**Hydroil, the opportunity to save leather**

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**1.Introduction**

Leather tanning is today an important industry were a secondary raw material of the food compartment, the hide, is transformed in a relevant product for the apparel chain, that is, from a slaughter waste to a versatile luxury product. Tannery process chemically transform the perishable collagen of the raw skin in a long-time stable product under the most severe conditions of use.1,2 With tanned leather it is possible to produce as many as possible product like clothes, gloves, shoes, bags, wall panels, seat covers and more. As all the industrial products, tanned leather must fit the demand of sustainability well issued by the 17 goals of the UN 2030 Agenda.3 Accordingly, the main challenge for the XXI century tanneries is to guarantee the sustainability of used processes and, unfortunately, the tanning step is one of the most critical ones within the whole leather chain (e.g., because the huge amount of chemicals and water used). Today, more than 85% of the hides are tanned with metals, in particular with chromium (III) salts. These salts are not toxic but the possibility of their not voluntary oxidation to chromium (VI) salts even at level of ppm rises issue about human health.4 Of course, there are other ways to tan leather, like with vegetal or synthetic tannins, aldehydes, oils or resins. However, all these different recipes cannot express the process flexibility and the product quality of the chromium-based recipe. This is because the unique very stable structure that is produced by the olation reaction between chromium (III) and collagen that creates an octahedral complex with six hydroxyl ligands as sketched in Figure 1.5



**Figure 1.** Complexing and olation mechanism of chromium.

In conclusion, there is a strong market demand for a final tanned product with the handy properties of the chromium tanned leather but obtained with a less critical process from the environmental and health issues.

Accordingly, the aim of this work is to present a new sustainable tanning agent that combine the properties described above.

**2. Hydroil**

The tanning agent here under investigation has the commercial name of Hydroil. It is a tanning agent derived from OMWW (Oil Mill Waste Water).6 This invention, disclosed a new kind of sustainable tanning element, derived from an environmental pollutant (i.e., OMWW)7 that it can be carefully dispersed in landfills because it can improve desertification8 for its very high COD and BOD5 values. Hydroil transforms this toxic product in a tanning agent that can be classified as a circular economy product. Moreover, OMWW is expected to exploit important properties of olive oil and scraps contained in this waste water like: (i) antibacterial activity (important in various steps of tanning industry); (ii) tanning characteristics of polyphenolic tannins with or without other tanning reagents; (iii) antioxidant activity thanks to hydroxytyrosol and some other compounds.9 These characteristics, permit to use it to protect leather from different types of degradation. It is significant to remember that tannins are important tanning agents because their capacity to perform olations between their hydroxy groups and the carboxyls of the collagen as sketched in Figure 2.10 It is well known that common vegetable tannins produce time stable leathers but with a very slow mechanical flexibility than that tanned with chromium salts. Hydroil tanning agent merge these characteristics: the leather handiness similar to that Cr(III) tanned, the product durability and the process sustainability.



**Figure 2.** Olation interaction mechanism of tannins.

**3. Methods**

This paper will investigate the potential of this source of new tanning agent with a series of test summarized in Table 1. Different hides were processed using various recipes and then, after tanning, were tested using consolidated qualification tests, whose aims are explained in detail below. In all test the compositions are expressed in kg hides/kg bath ratio.

E1: For the evaluation of antimicrobial effect, dry hides were processed in a rotating jar mill together with OMWW at different concentration (25-50-75-100%) and water (100%). They were agitated for 2 hours at 25°C and after that, the material was left for remaining wet on a plastic bag for 24 hours. Finally, it was done a common test to evaluate the possible formation of rot; by hair pulling and smelling (evaluation of significant malodorousness or not).11 The results were compared in parallel with blank test.

E2: For the evaluation of tanning capacity, the Folin-Ciocalteau and Chambort-Jamet methods were used. In particular, the first one is the most common test for polyphenols quantification, by firstly doing a basification with Na2CO3 and then using FCR (Folin-Ciocalteau Reagent), a mixture of phosphomolybdate and phosphotungstate; so, this solution could be analyzed by UV spectroscopy. The other method is the main one to know the capacity to absorb tanning species in hide powder. In particular, it was used standard leather Freiberg Hide Powder, bought in Forschungs institute für Leder und Kunststoffbahneng GmbH in Germany. The formula for quantification of tanning capacity expressed is:

*C.C.* = $\frac{C\_{i}-C\_{f}}{C\_{i}}x 100$

Where: C.C. is tanning capacity; Ci is the starting concentration and Cf is the final concentration, after the tanning time.

E3: To know if OMWW has a microbiological inhibition activity, 10 kg calfskin hides were used in testing drums of 50 liters. These hides were previously worked in wet and Pickle phase; the product concentration was 100% and it was significant the density adjustment to 6°Be by salt. After 2 hours, hides were checked and took on a horse for a few days. So, they were ready to be tested by warm humidity conditions (climate chamber) of 40°C with 60% humidity for 7 days. Also, it was valuated Tg by the standardized method UNI EN ISO 3380.11

E4: Then it was tested the capacity of OMWW to improve the metal-free tanning phase, by mixing with some other agents. One of the most important tests is using similar condition of the previous test for hides, in a batch with a pH of 2,8-2,9; 70% of product (OMWW) with 6% of glutaraldehyde, 1,5% of long chain sulfosuccinate and rolling the jars for 3 hours. After, it was added 2% of dihydroxydiphenyl sulphone and rolled for other 3 hours. Finally, it was putted inside jars 5% of tanning polyacrylic resin and rotated for 8 hours. Leathers were washed with 100% cold water, 1% sodium acetate and after a few hours wrapped in nylon bags, it was done a Tg analysis.12

E5: For a valuation of OMWW antioxidant activity, it was used wet-blue leather (chromium tanning) in a reproduction of retanning phase, by matching a vegetal tannin (Tara) and the Olive Mill Waste Water. After that, it was used as fatliquoring agent sulphited fish oil, really important to repeat normal passages to make a leather. The water was replaced with OMWW 150% p/p. It was used a jar, and after some rotation, leathers were lest to rest for one day. Then were done drying operations on vacuum machine, hot roller machine and on air. Finally, these were submitted in strong condition to develop Cr VI, a strong carcinogenic product:13

1. 24h under UV rays at 30 cm away from a UV iron halides lamp (JELOSIL HG200 L) at 30°C with 55% of humidity
2. 24h in climate chamber at 60°C with humidity of 90%.

The quantification of Cr VI was done with spectrophotometric method UNI EN 17075:2008.

**Table 1.** summary of experimental activity used to test Hydroil tanning agent

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Entry | Substrate | Phase | Instrument | Ingredients | Time | Temperature | Preparation | Evaluation test |
| Time | Place |
| E1 | Dry hides | Soaking | Jar mill | Water +OMWW | 2 h | 25°C | 24h | Plastic bag | Hair pulling + smelling |
| E2 | Hide powder | Tanning | Beaker | Water + OMWW | Like the evaluation method | Folin-Ciocalteau quantification | Chambort-Jamet method |
| E3 | Calfskin hides | Pickle | Testing drums | Water + Pickle bath + OMWW + salts | 2h | rt | 7 days | On a climate chamber | UNI EN ISO 3380 |
| E4 | Calfskin hides | Tanning | Jar mill | Pickle bath + OMWW + glutaraldehyde + sulfosuccinate + dihydroxydiphenyl sulphone + polyacrylic resin | 14h | rt | hours | On a nylon bag | UNI EN ISO 3380 |
| E5 | Wet-blue leather | Retanning | Jar mill | Tara or OMWW + water + sulphited fish oil | 1 day | rt | 48 hours | Over UV lamp and on climate chamber | UNI EN 17075:2008 |

**4. Results and discussion**

E1: The evaluation of OMWW bactericide feature was done in base of tannins antimicrobial activity. In fact, these are a natural defence for fruits and vegetal tissues, thanks by the inhibition activity of bacterial cell wall synthesis and of some peculiar enzymes with a reproductive control action.14 Of course, in case of OMWW there is a difference on tannins presence, depends by: olive species, seasons and climate. But, OMWW used, had 500-10000 mg/l gallic acid determined by Folin-Ciocalteau assay (the most common polyphenol tannins quantification) and it is enough to have a strong activity. More concentration takes more bactericide activity like it was demonstrated in this first experiment. This is valuable thanks by physical tests; olfactory evaluation of malodorousness and hair pulling. The principle is: if there is a bacterial contamination, the keratinolytic activity and bad smelling are due by some products made by different species like: Bacillus, Staphylococcus and Micrococcus.

E2: For a valuation of tanning capacity Chambort-Jamet is a really important standardized method. But to do that, it must be normalize the tannins quantity on OMWW, so a previous Folin-Ciocalteau is mandatory. This assay is based on the polyphenol oxidation at pH 10, thanks by reduction activity of molybdenum and tungsten compounds.15 Then the tanning capacity has an easy principle, based on quantification of how much substances are absorbed in standard hide powder, in a beaker lab bath. It is done by weighting, at the beginning and at the end, filtrated dried tannins. The results were surprising: 82,94% phenols absorbed are quite similar to commercial wood tannins, so it exhibited a very high tanning power.

E3: The evaluation of using OMWW as preservative adjuvant against microorganisms, could be very interest for its using in another part of the process. In this case it was applied climate chamber conditions to improve microbial growth after OMWW. For a good preparation of hides, it was followed some tips like: checking thickness and permeation by lightness of bath and to increase fixation process it was putted hides on a horse for a few days. The deterioration evaluation in this case was done by smelling and observing mold formation, but without negative changes in hides. To know contraction or gelatinization temperature it was used a standardized procedure, consisting on shrinkage determination of leather sample piece by heating at a specified rate in water. The result of 60°C means an exciting tanning activity by OMWW.

E4: The chromium-free vegetal-like tanning test, can improve leather characteristics by using OMWW in an optimized procedure. The acidification permits to tannins to enter inside the material by modifying hide isoelectric point. Furthermore, an acid pH permits chelation and aggregation of phenols, so a fixed tannins improvement.16 The wrapping of leather was done to avoid excessive drying and to absorb and distribute chemicals inside. The test was done with or without PA (polyacrylic acid) and Tg was 82°C and 78°C, an enthusiastic result, considering vegetal and chromium tanning leather have 80 and 100°C. The PA prove was the best one; may be the use of polymer can improve the structure stability.

E5: At the end, an interest step for consumers health is the application of OMWW for the Cr VI decrease. This is possible thanks by the presence of some antioxidant agents inside olive drupe. They act like defending agents from different climates, rays, temperatures and humidity conditions. Without them fruits or some other vegetal products, could be more susceptible and easily altered. In fact, olive waste water protects chromium tanning leather from oxidizing conditions and the results were very encouraging (mg Cr VI/kg leather):

* Tara retanning process: 1) 6,31; 2) 5,68
* OMWW retanning process: 1) 0,29 2) 0,16

The principle of this standardized method is the extraction and quantification by a colorimetric method in presence of particular indicator, oxidized by all Cr VI presents in sample.

**5. Conclusions**

These results demonstrated some good characteristics of OMWW and in base of them it was developed the product Hydroil.6

Every single day human activities footprint becomes high and high, and linked with its, all of these days natural disaster risk increase drastically in every region of world ascertained by UNDRR (United Nations Office for Disaster Risk Reduction).17 So, it is the hour to find a solution and try to exploit this problem to a new kind of products, with important characteristics and less costs; not only for environment but also for the industry. Only with this strategy, leather and some other sector could survive and update. Hydroil is the method, the chance to do that by becoming stronger and competitive than before.

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