COMPARATIVE STUDY ON THE LIGHT FASTNESS PROPERTIES OF DIFFERENT WHITE TANNING AGENTS

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The main causes of leather goods damage is fading as well as the damages caused by sweat and body grease, mechanical deformation and ageing. Tanning agents have varied efficiency on the UV durability and stabilization of collagen. It is because they have different bond strengths and binding mechanisms with leather. In this study, light fastness properties of the leathers tanned with the most commonly used white tanning agents were aimed to evaluate by using ATLAS XENOTEST ALPHA+ test instrument according to ISO 105-B02 standard test method and the leathers tanned with chromium tanning agent were used as a comparison. Blue wool test references were evaluated according to grey scale, and the evaluation of the color change for the tanned and dyed leathers against UV application of an artificial light source representative of natural daylight was carried out. In addition to light fastness test, colorimetric measurements of the treated samples and color changes before and after the UV application were also spectrophotometrically determined by Konica Minolta CM-3600d test device. The results showed that chromium tanned leathers provided the best light fastness results compared to other leathers tanned with white tanning materials. Zirconium and phosphonium tanned leathers had the same values and better than aluminum and vegetable tanned leathers.

Keywords: Leather, light fastness, tanning agents.

INTRODUCTION

Fading is one of the main causes of damage to leather goods, apart from damages caused by sweat and body grease, mechanical deformation and ageing. The light fastness of a material describes its resistance to fading by light, in particular by the constant radiation of UV light (Gülümser *et al.*, 2008). Sunlight is reaching to earth as electromagnetic radiation. The spectral form and intensity of light exposed on a dyed material have great effect on fading degree. The radiation between 290-400 nm is named as Ultra violet or UV. This radiation up to 400 nm have more energy and can break ionic, hydrogen and even covalent bonds in the material (Omur and Mutlu, 2016; Demir *et al.*, 2008). Materials that resist this effect are referred to be lightfast.

Leather products such as garment, upholstery and the leathers used for upper and automotive purposes are required a considerable fading characteristic during the daily use. Tanning operation plays a key role in improving the durability and stability of leather by strong crosslinks in the triple helical collagen matrix. It is the main process of leather manufacturing, which makes the hide and skin durable and less susceptible to decomposition (Heidemann, 1993).

In the leather industry, different tanning agents can be used to produce different types of leather products with different bonding mechanism. Nowadays mineral tanning is of technical importance for leather manufacturing considering the properties and performance (Covington, 1997). Mineral tannage is the preference in many leather types so that leathers become softer, lighter and more flexible as well as having higher hydrothermal stability as compared to vegetable tannage. The mineral tanned leathers are proper to dyeing process and can be finished in different methods. Among the

mineral tanning agents, chromium salts have known as ideal tanning agent considering the characteristics that provides to final leather (Covington, 2009).

Although chromium salts are the mostly used tanning agent due to their high hydrothermal stability and good organoleptic properties, their usage has been limited because of adverse effects on environment and human health. Therefore, recently alternative tannages have been replaced with chromium in order to make use of the mineral tanning advantages lacking with other organic tanning procedures (Ogata *et al.*, 2018; Moretto, 2015).

In today's trends toward chrome-free tanning technology (Madhan *et al.*, 2007); zirconium, aluminum, organic phosphonium salts and vegetable tannins are the alternative options to chromium tannage. Although mineral tanned leathers have advantages such as better durability, high performance and good dyeability, however they are not chemically stable and satisfactorily soft and flexible as well as having appropriate hydrothermal stability compared to chromium salts (Li *et al.*, 2006; Fathima *et al.*, 2006, 2005, 2003).

To reveal the tanning material effect on the light fastness properties of leathers, in this study, the light fastness properties of various white tanning agents such as aluminum, zirconium, phosphonium and tara were investigated in order to compare with the commonly used chromium salt.

MATERIALS AND METHODS

Materials

Commercially pickled Spanish sheepskins were used for tanning operations. Tanning agents used in the study were industrially produced, commercially available products: chromium salt from "Sisecam Chemicals," aluminum salt from "Zschimmer and Schwarz GmbH & Co. KG," phosphonium and zirconium salts from "Clariant" and tara tannin from "Silvachimica S.r.l." Other chemicals used in the production were provided from various suppliers.

Depickling, Tanning and Post-tanning Processes

Depickling process was applied for all leathers before tanning operations. Following the depickling process, the skins were tanned with chromium and different type of white tanning agents by conventional methods. Post-tanning processes were performed as shown in Table 1. Two independent processes were applied for each tanning agent.

Table 1. Post-tanning processes for differentiated tanning operations

Process	%	Chemicals	Temp (°C)	Time (min)	Remarks
Neutralization	100	Water	40		
	1	HCOONa		2x20	7 °Bé
	0.8	NaHCO ₃		3x20	pH 5.5
Washing x 3	200	Water	30	20	Drain
Retanning	100	Water	40		
	3	Syntan		20	
	4	Dicyandiamide resin		20	
	3	Acrylic syntan		20	
Fatliquoring	+50	Water	60		

Process	%	Chemicals	Temp (°C)	Time (min)	Remarks
	3	Synthetic fatliquoring agent			
	2	Phosphoester fatliquoring agent			
	2	Lanoline based fatliquoring agent			
	3	Sulphited natural fatliquor		60	
Dyeing	1	Dye auxiliary	40	20	
	4	Dyestuff		45	
	2.5	HCOOH		30	pH 4.0
Washing x 3	200	Water	30	20	Drain
Horsing-Drying-Dry drumming-Toggling					

Light Fastness Test of the Leathers

Light fastness tests of the leathers were performed by using ATLASXENOTEST ALPHA+ test instrument in accordance with the standard ISO 105-B02 in triplicates. A specimen of the leather to be tested is exposed to artificial light under controlled conditions, together with a set of reference materials. The colour fastness is assessed by comparing the change in colour of the test specimen with that of the reference materials used. Blue wool test references (1 to 8) were evaluated to the scale (according to grade 4 – contrast between the exposed and the unexposed portions of the specimen), then the grey scale was used for evaluation of the leathers colour change against UV application of an artificial light source representative of natural daylight (Xenon arc fading lamp) with ISO 105-A02.

Colorimetric Measurements

Konica Minolta CM-3600d brand spectrophotometer was used for measuring the colours of the leathers which were processed with different tanning agents. The effect of each tanning material on the leather colour has been examined before and after the UV application of an artificial light source representative of natural daylight. Then they were compared with the original samples. The colour differences between the control sample and the leathers processed with tanning agents were calculated according to CIE Lab-76 colour difference formula (CIE, 1976). Colorimetric measurements were carried out on both tanned and dyed leathers in triplicates.

RESULTS AND DISCUSSIONS

Colorimetric measurements and grey scale evaluations of the tanned leather samples before and after light fastness tests were given in Table 2. The tests were also performed after the post-tanning operations for the dyed leathers as provided in Table 3.

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Table 2. Colorimetric measurements and grey scale evaluations of the tanned leathers

Leather samples	Before analysis			After analysis			Color difference (ΔE)	Grey scale evaluation
	<i>L</i>	<i>a</i>	<i>b</i>	<i>L</i>	<i>a</i>	<i>b</i>		
Chromium tanned	79.13	-6.35	0.89	78.77	-7.74	1.47	1.55	4/5
Aluminum tanned	90.32	0.34	7.96	93.08	0.42	5.23	3.89	3
Zirconium tanned	92.03	0.23	7.55	94.11	0.29	4.95	3.32	3/4
Phosphonium tanned	91.35	0.12	7.95	93.38	0.11	5.84	2.94	3/4
Tara tanned	91.36	0.23	8.28	85.65	1.74	21.06	14.09	2

Table 3. Colorimetric measurements and grey scale evaluations of the dyed leathers

Leather samples	Before analysis			After analysis			ΔE	Grey scale evaluation
	<i>L</i>	<i>a</i>	<i>b</i>	<i>L</i>	<i>a</i>	<i>b</i>		
Chromium tanned	60.28	5.14	27.52	67.08	1.31	19.98	10.85	2/3
Aluminum tanned	56.87	10.16	32.33	65.81	6.63	25.97	11.52	2/3
Zirconium tanned	60.11	10.95	34.44	68.18	7.66	27.69	11.02	2/3
Phosphonium tanned	63.34	8.71	32.13	71.55	5.57	24.62	11.57	2/3
Tara tanned	54.44	10.55	29.41	61.06	8.30	26.51	9.57	2/3

The tanned leathers exhibited very slight differences in lightness values (*L*) except vegetable tanned leathers after the light fastness tests as indicated in Table 2. For yellowness (*b*) wet blue samples showed a slight increase, whereas aluminum, zirconium and phosphonium tanned leathers showed lower values than the original samples after the UV application. Tara tanned leathers gave the highest *b* value and exposed to high changes by increasing the yellowness value of the leathers. The colour differences (ΔE) showed that vegetable (tara) tanned leathers have the maximum ΔE values of 14.09. Besides, chromium tanned leathers yielded the minimum ΔE value of 1.55 which was the sign of minimum colour (ΔE) differences for the wet blue leathers as compared to control sample.

These differences were also observed and confirmed by the grey scale evaluations. Chromium tanning material provided the best light fastness value (4/5) compared to other white tanning materials. Zirconium and phosphonium tanned leathers had the same values (3/4) and better than aluminum (3) and vegetable tanned leathers (2).

After the post-tanning operations, no significant color differences between the leathers differentiated in tanning operations were observed. Minimum ΔE value was determined from vegetable tanned leathers while the highest value was seen from phosphonium tanned leathers. According to the grey scale evaluation, same light fastness values (2/3) were obtained for each dyed sample because of the dyeing process as seen in Table 3.

Most coloured materials can fade or change in color when they are exposed to light for prolonged periods of time. In a photochemical reaction it is necessary that at least one of the reacting molecules has absorbed light. This compound is then in an excited state. In systems in which the stability of a dyestuff is of interest, three basic types of photochemical reactions are possible. Firstly, the dye can absorb light and then decompose, because the dye molecules are not chemically stable in their excited form. Reactions with other substances present in the system are in this case not necessary for

the photodecomposition of the dye. A second possibility is that the photo-excited dye molecules are unstable only if certain other substances are also present in the system. These substances concerned are absent; the activated dye molecules are reconverted into their stable ground states by physical deactivation processes. Under these conditions no fading occurs. A third possibility is that substances, other than dyestuff, absorb the light and then react in their photo-excited state with the dyestuff (Ozgunay, 2008; Crews, 1987; Padfield and Landi, 1966).

The highest light fastness value was obtained with chrome tanned leathers as expected due to the strong covalent bonding between chromium and collagen. On the other hand, aluminum tanned leathers showed the poor fastness values among the white mineral and organic tanning agents since it forms only electrostatic interactions with collagen.

Aromatic organic structures tend to absorb high energy ultraviolet radiation and for this reason they are less radiation stable than aliphatic organic compounds. Tannins based on aromatic organic compounds cannot be high lightfast because of their nature. In our study it is also revealed that the lowest light fastness values were obtained from vegetable tanned leathers and their dyed forms.

CONCLUSION

In the study, the light fastness properties of sheep leathers tanned with different white tanning materials were aimed to determine to compare the results with the chromium tanned leathers and following conclusions have been drawn;

- a. The highest color difference was observed from the leathers tanned with tara vegetable tannin after the light fastness test.
- b. The leathers tanned with chromium salts gave the best light fastness value compared to white mineral tanning agents.
- c. Slight differences were determined after the light fastness test for the white mineral tanning agents.
- d. After the post tanning operations, high ΔE values were obtained compared to tanned leathers. But they showed only slight differences in terms of color change after the light fastness tests.

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