prepared tanning agents based on Ti-Al was carried out and the following results were obtained (Table 4).

Table 4: New Titanium-Aluminum tanning agents (powder form) metal contents (ICP-AES)

Element	
Ti-Al (%)	99.6
V (%)	0.13
Mg (%)	0.33
Fe (%)	0.03
Zr (%)	0.23

Most significant is the absence of Cr, Cd, Pb, Hg, Ni and As – non detectable.

3.2 New Wet-White leathers characterisation and evaluation

Full thickness semi-processed tanned leathers resulting from application of the new Titanium-Aluminum tanning agents as described here is white, with a smooth grain full and supple, as shown with the photographic image in Figure 2.

Figure 2.Wet-white leathers tanned with the new agent

Shrinkage temperature values determined for the different new tanning agent variants ranged from 68-82^{0}C, whereas wet white leathers were successfully processed through the subsequent mechanical operations of splitting – easily grain, middle and bottom split were obtained, as well as shaving, as demonstrated with the photographic image of Figure 3.

Figure 3 Wet-white split and shaved

Good hydrothermal stability of the prototype leathers was confirmed with measurements undertaken using the Micro-Hot table device, with Ts=70-80^{o}C, as shown in Figure 4.

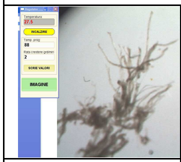
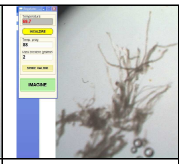
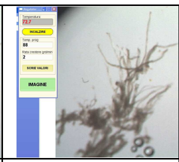
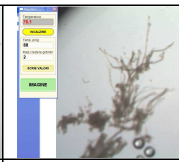
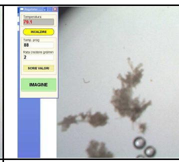
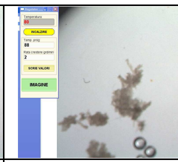
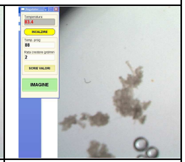
T_{in}	A1	B1	C	B2	A2	T_{fin}
°C						
						
27.5	69.7	72.7	**76.1**	79.1	80.0	83.4

Figure 4. Determination of shrinkage temperature by MHT method

Another confirmation of the thermal behavior of the new semi-wet type of leather tanned with white pre-tanning agents was obtained by using DSC analysis (differential scanning calorimetric dynamic analysis). A typical example of the thermographs recorded for samples taken from the prototype wet-white leathers tanned with the new Ti-Al based tanning agents is shown in Figure 5.

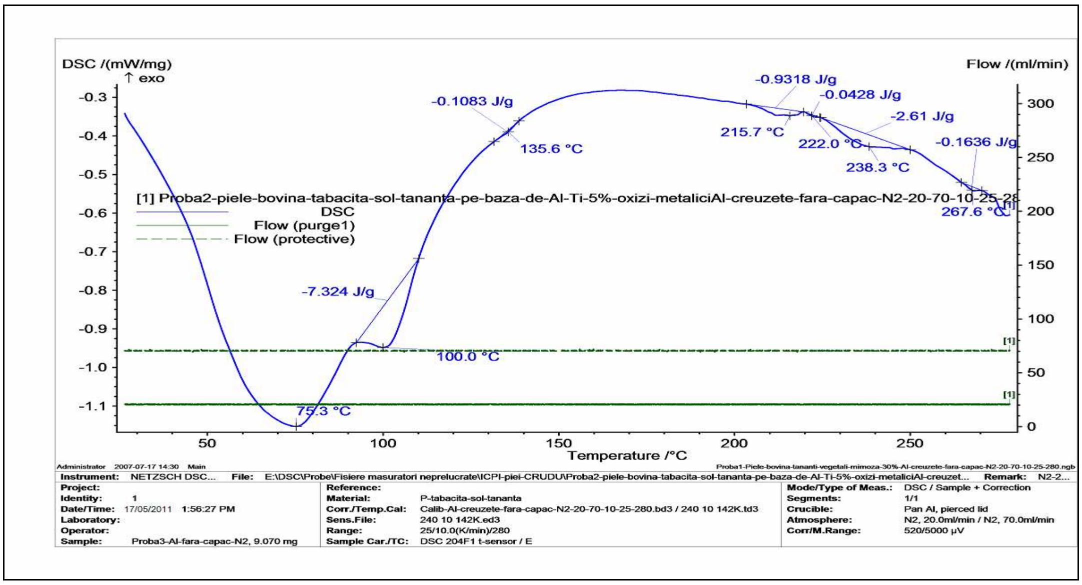


Figure 5.DSC-thermograph obtained for wet-white tanned with the new Ti-Al tanning agents

The endothermic transitions recorded for the new wet white leathers consists of at least three (3) peaks, indicative of consecutive denaturation processes. The first transition is recorded for temperatures within the range 50^{o}C and 125^{o}C. A second set of peaks is registered for temperature values between 130° and 250°C, strongly linked to the processing history of the material (in particular the degree of tanning); the denaturation process occurring can be tentatively explained by the crystalline-amorphous two-phase model of collagenic materials. According to this model the super-coiled triple-α helix is partially crystalline and embedded in an amorphous matrix. Consequently, the minimum of endotherm II is associated with uncoiling / melting of the crystalline region. In turn, the tanning process by inducing the formation of synthetic crosslinks, can result in increased stiffness of the matrix, and, thus, is responsible for the observed shift of the melting process to higher temperature values. Monitoring the temperatures at which process II occurs may, therefore, reveals the degree and effectiveness of tanning, whereαs for leathers tanned with Cr(III) –salts the second peak is not visible as it overlaps with the pyrolytic transition. Hence, DSC thermographs, as those recorded for wet-white prototype leathers and shown in Figure 5 are specific to each material and can be used as material –specific and unique «fingerprints» [18].

In order to characterize the new wet-white leather and prove the tanning potential of tanning potential of the newly synthesised compounds, chemical analyses has been carried out both on the split and grain layers of the product leathers and the results obtained are shown in Table 5.

Table 5: Wet-white grain and split leather chemical analyses

No.	Parameter	Layer	
		Grain	Split
1.	Volatile matters (%)	53.1	51.2
2.	Extractible (%)	1.58	2.35
3.	Ash (%)	10.4	10.9
4.	Metal Oxides (%)	8.2	8.3
5.	Shrinkage temperature (^oC)	77	75
6.	Shrinkage temperature (^oC -MHT)	76.1	73.9
7.	pH extract	3.98	4.0

Similar analytical values obtained for both layers tested have led to the conclusion that the penetration of the new tanning agents was not only complete but also uniform, assuring sufficient stabilisation of the wet-white for further mechanical or other chemical processing.

The evaluation of the modification of collagen by new tanning agents', and in particular topographic distribution – mapping - of the metal species in the prototype leathers, was obtained by means of scanning electron microscopic (SEM) and energy dispersive X-ray analysis (EDAX). These are most appropriate methods for the characterisation of surfaces and the results obtained confirm all previous assumptions about metal tanning agents uniform penetration and distribution, as well as provide semi-quantitative data of the mineral species topographic mapping (Figures 7 and 8)

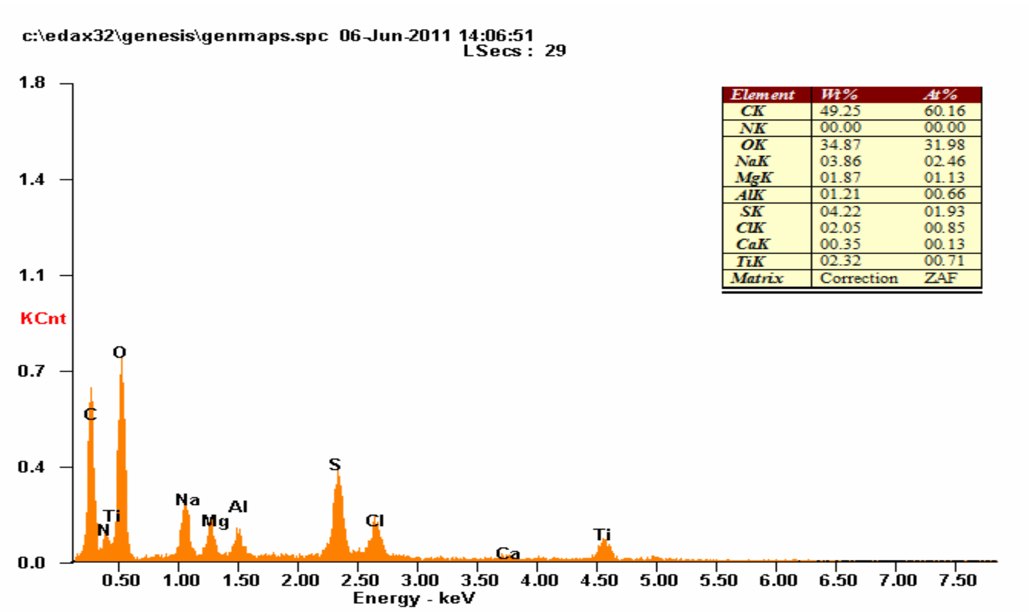
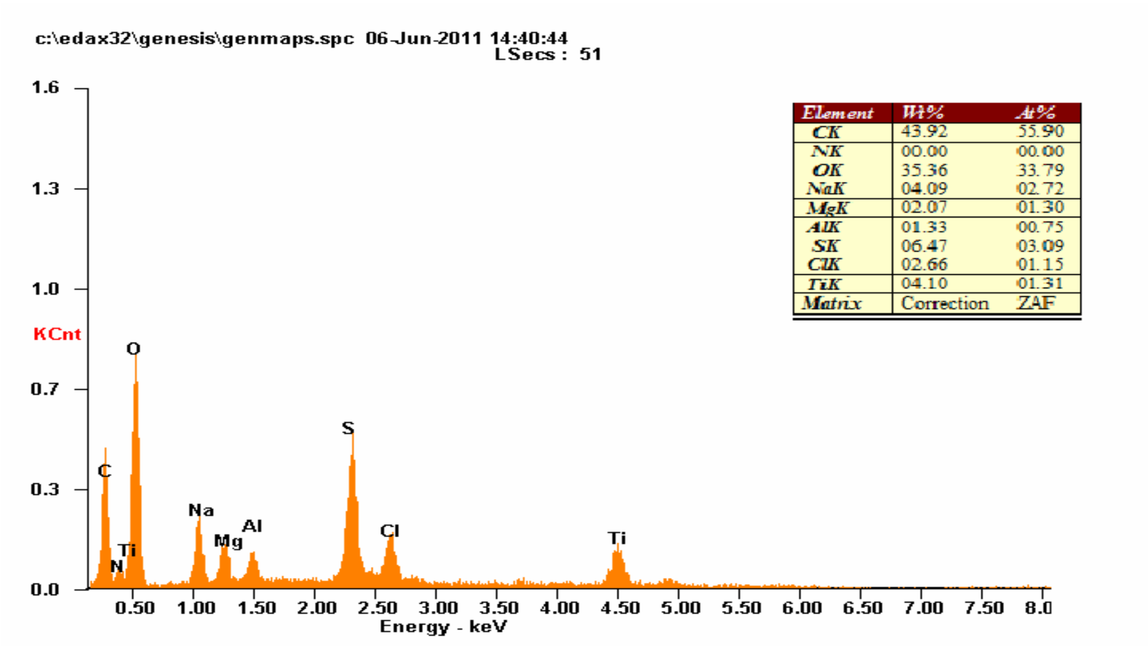


Figure 6. SEM-EDAX mapping of grain layer



Element	Wt%	At%
CK	43.92	55.90
NK	00.00	00.00
OK	35.36	33.79
NaK	04.09	02.72
MgK	02.07	01.30
AlK	01.33	00.75
SK	06.47	03.09
ClK	02.66	01.15
TiK	04.10	01.31
Matrix	Correction	ZAF

Figure 7. SEM-EDAX mapping of split

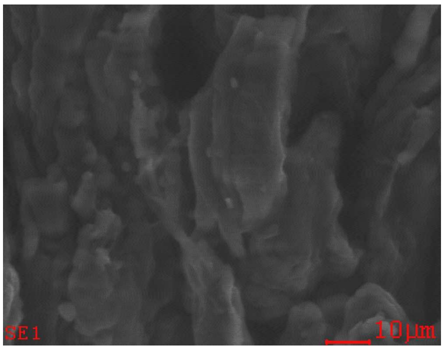


Figure 8. SEM – image of grain layer split of new leathers

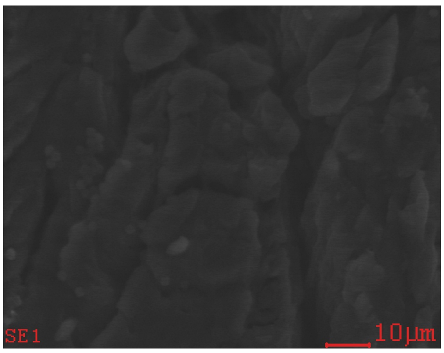


Figure 9. SEM – image of the bottom split of new leathers

4. Conclusions

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;
- 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
- increase in assortments diversity

The experimental results obtained so far in pretanning trials, are a clear witness that it is now possible at pilot scale to produce full substance bovine wet white with the desired smooth grain, that possesses the minimum hydrothermal stability for subsequent mechanical processing and further R&D ought to be carried out aiming at:

- improving the methods of waste processing to make them more efficient;
- a complete survey of environmental impact and LCIA of the products, effluent and waste generated
- obtaining quantitative yield and costing data from large scale lots
- the diversification and rendering more efficient the tanning materials, application processes, and wet-white leather semi-processed commodity products.

5. References

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