A technical feasibility study on titanium tanning to obtain upper quality versatile leather

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1. Abstract

The many advantages offered by chrome tanning justify its widespread use for production of almost all types of leather. However, the traditional chromium(III) tanning process is constantly under threat from the pressure of legislation and ever-tightening restrictions require to minimize chromium-containing effluents discharge and chromium-containing wastes production.

Recently, the manufacture and use of chromium(III) free tanning agents compounds have been studied intensively. Aluminum, zirconium and titanium compounds has been found to be an effective alternative to chromium salts. In particular, titanium is abundant in nature, easily obtainable and non-toxic. So, titanium tanning is one of the most promising replacements for chromium tanning in today's leather industry.

In this study we investigated the use of titanium salts as tanning agent for the production of high quality bovine upper leather. The technical feasibility of the innovative titanium tannage process was experimentally explored. Several experimental activities have been performed, carrying out tests of chrome and titanium tanning on two different types of skins to assess the quality of the finished leathers obtained by new titanium tannage compared to the leathers obtained by traditional chrome tannage. The results have shown that the finished leathers are appropriate for different final uses and are comparable to the ones obtained by the conventional chromium process in terms of physical-mechanical properties.

2. Introduction

Advancement of science and technology brings about newer tanning methodologies and materials. Initially, vegetable tanning was the tannage of choice, followed by inorganic tannages, which now have prime position in leather production. Among these tanning materials, chromium takes first place, seeming to offer more advantages; it is commonly regarded as a "perfect" tanning agent in terms of leather performance. However, the biotoxicity of chromium has been a subject of active discussion. The biological implications of chromium are known to vary with the oxidation state of the metal ion [1]. The implication of chromium(III) in glucose metabolism has been considered beneficial [2] while oxyanions like chromates are well established human carcinogens [3]. In view of the potential toxicity of some forms of chromium, the environmental regulatory norms stipulate that the levels of chromium in wastewaters must be controlled. For this reason, other inorganic tannages, such as aluminum, silicates and titanium, are of interest for many researchers. Silica has long been examined as a tanning material, however, self-tanning potential of silicate is yet to be established and sodium silicate has been used successfully more as a filler in chromium leathers than as a tanning material. Aluminium tanning, as silica , is considered to be an incomplete tannage: without chromium aluminium does not form stable coordination complexes [4]. Unlike the two different tanning agents described above, titanium tanning is considered one of the most promising substitutes for chrome tanning in the leather industry. Research on titanium tanning has been well documented in the literature over the past century and various titanium tannage were patented, using different methodologies and materials, as: titanium chloride, titanium oxalate and titanium gluconate, obtaining results non very satisfactory. A breakthrough came in Russia, in the 1970, with the patenting of ammonium titanyl sulfate, nowadays, the commonly used titanium salt in the tanning process, with the production of leathers with the same performances of those chrome tanned.

From chemical point of view, similar to chromium, titanium exploits the nucleophilic reaction with the carboxyl groups of the skin to bind to the dermis. However, there are important differences between titanium and chrome tanning, founded in different oxidation states of metals: Cr (III) and Ti(IV). This implies a much higher penetration rate of chrome into the skin, easily allowing the full saturation of the carboxyl groups and without leading to the stiffening of the structure at the same time. Titanium, being a much larger molecule, can't reach full saturation of the carboxyl groups, obtaining a leather with greater rigidity than a chrome tanned leather. Other problems in tanning process with titanium salts are the high reactivity of titanium towards the surface of the skin, the extensive hydrolysis during basification and the lower precipitation pH of tanning agent, compared to that one which characterizes chrome salts. These drawbacks can be reduced by using some specific expedients. The use of organic masking products is useful to aid the penetration of the tanning agent through the section, decreasing the reactivity with the surface of the skin. Reduction of the salt hydrolysis during basification occurs by using a basifier agent that reacts slowly, as magnesium oxide.

Chrome tanning process presents clear advantages, however, titanium tanning has been reassessed because by this process is possible to obtain crust leathers with physical properties comparable with the conventional chrome tanned crust leathers [5]. Moreover, the use of titanium as tanning agent could eliminate the use of chromium with the following advantages:

- absence of chromium in the exhausted floats, avoids the presence of heavy metals in wastewaters process; besides, as reported in literature, the presence of titanium oxide particles during purification, catalyzes the degradation of organic molecules [6];
- production of chromium free waste, which can be more easily managed in disposal phase;
- improved quality of the product in terms of allergenicity; salts of titanium are completely harmless and have no problems of skin or mucous membranes sensitization.

In the present study, an innovative titanium tanning procedure based on the use of titanyl sulfate instead of the commonly used ammonium titanyl sulfate has been investigated on pilot scale. The tanning procedure has been optimized and validated on two different kind of skins, sheep skins and calf hides, in order to assess the quality of the finished leathers obtained by new titanium tannage compared to the leathers obtained by traditional chrome tannage.

3. Materials and method

Experimental tests were conducted on calf hides and sheep skins in a pilot-scale drum (1 m diameter, 0.5 m length). Calf hides after soaking, liming, deliming and bating, were divided into two sides: one side was conventionally pickled and tanned with chrome, the other side was pickled and tanned according to the innovative recipe (the procedures are reported in Tables 1 and 2).

Sheep skins previously pickled, after depickling, bating and degreasing operations were divided into two sides. One side was conventionally pickled and tanned with chrome, the other side was pickled and tanned according to the innovative recipe (the procedures are reported in Tables 3 and 4).

After tanning, the skins followed the traditional re-tanning to produce upper leathers.

Table 1. Calf hides: steps of conventional pickle and chrome tanning process (offers: wt.% based on fleshed hide)

%	*Product*	*Operations & controls*
50	Water 20°C	
9	Sodium chloride	Bé control [9-9.5]
0.6	Formic acid (1:10 w/w)	slowly during the rotation pH control [4.1-4.3]
0.8	Sulfuric acid (1:20 w/w)	slowly during the rotation pH control [2.9-3.1]
4.5	Basic chrome sulphate	Section control
1	Sodium acetate	pH control [2.2-2.4]
4.5	Basic chrome sulphate	Section control
50	Water 40°C	
0.6	Basifier agent (MgO)	pH control [3.6-3.8]

Table 2 .Calf hides: steps of innovative pickle and titanium tanning process (offers: wt.% based on fleshed hide)

%	*Product*	*Operations & controls*
50	Water 20°C	
6	Sodium chloride	Bé control [8-8.5]
1	Formic acid (1:10 w/w)	slowly during the rotation pH control [3.9-4.1]
1	Citric acid	slowly during the rotation pH control [3.1-3.3]
0.8	sulfuric acid (1:20 w/w)	slowly during the rotation pH control [2.1-2.3]
12	Titanyl sulfate (TiO_2 29%)	Specific addition* Section control
2.5	Basifier agent (MgO)	pH control [3.4-3.6]

* Titanyl sulfate was added by a specific methodology in the process of patenting

Table 3. Sheep skins: steps of conventional pickle and chrome tanning process (offers: wt.% based on doubled pickled weight)

%	*Product*	*Operations & controls*
50	Water 20°C	
8	Sodium chloride	Bé control [8.5-9]
0.8	Formic acid (1:10 w/w)	slowly during the rotation pH control [3.9-4.1]
1.2	Sulfuric acid (1:20 w/w)	slowly during the rotation pH control [2.3-2.5]
4.5	Basic chrome sulphate	Section control
0.5	Sodium acetate	pH control [2.1-2.3]
4.5	Basic chrome sulphate	Section control
50	Water 40°C	
0.6	Basifier agent (MgO)	pH control [3.6-3.8]

Table 4. Sheep skins: steps of innovative pickle and titanium tanning process (offers: wt.% based on doubled pickled weight)

%	*Product*	*Operations & controls*
50	Water 20°C	
6	Sodium chloride	Bé control [8-8.5]
1.2	Formic acid (1:10 w/w)	slowly during the rotation pH control [3.9-4.1]
1.5	Citric acid	slowly during the rotation pH control [2.7-2.9]
0.2	sulfuric acid (1:20 w/w)	slowly during the rotation pH control [2.1-2.3]
12	Titanyl sulfate (TiO_2 29%)	Specific addition* Section control
2.5	Basifier agent (MgO)	pH control [3.4-3.6]

* Titanyl sulfate was added by a specific methodology in the process of patenting

The final leathers obtained were characterized by their main mechanical and technical properties. Physical testing was conducted according to Italian standards (UNI 10594) for upper leather. The extension and load at tear was determined according to the UNI-ISO 3377-2 method using an electronic dynamometer (Pegasil, Mod. Marte). The data reported are the mean of three determinations. The extension and load at grain crack was determined according to the UNI-ISO 3379 method using a lastometer Pegasil Mod. EL-51E. The data reported are the mean of three determinations. The measurement of Shrinkage temperature was carried out using a shrinkage tester according to IULTCS official testing method IUP16. Technical properties were assessed by the expertise personnel of PO.TE.CO.

The exhausted floats after tanning were sampled; their titanium and chrome content was performed by a ICP-AES with a Perkin Elmer 400.

Chrome and titanium distribution in the section of the tanned skin was analyzed by scanning electron microscopy (SEM) coupled with energy x-ray dispersion (EDX) by using a JEOL 5600 LV electron scanning microscope.

4. Results and discussion

The innovative titanium tanning process is based on the specific procedure of titanyl sulfate adding, that allows a greater penetration of the tanning agent into the collagen fibers. The results of the mechanical properties of the crust leathers are reported in Tables 5 and 6 for calf hides and in Tables 7 and 8 for sheep skins. The final leathers obtained by innovative titanium tanning are characterized by physical properties comparable with the conventional chrome tanned crust leathers and they comply with the standards required for high quality upper leather.

Table 5. Extension and load at tear of the crust leather obtained by calf hides

Sample	*Thickness (mm)*	*Extension (mm)*	*Load (N)*	*Load/thickness (N/mm)*
Traditional chrome tanning	1,52	35,09	115,0	75,9
Innovative titanium tanning	1,43	45,4	113	79,3

Table 6. Extension and load at grain crack of the crust leather obtained by calf hides

Sample	*Extension at break (mm)*	*Load at break (N)*	*Extension at crack (mm)*	*Load at crack (N)*
Traditional chrome tanning	8,05	325,64	9,94	536,81
Innovative titanium tanning	7,30	149,5	11,28	415,8

Table 7. Extension and load at tear of the crust leather obtained by sheep skins

Sample	*Thickness (mm)*	*Extension (mm)*	*Load (N)*	*Load/thickness (N/mm)*
Traditional chrome tanning	1,06	32,09	37,4	35,28
Innovative titanium tanning	0,95	46,8	27,3	28,9

Table 8. Extension and load at grain crack of the crust leather obtained by sheep skins

Sample	*Extension at break (mm)*	*Load at break (N)*	*Extension at crack (mm)*	*Load at crack (N)*
Traditional chrome tanning	8,15	186,5	10,94	324,5
Innovative titanium tanning	7,45	102,5	13,13	201,7

The results of the assessment of the technical properties of titanium tanned crust leathers, in comparison with chrome tanned ones, are reported in Table 9 for calf hides and in Table 10 for sheep skins. It may be observed that the crust leathers obtained by innovative titanium tanning process and the conventional chrome tanning process show quite similar technical properties. The high value of dyeability for titanium tanned leathers could be related to titanium tanning agent that gives whiteness as a base colour improving the brilliancy and dyeing properties.

Table 9. Technical properties of the crust leather obtained by calf hides

Technical properties	*Traditional chrome tanning*	*Innovative titanium tanning*
Softness	100	90
Fullness	100	90
Opening-up	100	100
Grain blowing	100	100
Dyeability	100	120

Table. 10. Technical properties of the crust leather obtained by sheep skins

Technical properties	*Traditional chrome tanning*	*Innovative titanium tanning*
Softness	100	80
Fullness	100	90
Opening-up	100	100
Grain blowing	100	100
Dyeability	100	110

Shrinkage temperature of the leathers titanium and chrome tanned are shown in Table 11 for calf hides and in Table 12 for sheep skins. The results indicate that the shrinkage temperature of 84°C was achieved for the crust leathers obtained by titanium tanning of the calf hides, and a higher shrinkage temperature (90°C) was reached for the crust leathers obtained by titanium tanning of the sheep skins. The shrinkage temperatures achieved by titanium tanning, although lower than ones obtained by chrome tanning, can be considered enough high and acceptable.

Table. 11. Shrinkage temperature of the crust leather obtained from calf hides

Sample	Shrinkage temperature
Traditional chrome tanning	103°C
Innovative titanium tanning	84°C

Table. 12. Shrinkage temperature of the crust leather obtained from sheep skins

Sample	Shrinkage temperature
Traditional chrome tanning	105°C
Innovative titanium tanning	90°C

The titanium and chrome content of the exhaust baths of tanning processes is reported in Table 13 for calf hides and in Table 14 for sheep skins. Values of remaining titanium in the bath tanning are lower than the residual chrome, thus a higher amount of titanium penetrated into the collagen fibers.

Table. 13. Concentration of tanning agent in the exhaust baths of the calf hides

Sample	Tanning agent (mg/l)
Traditional chrome tanning	5450
Innovative titanium tanning	2350

Table. 14. Concentration of tanning agent in the exhaust baths of the sheep skins

Sample	Tanning agent (mg/l)
Traditional chrome tanning	4640
Innovative titanium tanning	1520

Figure 1 reports the SEM pictures of the cross section of the traditionally chromium tanned crust leather and the SEM-EDX distribution of chrome. A good compactness of the fibril bundles and a uniform penetration of chromium may be observed. In Figure 2 is shown the SEM pictures of the cross section of the titanium tanned crust leather obtained and the SEM-EDX distribution of titanium. It can be observed a lesser compactness of the fibril bundles in comparison with the chromium tanned leather. Besides titanium does not distribute uniformly along the section, but it is mostly fixed on the surface region of the leather.

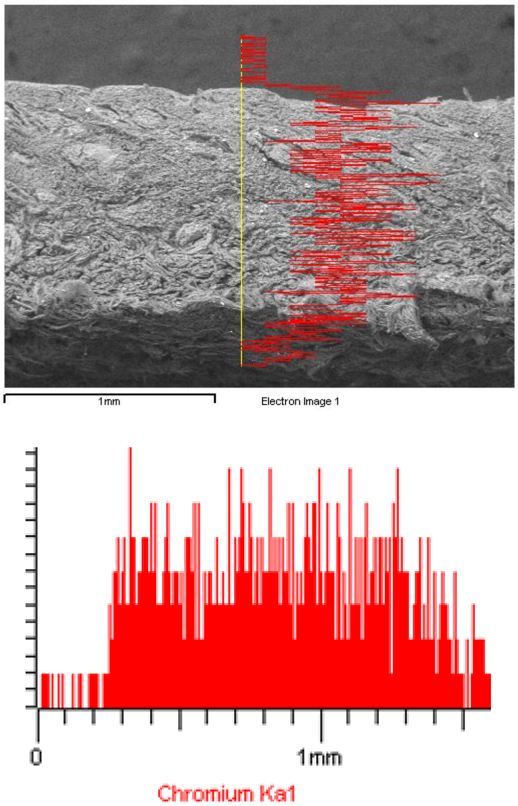

Fig. 1. SEM and SEM-EDX pictures along the section of the traditionally chromium tanned crust leather

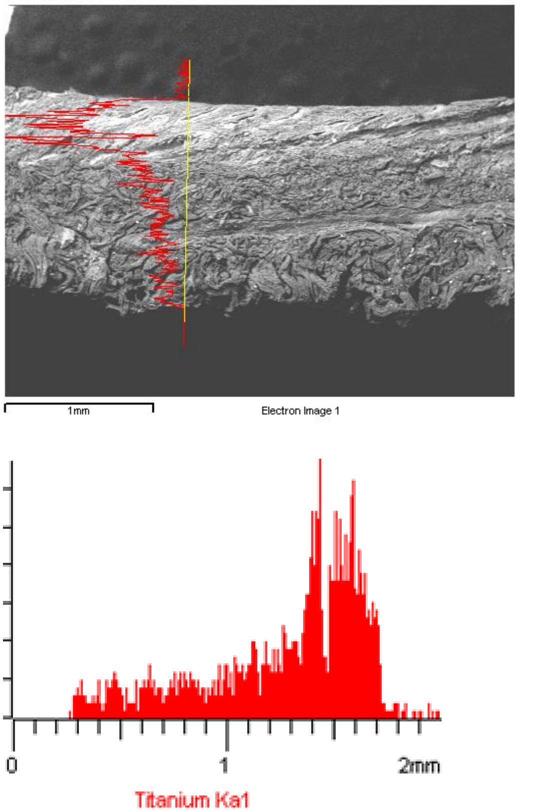

Fig. 2. SEM and SEM-EDX pictures along the section of the innovative titanium tanned crust leather

4. Conclusions

In the present study, an innovative titanium tanning procedure has been assessed on pilot scale. The obtained results clearly indicate that the use of titanium in the tanning process of upper leathers provides leathers with physical, chemical and functional properties comparable with the conventional chrome tanned leathers; besides, dyeing characteristics of the titanium tanned leathers are found to be better as compared with chrome tanned leathers. The SEM pictures and the SEM-EDX distribution of titanium show a greater fixing of titanium on the surface region of the leather. Thus, the innovative methodology can be further improved, although the results regarding the quality of the finished leather are satisfactory.

In the innovative titanium tanning, the use of a lower amount of sodium chloride involves a significant reduction of chlorides in the exhaust baths and the use of titanyl sulfate instead of the commonly used double ammonium sulfate, avoids the presence of ammonium ions in the wastewaters, reducing the environmental burdens.

The outcomes are interesting and reliable as they carried out in pilot scale, using small lots of skins, therefore, the process should be tested in semi-industrial scale to validate the results.

5. References

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