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Valorization of titanium metal wastes as tanning agent used in leather industry

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ABSTRACT

The development of new tanning agents and new technologies in the leather sector is required to cope with the increasingly higher environmental pressure on the current tanning materials and processes such as tanning with chromium salts. In this paper, the use of titanium wastes (cuttings) resulting from the process of obtaining highly pure titanium (ingots), for the synthesis of new tanning agent and tanning bovine hides with new tanning agent, as alternative to tanning with chromium salts are investigated. For this purpose, Ti waste and Ti-based tanning agent were characterized for metal content by inductively coupled plasma mass spectrometry (ICP-MS) and chemical analysis; the tanned leather (wet white leather) was characterized by Scanning Electron Microscope/Energy Dispersive Using X-ray (Analysis). SEM/EDX analysis for metal content; Differential scanning calorimetric (DSC), Micro-Hot-Table and standard shrinkage temperature showing a hydrothermal stability (ranged from 75.3 to 77 °C) and chemical analysis showing the leather is tanned and can be processed through the subsequent mechanical operations (splitting, shaving). On the other hand, an analysis of major minor trace substances from Ti-end waste (especially vanadium content) in new tanning agent and wet white leather (not detected) and residue stream was performed and showed that leachability of vanadium is acceptable. The results obtained show that new tanning agent obtained from Ti end waste can be used for tanning bovine hides, as eco-friendly alternative for chrome tanning.

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” (Covington, 2008).

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 (2–7 g 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 fat liquoring 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 re tanned with chromium (III) tanning agents.

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These practical and operational constraints have stimulated research efforts to find an alternative to chromium (III) tanning German, 2010 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. Accordingly, Al (III), Zr (III) Hancock et al., 1980; Waldo et al., 1983, Ti (III and IV) Peng et al., 2007; Adiguzel Zengin et al., 2012; Mutlu et al., in press, Fe –salts (Kleban), their mixed salts (Covington, 1988), and most recently nano-silicates (Liu et al., 2010) and sodium water glass (WASSERGLAS) 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 Life Cycle Inventory Assessment (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 (Covington et al., 1989) 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 (Ioannidis et al., 1989) which, on the other hand, were never taken up by the Industry, due to emerging renewed 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 treatment plant.

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 characterized as potentially toxic or hazardous.

2. Materials and methods

2.1. Materials

Chemicals for synthesis of tanning agents: All chemicals used were of technical grade. Aluminum sulphate, $Al_2(SO_4)_3{\cdot}18\ H_2O$ (15.3% Al_2O_3, 8.55% Al) (SR EN 878/2004); sodium citrate (STF 116/2000); sodium tartrate (STF 34/1999); ammonium sulfate (STAS 450-1975); magnesium oxide (STAS 4995-1980); sulphuric acid (95–97% -STAS 97-1980).

Ti-end unrecyclable waste from the Ti-metallurgic industry with a composition of min. 90% content of titanium.

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

2.2. Methods

Ti–Al tanning agent synthesis: For the solubilisation of Ti-end waste in order to obtain tanning agents, an antacid reaction vessel equipped with jacket for temperature control, with a VELP SCIENTIFIC mechanical stirrer and gas outlet for gases resulting during synthesis was used. In-house design laboratory equipment with vacuum ILMVAC type was used for the filtration of titanium solution resulted by dissolving wastes.

Tanning trials were undertaken using pickled bovine pelts and a DOSEMAT micro pilot DOSE MAT inox-drum. The tanning brine bath length varied from 200% to 400% on pickled weight and the initial float pH = 3.1–3.2, before the adding of the tanning agent. The temperature of the tanning bath was about 25 °C and the drum rotational speed was 15 rpm. Ti- tanning agent was added with offers ranging from 2% to 10% w/pickled weight. The pH of the bath after the addition of the tanning agent was pH = 2.2–2.3. The tanning bath had a characteristic purple colour and the section of the pelt was fully penetrated after 10–25 min (visual control). Basification of the bath was initiated using 2–3% w/pickled weight MgO based products for this purpose. After 30–60 min – with heating of float from 25-to-35 °C – 2–3% w/pickled weight cationic fatliquor was added and the drum run to reaction completion over a period of 1–6 h with the tanning bath fully de-coloured and pH = 3.4–3. Leathers are then retanned and finished in the traditional manner (Crudu et al., 2011).

2.3. Characterization

Ti-end waste: Metals' content was determined using inductively coupled plasma mass spectrometry device (ICP-MS).

Ti based tanning agent was analyzed as solution and as powder by chemical analysis and ICP-MS analysis.

Kinetic of tanning process was performed by varying the offer of Ti based tanning agent from 2%, 4%, 6%, 8% and 10% related at weight of pickled pelt and by measure metal oxides content of initial and final tanning floats. The exhaustion index (Ie, %) was calculated by formula:

$$\mathrm{Ie} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i is metal oxides content of the initial float, and C_f is metal oxides content of the final float.

Chemical analysis of leather tanned with Ti based tanning agent (so called wet-white leather because of light colour). After wet white leather was split in tree layers (grain, median and bottom split) was performed chemical analysis for determination of volatile meter, extractible, ash, metal oxides, total soluble, pH on each layer of leather.