

LIGHTFASTNESS PROPERTIES OF LEATHERS TANNED WITH VARIOUS VEGETABLE TANNINS

by

H. OZGUNAY*

Ege University, Faculty of Engineering, Department of Leather Engineering
35100 BORNOVA-IZMIR - TURKEY

ABSTRACT

The color changes of bovine leathers, tanned with commonly used hydrolysable and condensed vegetable tannins, were measured colorimetrically as a function of prolonged irradiation with Xenon test light. The results showed that hydrolysable and condensed tannins exhibited differences in their light fastnesses. The color change of hydrolysable tannins under the effect of light was considerably low when compared to the condensed tannins. Gambier and quebracho tannins, among the condensed tannins, exhibited a rapid color change in the direction of red and yellow, while mimosa showed a slower color shift. Tara, among the hydrolysable tannins, exhibited a slower color shift than the others. At the end of 24 hours, the color changes, observed as darkening in all the tannin groups reached a maximum point after which color lightening was observed with extended time.

RESUMEN

Los cambios de color de cueros bovinos, curtidos con taninos vegetales condensados e hidrolizados de uso común, se midieron colorimétricamente como una función de irradiación prolongada a la prueba con la luz de xenón. Los resultados mostraron que los taninos hidrolizables y condensados muestran diferencias en su solidez a la luz. El cambio de color de los taninos hidrolizables bajo el efecto de la luz es considerablemente baja si se la compara con los taninos condensados. Taninos de gambir y quebracho, entre los taninos condensados, exhibieron un rápido cambio de color en la dirección de rojo y amarillo, mientras que la mimosa mostró un lento cambio de color. Tara, entre los taninos hidrolizables, exhibieron un cambio de color más lento que los demás. Al término de 24 horas, los cambios de color observados como oscurecimiento en todos los grupos de tanino alcanzaron un punto máximo, luego del cual un aclaramiento fue observado en un tiempo extendido.

INTRODUCTION

In recent years, the use of vegetable tanning materials has notably increased due to greater interest and demand towards natural products. Vegetable tanning materials are polyphenolic materials with molecular weight ranging from 500 to 3000-4000¹. They are classified into two groups; as pyrogallols, or hydrolysable tannins; and catechols, or condensed tannins². Quebracho, mimosa and gambier, among the condensed tannins; tara, chestnut and valonea among the hydrolysable tannins, are widely used in the Leather Industry.

The individual color properties of vegetable tannins and colors they confer to resultant leathers have great importance when natural colored leather manufacture is taken in consideration. Additionally, these types of leathers should preserve their colors without change during their usage time in manufactured products. With increased usage of ultraviolet producing fluorescent lighting in most environments, light induced degradation of colors has become more critical in recent decades. This constitutes a problem for today's customers demanding high performance and strict color specification.

The tanner prefers vegetable tannages because of the pleasing firm handle they confer to the leather, combined with good embossing, air and vapor permeability, natural look and feel properties. However, it is essential to be aware of their light fastness behavior for the reasons mentioned above.

Most colored 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 react with the photo-excited dye molecules, thereby converting them into other compounds. If the substances concerned are absent, the activated dye molecules are reconverted into their stable ground states by physical deactivation processes. Under these circumstances no fading occurs. A third possibility is that substances, other than the dyestuff, absorb light and then react in their photo-excited state with the dye stuff³.

Aromatic organic structures tend to absorb high energy ultraviolet radiation and for this reason they are less radiation stable than aliphatic organic compounds. Tannins and dyes, based on aromatic organic compounds cannot be very lightfast because of their nature.

Most natural dyes have poor to moderate light-fastness, while synthetic dyes represent the full range of light fastness properties from poor to excellent^{3,4,5}. These observable differences in light fastness are due to differences in their chemical and physical properties. The analysis of the natural dyes listed in Color Index revealed that almost 50% of all natural dyes used to color textiles are flavonoid compounds, which are not very light fast⁴. However, synthetic dyes can be produced from the compounds, which have good light fastness and resistance to photochemical degradation, i.e. metallized dyes show very good light fastness because of their strong molecular forces which hold the atoms in the molecule together.

The loss of, and change in color of dyed textiles upon exposure to light is a complex reaction affected by both the chemical and physical state of the dye^{3,4,6,7}.

Factors which have an influence on the fading of colored materials can be classified as:

1. Internal factors
2. External factors

Internal factors are the constitutions and properties of the dyes, the constitutions and properties of materials to which the coloring matter has been applied, the physical state in which the dyes are present, the properties of other substances present in the system, etc.

The main external factors are the humidity of the atmosphere, spectral distribution of the radiation to which the samples are exposed, and the temperature³.

It is practically known that hydrolysable tannins are more stable to light than condensed tannins⁸. However, there are not many detailed studies on the evaluation and comparison of the light fastness properties of tannin groups and of individual tannins. Vegetable tannins belonging to either hydrolysable or condensed tannins might have individual characteristics, behavior, color, and fastness properties besides the characteristics of the group they belong to.

In this study, except the vegetable tannins used for tanning the hides, the internal and external factors were kept constant. 3 different tannins were selected to represent each tannin group. These 6 tannins were used in tanning hides. The changes in the colors of the leathers tanned with different vegetable tannins were monitored spectrophotometrically as a function of time.

EXPERIMENTAL

Materials

Two limed/split, pickled hides were used as research material. Samples were cut out from the coupon areas, each measuring 11" x 8.5". These samples were used for the tanning trials. 3 hide samples were tanned with each vegetable tanning material.

The vegetable tannin extracts used for the study were industrially produced, commercially available products: three condensed tannins: quebracho (72% tannin, Silvachimica S.r.l. Cuneo, Italy), mimosa (72% tannin, Silvachimica) and gambier (min. 50% tannin, Silvachimica) and three hydrolysable tannins: tara (min. 48% tannin, Silvachimica), chestnut (72% tannin, Silvachimica) and valonea (68% tannin, Ar-Tu Kimya San. ve Tic. A.Ş. Manisa, Turkey). These are well-known vegetable tannins used in the Leather Industry, all supplied in the form of spray-dried powders.

Method

The tannins selected for the evaluation of their color and light fastness on leather were used in the tanning of sample hides according to the recipe given in Table I. The pH's of the pelts were adjusted to 4.0 - 4.2 before the tanning process for the hydrolysable tannins (tara, valonea, chestnut) that have more acidic character. pH's of the pelts were adjusted to 5.0 - 5.2 for condensed tannins (quebracho, mimosa, gambier). Since the tannin content of each commercial vegetable tanning material is different from others, 14.4% tannin amount was calculated based on the pelt weight, and used for the tanning.

Testing of Light Fastness

ATLAS XENOTEST ALPHA test equipment (Atlas Material Testing Technology, Chicago, USA) was used for measuring the light fastness of samples. The tests were conducted according to ISO 105-B02 standard method 2,⁹: 50 °C, 65% RH, Xenon arc test lamp, 7 IR filter, 42 W/m².

Colorometric Evaluation of Light Fastness

Minolta CM-508d spherical spectrophotometer (Minolta Co. Ltd. Japan) with 8 mm diameter of measurement area was used for measuring the colors of the leather samples. Spectral reflectance values were measured between 400-700 nm range with 20 nm intervals, and 16 readings were obtained for each sample. The measurements were done under the conditions of CIE 10° standard observer angle and CIE standard D₆₅ light source. The reflectance readings were

* Corresponding Author - Email: hasan.ozgunay@ege.edu.tr

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TABLE I
Tanning recipe

Process	Amount	Product	Time
Depickle	300%	Water 6 Be	5 min.
	1.5%	HCOONa	30 min.
	X%	NaHCO ₃	120 min.
			pH 4 - 4.2 Hydrolysable pH 5 - 5.2 Condensed
Drain&Wash Tanning	150%	Water	
	X %	Vegetable Tanning Material	45 min.
	X %	Vegetable Tanning Material	30 min.
	0.5%	Fatty alcohol sulfate soap	
	1%	Synthetic Fatliquor*	30 min.
	X%	Vegetable Tanning Material	30 min.
	0.5%	Fatty alcohol sulfate soap	
	3%	Synthetic Fatliquor*	5 h.
X%	HCOOH	1 h. pH 3.5	

Drain&Wash

*A commercial synthetic fatliquor with good lightfastness

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

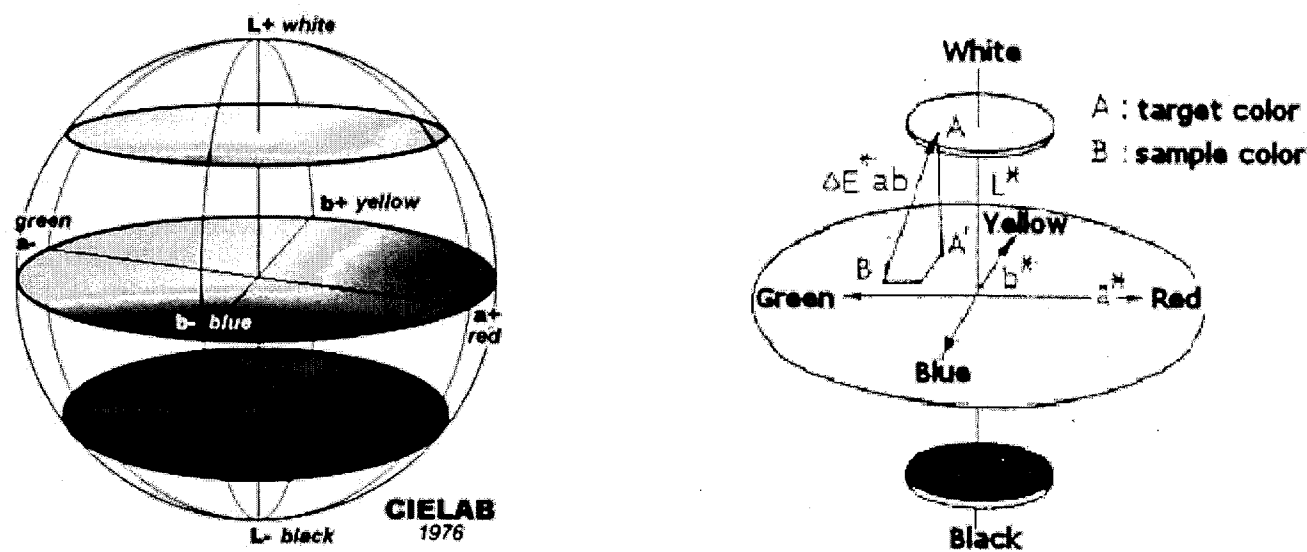


Figure 1: CIE LAB Color System and illustration of ΔE

converted to CIE L*a*b* values by using related formulas, and color differences were calculated by CIELAB 1976 color difference formula¹⁰.

The CIELAB 1976 color difference formula calculates the linear distance between the coordinates of the sample and target color, and this difference is shown by ΔE ¹⁰, Figure 1.

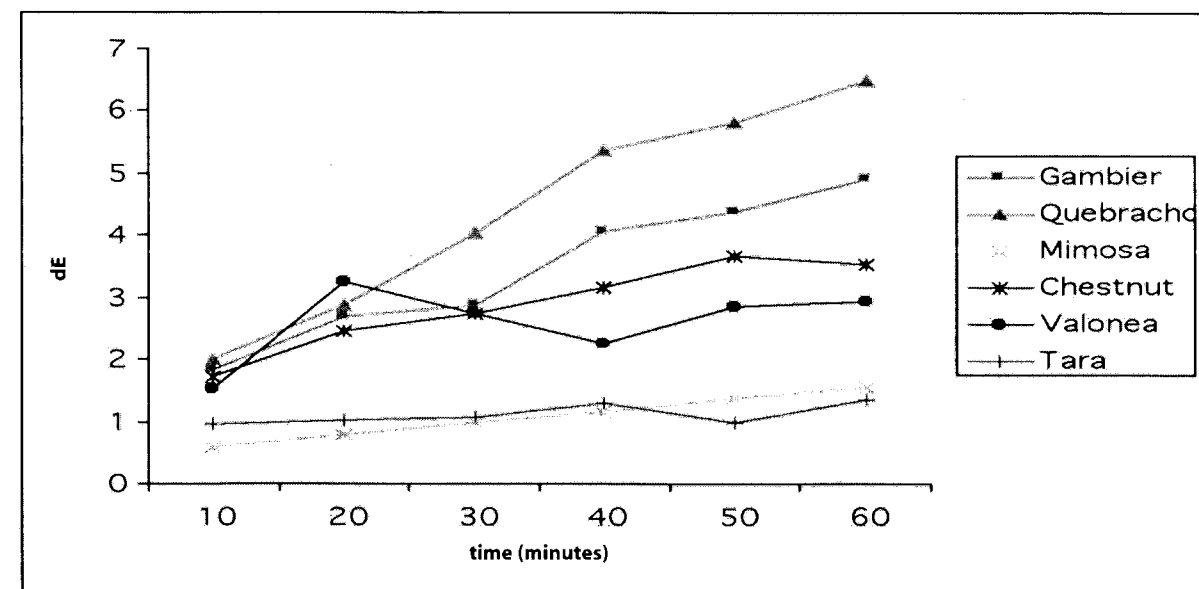


Figure 2: Color changes of samples in 0 - 60 minutes

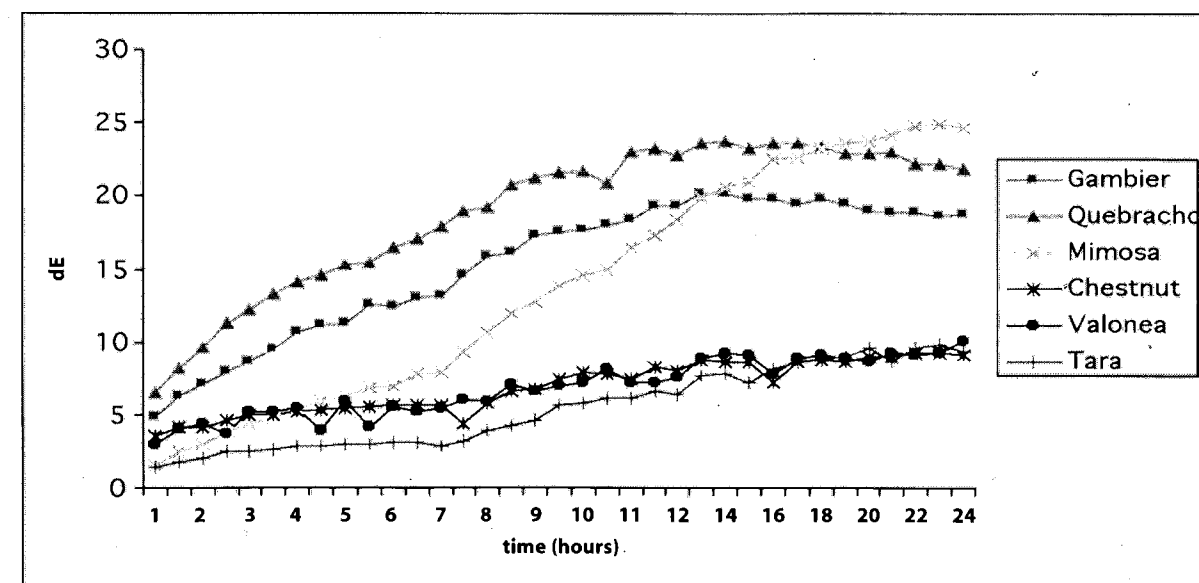


Figure 3: Color changes of samples between 1-24 hours

RESULTS AND DISCUSSION

The color changes (dE) of leather samples under Xenon arc test lamp related to time are given in the following figures.

Considering the color changes of samples in the first hour (Figure 2), the greatest color changes were observed respectively in quebracho, gambier, chestnut, and valonea tanned leathers. The leather samples tanned with tara and mimosa have shown the least color change.

When the color difference values between 1 - 24 hours were investigated (Figure 3), it was seen that all the colors of vegetable tanned leathers had shown color change due to

their aromatic organic nature. In this period, the color changes of condensed and hydrolysable tanned samples differed noticeably. So here, we can pronounce the common fact that hydrolysable tannins have higher light fastness properties than condensed tannins, which is clearly seen in Figure 4.

The sample tanned with mimosa showed less color change than the other condensed tannins, until around 6 hours. However, after 6 hours, the color of the sample increasingly changed and attained values similar to the other condensed tannins after 24 hours. It is thought that this behavior is related with the chemical structure of the mimosa tannin. Pasch *et al.*, have shown that mimosa is composed of

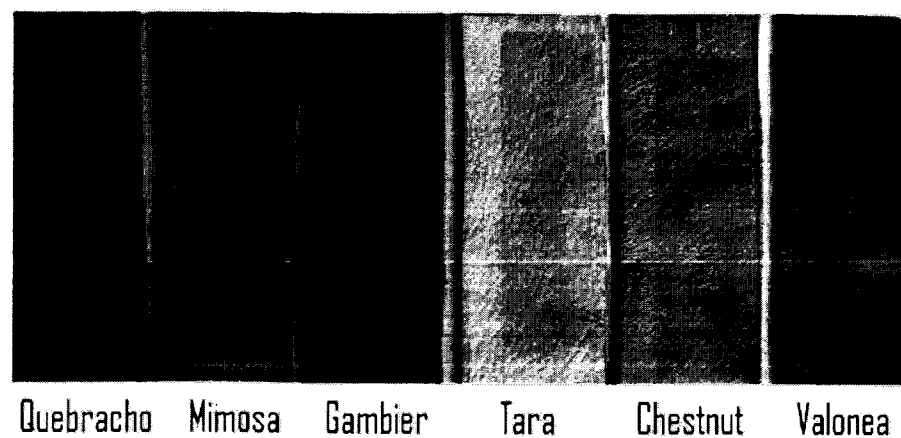


Figure 4: Color change variations among tannins (Ed Note: For figure in color contact the authors or JALCA editor).

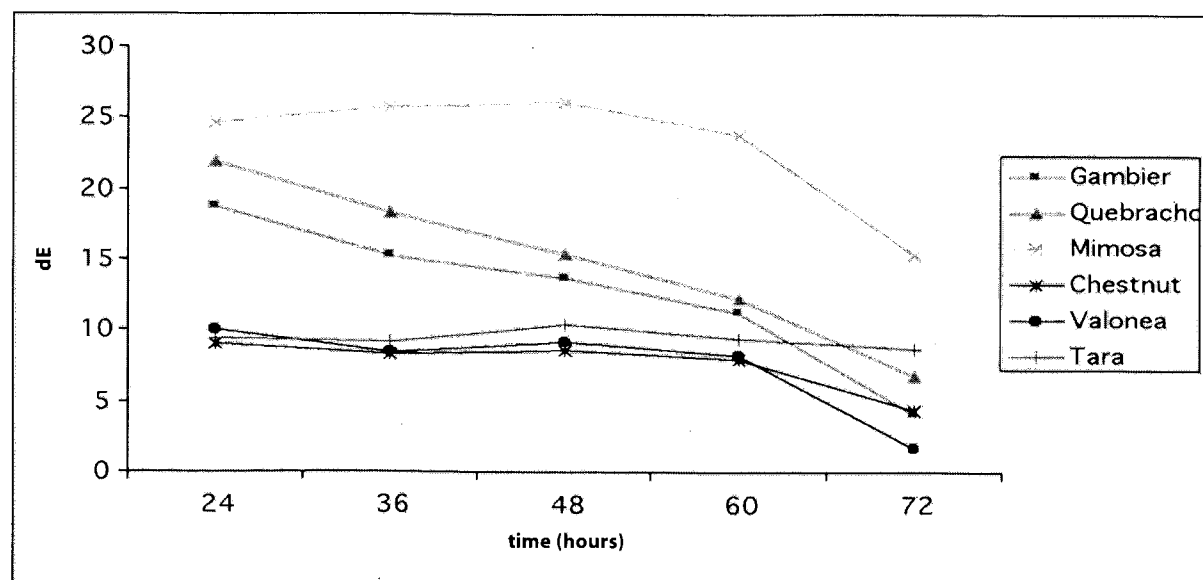


Figure 5: Color changes of samples between 24-72 hours

prorobinetinidins while quebracho is composed of profisetinidins, and mimosa is heavily branched while quebracho is almost completely linear, which makes it more easily hydrolysable, while mimosa is completely stable to hydrolysis because of its interflavonoid link¹¹.

Considering the hydrolysable tannins, chestnut and valonea showed similar behavior against the exposed light in all periods. The reason for this is attributed to their very similar chemical structure¹². The sample tanned with tara showed less color change than the other hydrolysable tannins in the first 8 hours, however the color change then began to increase and attained values similar to the other hydrolysable tannins at the end of 16 hours. After 24 hours, no significant color difference was observed among the samples tanned with hydrolysable tannins.

After 24 hours, the change in color difference values had maximized and had begun to decrease over prolonged time (24 – 72 hrs, Figure 5).

The color changes of samples during the whole period of trial are presented in Figure 6 to demonstrate the whole picture. Considering the overall period, all the color changes in leather samples showed an increasing slope in the first hours. However, after 12 hours, this increase began to slow down. After 24 hours, the changes began to decline and this behavior was symmetrical to the initial incline in the change of colors. For example, two tannins – quebracho and gambier – showing the most rapid color change in the first hours showed the maximum decrease in color difference after 24 hours. As in the initial hours, hydrolysable tannins did not show rapid change in color after 24 hours.

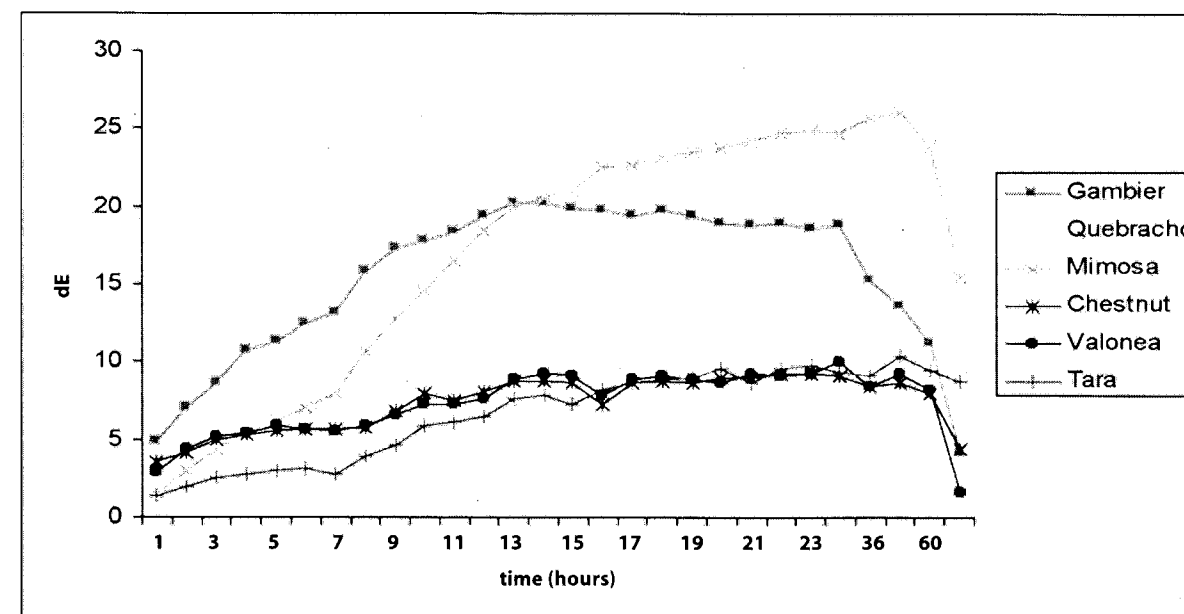


Figure 6: Color changes of samples in the whole period of time (0-72 hours)

TABLE II
Color difference values of samples at 12 and 24 hours

Time	Gambier				Quebracho				Mimosa			
	L	a	b	ΔE	L	a	b	ΔE	L	a	b	ΔE
0	61.40	11.44	30.53		68.48	14.14	24.68		71.49	8.32	17.02	
12h	46.06	20.09	38.54	19.34	49.57	22.30	34.48	22.81	55.43	16.17	21.52	18.44
24h	46.79	19.77	38.86	18.77	50.28	21.12	34.58	21.86	51.59	18.51	27.56	24.72
Δ12h	-15.34	8.64	8.01		-18.91	8.16	9.80		-16.06	7.85	4.50	
Δ24h	-14.61	8.33	8.33		-18.20	6.98	9.89		-19.90	10.19	10.54	
Time	Chestnut				Valonea				Tara			
	L	a	b	ΔE	L	a	b	ΔE	L	a	b	ΔE
0	69.05	6.03	22.47		56.18	6.14	25.91		78.98	3.56	15.16	
12h	61.32	5.95	24.68	8.04	49.31	7.09	29.01	7.60	73.75	6.62	17.31	6.43
24h	61.00	6.14	26.71	9.10	47.91	7.68	31.49	10.09	72.19	7.45	20.35	9.39
Δ12h	-7.73	-0.08	2.20		-6.88	0.94	3.10		-5.23	3.06	2.15	
Δ24h	-8.05	0.11	4.24		-8.27	1.54	5.58		-6.80	3.88	5.19	

Table II shows the CIE L, a, b values of leather samples at 0, 12 and 24 hours and the CIE Lab color difference values between 0-12 hours and between 0-24 hours. When the values are considered, it is seen that CIE L values of all leather samples show a decrease, which is more in condensed tannins and less in hydrolysable tannins. CIE a and b values of condensed tannins' have a tendency to increase, which means an increase in red and yellow tones when exposed to light. However, the color changes are not so drastic in hydrolysable tannins; only CIE b values of hydrolysable tannins have a tendency to increase, which means an increase in yellow tones when exposed to light.

CONCLUSIONS

In the light of the results above, we have reached the following conclusions:

- All vegetable tannins change their color when they are exposed to light due to their aromatic organic nature. The color changing reaction generally darkening of the vegetable tanned leather is due to formation of quinones on the phenolic structure of the vegetable tannin¹³.

- Condensed tannins change their color more, and more rapidly, than hydrolysable tannins due to their polyflavonoid structures.
- Among condensed or hydrolysable tannins, depending on their different chemical nature, some tannins can behave individually against light; for example mimosa from condensed tannins and tara from hydrolysables.
- The color changes in condensed tannins are in the direction of red and yellow that results in redder color, and in the direction of yellow for hydrolysables that causes yellowier color.
- All the color differences of vegetable tannins change to a limit, and after a particular time the change begins to decrease in parallel speed to initial increase. This lightening reaction is due to photodegradation of the system as cited before by Pizzi¹³.

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