PROPERTIES OF LEATHERS TANNED WITH TI-AL BASED TANNING MATERIALS OBTAINED FROM THE WASTES OF METAL INDUSTRY

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Although chromium tanning is the most popular tanning system worldwide, it is held under the microscope due to increasing requirements on disposal of chromium tanning effluents, by-products and sludge. For this reason; in last decades, researches on alternative tanning materials which will decrease or replace chromium usage take a great share among the main topics in the area of leather researches. In this research, a newly produced titanium based tanning agent, obtained from processing wastes from the industry of nonferrous metals was used as an alternative to chromium tanning agent. The new titanium tanning agent was experimented with 1%, 2.5%, 5%, 7.5 and 10% dosages. Physical tests and chemical analysis of the produced chromium-free leathers gave comparable results to leathers tanned with basic chromium sulphate. 5% usage of titanium tanning agent was found to be optimal.

Keywords: chromium-free leathers, titanium, tanning.

INTRODUCTION

When we talk about tanning today, the topic is usually raised in connection with environmental compatibility. Due to the increasingly stringent requirements governing tannery effluents as regards their chrome content, and due to a variety of problems involved in the disposal or utilization of by-products containing chrome, chrome tannage in particular has recently come under criticism (Germann, 1994).

The chromium salt tanning system, which is still the most popular leather tanning procedure is under continuous pressure from environmental groups and international regulations due to pollution and toxicology reasons unfairly associating the Chromium (III) commonly used with hazardous Chromium (VI) (Adiguzel Zengin et al., 2011)

The environmental regulatory agencies in many countries have come out with stringent stipulations for permissible levels of chromium in wastewater which are in the range of 0.3–2.0 ppm. In recent years, there has been a growing social awareness to contain chromium discharge in wastewaters. Conventional treatment systems adopted for the removal of chromium from waste streams produce large quantities of chrome-containing sludge, which has been listed among the hazardous wastes. Further, the cost escalation in leather processing on the one hand, and the increasing price of the chrome-tanning salts on the other, have rendered the better management of chromium in tanneries a vital economic priority (Sundar et al., 2002).

Under these circumstances, quest for new alternative tanning materials which will decrease or replace chromium use is inevitable. In this research, a newly produced titanium based tanning agent, obtained from processing wastes from the industry of nonferrous metals was used as an alternative to chromium tanning agent. Physical tests

and chemical analysis of the produced chromium-free leathers are compared with the leathers tanned with basic chromium sulphate.

MATERIAL AND METHOD

Six pickled sheep skins were used as material. The leathers were cut into four pieces from backbone line and a perpendicular line to the backbone, to increase the repetition of trials. Each leather sample was coded and processed in a different tanning drum. Each trial was made with 4 repetitions. The leather samples were processed with a standard clothing leather production recipe except the Titanium-Aluminum containing tanning material TMW/2 which was a product produced by using the wastes from the industry of nonferrous metals (Crudu, 2010). Various amounts of tanning materials were used in tanning process according to the Table 1.

Table 1. Experimental design for various amounts of tanning material

Trial Name	Parameter
T0	Blank (Chromium tanned leather)
T1	% 1 Titanium tanning material
T2	% 2.5 Titanium tanning material
T3	% 5 Titanium tanning material
T4	% 7.5 Titanium tanning material
T5	% 10 Titanium tanning material

Physical tests and chemical analysis were carried out in the laboratories of Department of Leather Engineering in Ege University, Izmir by using the following equipment: tensile tests with Shimadzu AG-IS, color measurements with Minolta CM-3600d, formaldehyde analysis with Agilent Technologies 1200 Series HPLC, titanium amounts in leather with Perkin Elmer Optima 2100 DV ICP-OES.

Leather samples were prepared in accordance with “sampling location” and conditioned according to “sample preparation and conditioning” standards TS EN ISO 2418 and TS EN ISO 2419 (Anon. 2006b and 2006c).

For determination of the chemical and physical properties of the chromium-free leathers, TS 4119 EN ISO 3376: tensile strength (Anon. 2006a), TS 4119 EN ISO 3376: elongation at break (Anon. 2006a), TS 4118-2 EN ISO 3377-2: tear strength (Anon. 2005a), color measurement of surface with spherical spectrophotometer, TS EN ISO 17226-1: formaldehyde determination with HPLC (Anon. 2009d), TS 4120 EN ISO 3380: shrinkage temperature (Anon. 2005b), TS EN ISO 4045 pH value (Anon. 2009b), TS 4125 EN ISO 4047: ash content % (Anon. 2009a), TS EN ISO 4048 determination of matter soluble in dichloromethane (%) (Anon. 2009c), and TS 4126 chromium oxide (%) (Anon. 1985) tests were performed.

RESULTS AND DISCUSSION

The amount of tanning material as titanium content in leather samples are given in Table 2. It should be expected that there should be a change in Titanium content because of changing amounts of offered tanning material; however there is not a straight correlation. The titanium content of leathers increases proportionally with 1%, 2.5% and 5% tanning material offers. But this increase slows down for 7.5% and 10% tanning

material offers. This shows that, we cannot bind all of the tanning material to collagen after 5% metal oxide offer.

The shrinkage temperatures of leathers tanned with varying amounts of tanning materials can be seen in Figure 2. The average shrinkage temperatures of leathers are 75.5, 79.8, 80.4, 80.3 and 81 for tanning material offers of 1%, 2.5%, 5%, 7.5% and 10% respectively. It is seen that there is not a considerable difference for 5% and more amounts. High shrinkage temperatures, like 90°C, can be achieved with Titanium solo tanning, however, this requires large quantities and this causes the leather to be overfilled, and yet remain soft (Covington 2006). Peng et al. (2007) have tanned goat skins with a 7.5% TiO_2 offer and the ending shrinkage temperature was 84°C after tannage. Galiana et al. (2011) have obtained 85°C shrinkage temperature with SANOTAN, a new type of titanium-based tannage.

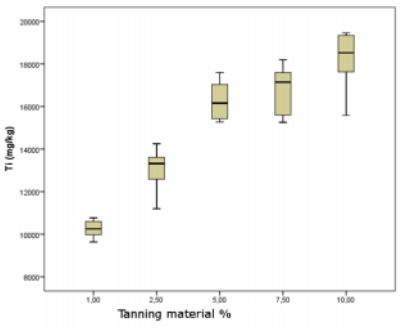

Figure 1. Titanium content of leathers tanned with various amounts of tanning materials

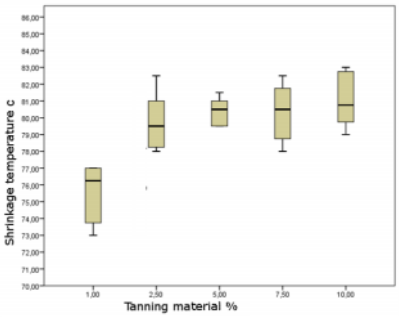

Figure 2. Shrinkage temperatures of leathers tanned with various amounts of titanium tanning agents

When the results of titanium content in leathers and shrinkage temperatures are considered together, it can be claimed that increasing the titanium content up to 5%, also increases the shrinkage temperature proportionally, but this increase loses its importance over 5% titanium content. Shrinkage temperature is one of the key indicators of tannage, however it is not enough alone. The physical and chemical changes of leathers also should be considered.

Table 2 shows the results of physical tests applied to the leathers tanned with chromium and varying amounts of titanium tanning agents. The average of tensile strengths of leathers tanned with titanium tannin is 21 N/mm^2 which is equal to the tensile strength of chromium tanned leather sample. However the elongations of titanium tanned leathers at break are considerably below than the chromium tanned sample. It can be concluded that titanium solo tannage causes low elongations, a pretanning is recommended. When the tear strength values of titanium tanned leathers are considered, their average is 70 N/mm, which is 3.3 times higher than the chromium tanned leathers. UNIDO offers a minimum of $10N/mm^2$, 15 N/mm^2, and 20 N/mm^2 of tensile strength for chromium tanned garment leathers, linings, and shoe upper leathers respectively. Also, UNIDO offers a minimum of 15N/mm, 25 N/mm, and 30 N/mm of tear strength for chromium tanned garment leathers, linings, and shoe upper leathers respectively. The mechanical properties of leather tanned with titanium are compatible with the acceptable quality standards advised by UNIDO (1996).

Table 2. Physical properties of leathers tanned with varying amounts of titanium tanning agents

Trial	Tensile Strength (N/mm^2)	S.D.	Elongation at Break (%)	S.D.	Tear Strength N/mm	S.D.
T0	21	6	77	16	21	3
T1	29	5	28	3	81	6
T2	21	5	30	7	71	14
T3	19	5	31	3	67	13
T4	21	3	30	5	69	10
T5	17	2	29	4	61	7

Another effect of a tanning material to the leather is the color. Tanning materials give their natural color to leather. Covington (2009) stated that the leathers tanned with titanium (IV) salts were initially colorless although it tended to go pale yellow with aging. In Table 3, colors of leathers tanned with chromium and changing amounts of titanium tanning agents and their color differences to white color (ΔE) are given. The pseudo colors are generated by the color measurement software. The color difference of 1% titanium containing leather to white color is similar to the chromium tanned leather as ΔE values. However the colors are different, which can be seen from pseudo colors and L, a, b values. As it is seen in Δb values there is an increase in yellow tones in titanium tanned leathers. But neither color difference nor yellowness increase proportionally with the increase in tanning agent amount.

Table 3. Color measurement values of leathers tanned with chromium and varying amounts of titanium tanning agents

Trial	L	a	b	ΔL	Δa	Δb	ΔE	Pseudo Color
White	98.92	-0.11	-0.36					
T0	78.92	-2.98	3.90	-20.00	-2.87	4.25	20.65	
T1	84.46	-2.29	13.72	-15.05	-2.27	14.66	21.14	
T2	83.27	-1.21	19.66	-15.64	-1.10	20.01	25.58	
T3	82.77	-1.52	18.10	-16.14	-1.41	18.45	24.78	
T4	84.54	-1.52	17.76	-14.37	-1.41	18.11	23.31	
T5	80.82	-1.61	18.45	-18.09	-1.50	18.80	26.43	

Chemical analysis results of leathers tanned with chromium and varying amounts of titanium tanning agents are given in Table 4. The average fat content of titanium tanned leathers is19.97%, which is very similar to chromium tanned leather. When we consider this data with the physical properties in Table 3, we can say that the strength values are due to the tanning agent change; because strength properties of leathers are a result of behavior of collagen fibers which are mainly affected by tanning and fatliquoring agents. Although the tanning takes place in a very acidic medium, the pH values of titanium tanned leathers are around 4.2 because of the basification process. The ash contents of leathers are indication of inorganic materials in leather and these increases

with the inorganic tanning material offer. The free formaldehyde content of leathers are approximately 12.15ppm which is below the limits. It is not recommended that the products for general applications, products in contact with skin, and baby leather products contain formaldehyde higher than 200, 75, and 20 ppm respectively (Anon. 2008).

Table 4. Chemical properties of leathers tanned with varying amounts of titanium tanning agents

Trial	Fat (%)	S.D.	pH	S.D.	% Ash	S.D.	Formaldehyde ppm	S.D.
T0	22.19		4.21		4.14		5.88	
T1	16.98	0.98	4.34	0.19	3.82	0.13	9.48	0.55
T2	20.36	1.30	4.06	0.18	5.18	0.64	13.69	1.89
T3	19.63	1.08	4.10	0.04	5.11	0.12	10.46	1.30
T4	20.16	3.75	4.12	0.07	5.40	0.16	13.82	0.90
T5	19.74	3.93	4.34	0.03	5.95	0.21	13.28	1.87
Mean (T1, T2, T3, T4, T5)	19.97	2.74	4.19	0.17	5.09	0.77	12.15	2.27

CONCLUSION

In this research, it was demonstrated that a material obtained from wastes of metal industry could be used as a tanning material in leather industry. Although the shrinkage temperature was around 80°C, physical and chemical properties of titanium tanned leathers gave comparable results to chromium tanned leathers, but with more yellowish color and less elongation. Although the tensile strength values of titanium tanned leathers are same with the chromium tanned samples, the tear strength values are considerably higher. So these leathers can be used in production of articles where high strength values and form stabilization are required, such as shoe uppers, leather crafts or upholstery leathers.

Titanium containing tanning materials in concentration of 1%, 2.5%, 5%, 7.5% and 10% were offered to leathers. The properties of leathers increased did not increase proportionally with the tanning material offer after 5%. So, a tanning material usage containing 5% titanium can be advised for tanning to get optimal results.

The project has two outcomes: First, a waste of metal industry is evaluated in another industry. Second, environmental load of leather wastes are decreased by using an alternative tanning agent rather than highly discussed chromium.

The chromium free leathers produced under this project have many application advantages as:

- No chromium in effluents;
- Shavings and cuttings can be recycled;
- Leathers are light colored and can be dyed to fashion colors easily;
- Leather have high strength values;
- An efficient quality assort can be made at wet-white stage.

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