Tannin Antioxidant Characteristics in Leather Versus Leather Light Stability: Models

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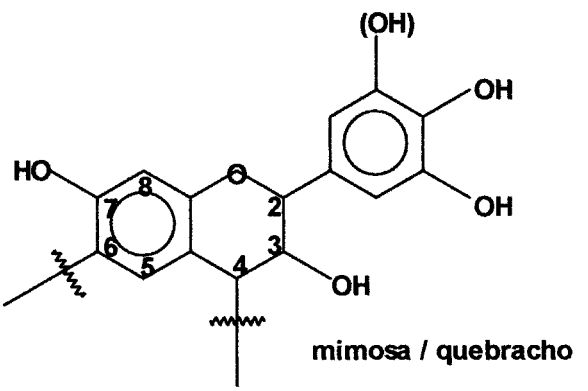
ABSTRACT: The variation of leather color as a function of aging time on prolonged irradiation with UV light of the leather produced by tanning with different polyflavonoid and hydrolyzable vegetable tannins is reported. A predictive model and two equations for the variation of leather color as a function of UV-irradiation time and as a function of the different vegetable tannins used was also established. This technique appears to describe well the overall phenomenon of oxidation and color change *in situ* observable in vegetable-tanned leathers. The variation of leather color as a function of aging time on prolonged irradiation with UV light of the leather produced based on different vegetable tannins was found to be composed of two main effects: The first one of these is the darkening reaction of the leather. This is due to the formation of quinones on the phenolic structure of the vegetable tannin. The second one is the leather-lightening reaction due to the photodegradation of the system. These two phases were equated and correlated with the radical uptake reaction and radical stabilization/decay reaction observed by ESR for UV-irradiation of pure tannin in the solid form and of the leather produced using the same. Thus, correlation among the antioxidant capability of tannins in the solid form, their antioxidant capability once included in the leather, and the color variation (darkening and lightening) of leather by colorimetry was established. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1030–1040, 2004

Key words: antioxidants; ageing; tannins; proteins; stabilization; renewable resources; irradiation

INTRODUCTION

The capability of phenols to produce rather stable phenoxyl radicals, by retarding or even inhibiting the progress of radical reactions, is well known.[1,2] Vegetable tannins present polymeric phenolic structures. The characteristic structures of the repeating units of polyflavonoid tannins[3,4] and the polymeric structure of the chestnut ellagitannins main component are shown below:



mimosa / quebracho

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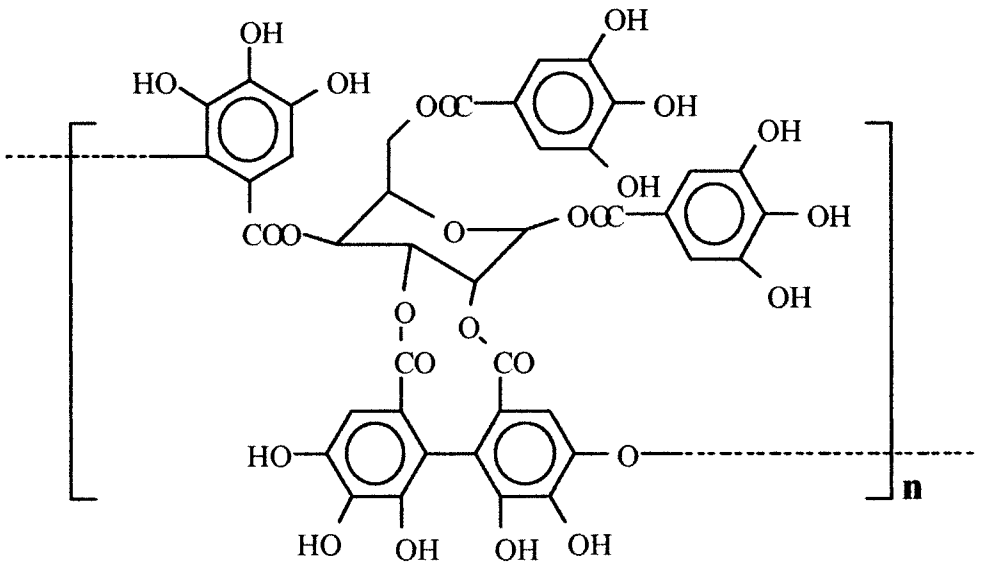


Recently, natural polyphenolic vegetable tannins have been shown, by use of electron spin resonance (ESR) analysis[2,5–7] and by stopped-flow techniques,[8] to be capable of similar, intense antioxidant effects. These studies were conducted on several natural tannin extracts[2,5,7] of the hydrolyzable and polyflavonoid types. Comparative kinetics were determined for both radical formation and radical decay reactions induced by both light-induced radicals and radical transfer from a less stable chemical species.[7] The parameters having a bearing on these reactions were identified. These studies were all carried out on vegetable tannin extracts alone—hence, not in the presence of any of the materials in which they are used. Thus, an effect or reactions that can be of considerable importance on just pure tannin extract may influence to a very different extent the material in which the tannin is used as an antioxidant. One of the main uses for vegetable tannins has been, for centuries, in the manufacture of leather, where among others their antioxidant capability is put to use.

The leather-tanning industry is one of the most ancient in operation. Although the technology of leather manufacture has evolved over centuries and even in recent years, the basic principles for the production of leather have remained the same. Hide proteins, mainly collagen, are rendered insoluble and dimensionally more stable by treatment with chemical products able to fix on them and render them both more resistant to mechanical wear and less susceptible to biological and other types of attack. Forestry-derived, natural polyphenolic tannins, such as chestnut and polyflavonoid extracts, used mainly for the manufacture of heavy, rigid, and hard leathers for shoe soles, saddles, belts, and other implements subject to high wear, are one of the main products still used today for leather tanning. Natural polyphenolic tannins have a strong astringent effect (they fix very effectively on the collagen structure) and give considerable "body," hardness, and toughness to the leather produced with them. They present, however, among others, the considerable disadvantage to have marked darkening problems when exposed to light. In the case of natural tannins, their capacity of photooxidation limits their use to applications where such a characteristic is of no consequence. It is the phenolic structure of the tannin itself which renders photooxidation possible.[7,9,10] Photoxidation and radical capture and retention by polyphenolic tannin structures have been shown to be closely related.[7] The main unknown is still the extent of the variation of leather color and its stability to UV-irradiation for prolonged periods and what type of law it follows.

This article then deals with

(i) The study of the rate of increase and decay of tannin phenoxyl radicals *in situ* in leather tanned with tannin extracts alone under prolonged UV-light irradiation, both by ESR and colorimetry.
(ii) Correlations to be deduced between the two methods.
(iii) The variation of tannin radical concentration and leather color as a function of photooxidation and aging time on prolonged irradiation with UV light. This for leather produced with pure vegetable tannin extracts.
(iv) Establishment of a predictive model and equation for the variation of leather color and light stability as a function of oxidation induced by accelerated UV aging.

EXPERIMENTAL

The vegetable tannin extracts used for this study were industrially produced, commercially available ones:

two polyflavonoid tannins and a hydrolyzable tannin. These three are the most used commercial ones for leather manufacture. Of the polyflavonoid tannins, unsulfited mimosa tannin extract, from the bark of the black mimosa tree (*Acacia mearnsii*, formerly *mollissima*, de Wildt) ex Tanac (Brazil), and sulfited quebracho tannin extract, from the wood of the quebracho tree (*Schinopsis balansae*) ex Indunor (Indusol Ato type, Argentina), were used. Their tannin content was 74%. The hydrolyzable tannin extract used was chestnut tannin, from the wood of the chestnut tree (*Castanea sativa*) ex Silva (Italy), with a tan content of 79%. All the tannins were in the form of spray-dried powders easily dissolvable in water.

Leather-tanning procedure

The hides to be tanned were weighed (weight = x), and 1.6 x parts by weight of water on hide weight were added, to which had been predissolved a given quantity y of vegetable tannin extract. The pH was adjusted to 5 and the whole continuously shaken overnight in a laboratory-sealed revolving tanning drum at ambient temperature. The pH was readjusted to 5 with an 8.5% formic acid solution, if required, and the whole shaken continuously for 4 h more at 50°C in a laboratory-sealed revolving tanning drum. The total by weight was then x parts of pelt, 2 x parts of tanning solution, and 1.6 x parts of water. Just for the ESR trial samples on leather samples, a 10% quantity on the tannin solids content of a melamine–urea–formaldehyde resin was added to the tanning cylinder just before the pH was readjusted to 5 with an 8.5% formic acid solution. The rest of the procedure remained the same.

The mechanical laboratory tanning setup used was composed of a metallic revolving rig having three fixed arms at 120° from each other. To these arms were fixed three plastic containers, one for each arm, of 1 L capacity each, and having a rounded corner rectangular section. The rig revolved by the aid of an electric motor at 58 rpm. The rig was maintained within a convection oven in order to be able to maintain a temperature of 50°C during the final treatment. The rotation of this rig gave rise to a complex shaking and tumbling movement of the hide specimens in the tanning solution.

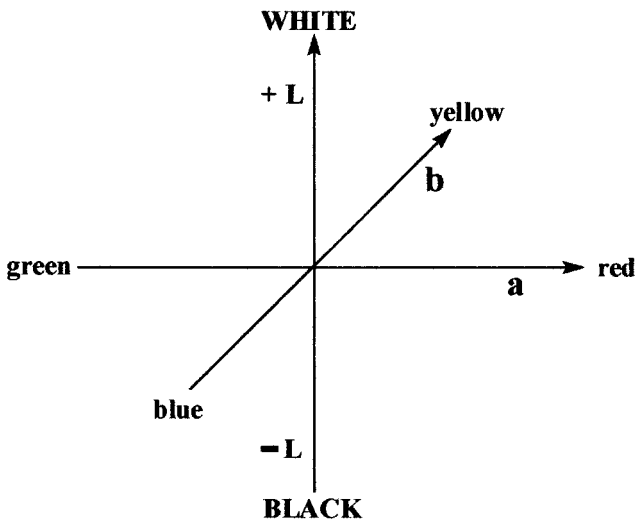
Stability to light and colorfastness testing by colorimetry

Color

Color depends on three parameters: L (black/white) (y); red–green = a (x–y); yellow–blue = b (y–z) as the components used to define the way color is perceived and described. Colorimetry is the objective and quantitative measure of the color of an object to define it in a conventional system of classification of color. The International Lighting Commission [Commission Internationale de l'Eclairage (CIE)] has defined a standard for color evaluation derived by extensive experiments.[11–14]

CIE lab 1976 color-evaluation system[11–14]

In this internationally agreed and recognized color-evaluation system, the axes green–red and blue–yellow define a chromatic plane. The axis perpendicular to this plane and passing for the intersection of the first two axes defines the clarity. In this manner, any color point can be exactly defined by its three coordinates L, a, and b:



where L represents the clarity; a, the chromatic component green–red; and b, the chromatic component blue–yellow. The system can equally be represented by its cylindrical coordinates L, C, and h, where L represents the clarity; C, the color saturation: $C = (a^2 + b^2)^{1/2}$; and h, the tonality (angle of color hue): h = arctan (b/a).

This system allows one to obtain the correct correlation between the differences between any two points of color and the difference in color effectively observed by a normal human observer. This allows one to define geometrical distances in the measuring system space which lead to several parameters of color variation, these being ΔL = the variation in clarity; $\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$, the total color difference, including intensity; $\Delta C = [(\Delta a)^2 + (\Delta b)^2]^{1/2}$, the chromatic difference; and $\Delta h = |(\arctan (b/a)_A - \arctan (b/a)_B)|$, the difference in hue, calculated as a numerical difference.

The measures in our case were made on samples of leather of 5-cm diameter before exposure in an UV weatherometer equipped of four medium-pressure mercury vapor lamps that allows the reproduction of

TABLE I
ESR Description and ESR-derived Kinetic Parameters for Vegetable Tannin-treated Leathers

Tannins	χ^2	X_0	Y_0	A_1	$t_1 = \tau$ (min^{-1})
Chestnut C, control	0.00162	0	1.391	−1.174 ± 0.101	7.09 ± 1.25
Mimosa, control	0.00092	0	0.511	−0.449 ± 0.020	17.19 ± 1.56
Quebracho, control	0.00052	0	0.326	−1.278 ± 0.016	13.95 ± 1.55

natural photometric aging. All radiation of wavelength lower than 290 nm absent from the sun spectrum is eliminated. The samples are fixed on a slowly rotating spindle that assures equal exposure to the UV radiation. Light flux at 360 nm was of 4.5 mW/cm^2, which, for the samples, is equivalent to a light radiation 45 times greater than that of sunlight. The variation of the parameters ΔL, ΔE, a, b, ΔC, and Δh was continuously monitored for all the experimental leathers throughout the 800 h of irradiation.

The colorimeters used were a portable Labomat Essor spectrocolorimeter, namely, the Spectrocolor Dr Lange Model and a Hunter Lab Color Quest with an integration sphere (having measurement geometry 0°/8°), allowing diffuse lighting of the samples and measurement of the light reflected at 8° in relation to the normal. It comprises a measuring probe and a spetrocolorimeter linked to a PC. It analyzes, wavelength by wavelength, the light energy reflected or transmitted by a specimen and determines also its spectral reflectance curve. A concave holographic diffraction network directs the light from the object under examination toward a small rod composed of 32 silicon detectors. The light-energy measure is then carried out for 32 wavelengths in 10 × 10 nm in the 400–710 nm range (corresponding to the visible range). From this reflectance spectrum, the PC calculates the various parameters of the color and for the lighting chosen.

ESR of leather and radical decay as a function of time of irradiation

ESR spectra were recorded at room temperature with a Brücker ER 200 D spectrometer. The samples were directly irradiated in a TE 102-type cavity by the emitted radiation from a Xe vapor lamp (OSRAM XBO 1000W). The radical concentration increase of some irradiated leathers was followed as a function of time. The kinetics were found to be of first order,[2,5,15–17] that is:

$$I(t) - I_0 = (I_\infty - I_0)(I - e^{-t/\tau}), \quad \text{with } \tau = \text{time constant (min}^{-1}) \quad (1)$$

where I_0 is the intensity of the signal before irradiation, and I_∞, the signal intensity at the steady state reached (thus, the value of the intensity to which the intensity value tends asymptotically).

The higher the time constant, the faster is the increase in radical concentration. In fact, both straight $I(t) - I_0$ values as well as the values obtained by dividing the left and right terms of the equation by I_0 in order to normalize all spectra and render comparison easier and more significant were charted.

To calculate $I(t)$, half of the signal height is measured carefully on the spectrum and then introduced into the following relationship:

$$I(t) = (1/2 \text{ height} \times Y \text{ scale})/\text{length of a scale division} \quad (2)$$

The data treatment was carried out by using Origin V software[18] according to the equation

$$Y = Y_0 + A_1 e^{\left(-\frac{X - X_0}{t_1}\right)} \quad (3)$$

The results obtained for the samples examined are shown in Table I. χ^2, in Table I, is a statistical value of conformity, a weighed mean of the squares of the differences between experimental and modeled values. The smaller the value of χ^2, the better will the model fit to the experimental reality.

RESULTS AND DISCUSSION

ESR of tannins alone

When talking of correlating the color change of leather and tannins with their photooxidative capability—hence, their antioxidant effectiveness—it is necessary to define what is intended for the antioxidant capability of tannin. This is not easy to answer because different aspects of this property are of use, to a different extent, according to the application. The antioxidant capability of tannin is a sum of effects, which can be defined as depending on the measurement of three parameters,[5] namely:

1. The rate at which a tannin is able to form a radical on irradiation.
2. The rate at which the tannin is able to form a radical when this is determined by the rate of radical transfer from a preexisting radical spe-

TABLE II
First-order Kinetics Obtained by ESR of Radical Formation, Radical Transfer, and Radical Decay of Three Pure Tannin Extracts

						Radical peak intensity ($\times 10^{-5}$)			
		Parameters				Max	Start	Difference	
Tannin	Cell	a	$k(s^{-1})$	r^a	$t_{1/2}$(s)	(60 min)	(0 min)	Units	%
Radical formation (first phase)									
Mimosa	Quartz	1.4974	1.549×10^{-4}	0.809	4474	95	41	54	132
	Glass	1.5069	1.510×10^{-4}	0.786	4604	67	29	38	131
Quebracho	Quartz	1.5546	1.513×10^{-4}	0.784	4580	191	80	111	139
	Glass	1.6545	1.605×10^{-4}	0.770	4316	164	63	101	160
Chestnut	Quartz	1.1748	0.610×10^{-4}	0.792	11,360	222	160	62	39
	Glass	1.2057	0.581×10^{-4}	0.742	11,927	182	128	54	42
Radical decay (second phase), after direct irradiation									
Mimosa	Quartz	0.909	0.874×10^{-4}	0.920	7931				
	Glass	0.928	0.639×10^{-4}	0.900	10,839				
Quebracho	Quartz	0.901	0.559×10^{-4}	0.910	11,571				
	Glass	0.846	0.379×10^{-4}	0.810	18,294				
Chestnut	Quartz	0.931	0.102×10^{-4}	0.740	68,177				
	Glass	0.934	0.197×10^{-4}	0.710	35,012				
Radical transfer from DPPH: Radical decay (second phase)						Radical formation (ESR) by stopped flow			
									[$t_{1/2}$ (s)]
Mimosa		0.972	17×10^{-4}	0.952	40,765	5	Too fast to measure		0.4
Quebracho		1.092	83×10^{-4}	0.978	8349	38	15 intensity units/1200 s		1.1
Chestnut		0.934	19.6×10^{-4}	0.708	35,357	21	Too fast to measure		20.6

[a] Coefficient of correlation.

cies. For example, the transfer to the tannin of a radical formed on a substrate, that is, collagen in leather, by irradiation.

3. The rate of radical decay of the tannin phenoxyl radicals formed.

The first parameter defines the ease with which a radical is formed preferentially on the tannin rather than on the substrate—hence, to collagen—in the case of leather. The faster the radical is formed on the tannin rather than on the substrate, the better protected is the substrate and the better is the macroscopic, noticeable antioxidant effect of the tannin.

The second parameter defines the ease and readiness of the tannin in subtracting a radical from a substrate, that is, collagen in leather, in order to protect it. The easier and the more rapid this transfer, the greater are the antioxidant capabilities of the tannin.

The third parameter defines how stable is the tannin phenoxyl radical formed. The more stable the radical formed, the slower is the rate of radical decay. This means that the inhibition of radical degradation of the substrate is more marked—hence, the better are the antioxidant properties of the tannin. A fourth effect, namely, the joint quenching of two tannin radicals with each other, while possibly of importance in pure tannin kinetics,[5] is of no consequence in the presence of the preponderant proportion of the substrate, such as in the leather case.

Comparisons of the rate constants or of the semi-transformation time $t_{1/2}$ for the UV-irradiation of tannin extracts only, obtained by ESR, are shown in Table II. The results in glass and quartz cells are comparable. Furthermore,

1. In presence of singlet oxygen (in air), on straight irradiation, mimosa and quebracho polyflavonoid tannins present the faster radical formation reaction while hydrolyzable chestnut tannin is slower (effect 1).

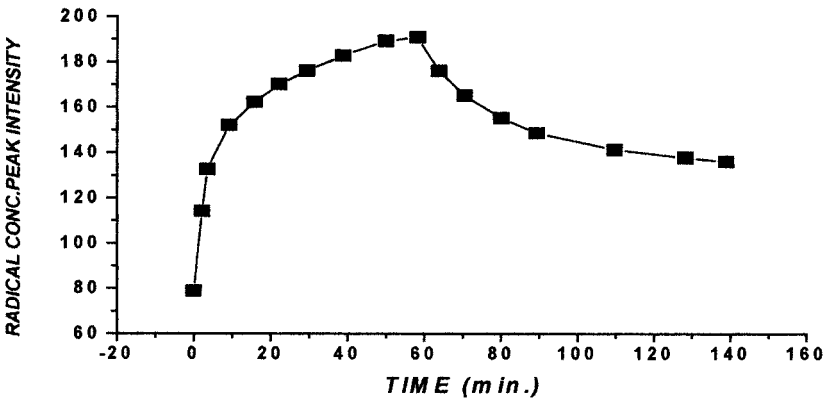


Figure 1 Typical example of the intensity increase and decrease of the average of the two opposite symmetrical phenoxyl radical peaks representing the ESR signal during UV-irradiation experiments of only quebracho flavonoid tannin extract powder in air and a quartz cell. The initial part of the curve up to the maximum of intensity describes the increase in radical concentration as a function of time during irradiation, while the decreasing intensity phase describes the radical decay reaction from the moment the UV lamp has been switched off.

2. The radical decay reaction in the presence of singlet oxygen (in air) indicates that chestnut tannin maintains the radical for much longer and, hence, is superior to quebracho and far superior to mimosa tannin (effect 3). This appears to be the most important effect.
3. The reaction of transfer of the radical from DPPH to the tannins was so fast in all three cases that it was impossible to measure it by ESR. This indicates that, for radical transfer, all the three tannins appear to be almost equally effective (effect 2). This effect can then be disregarded because the rate of formation of radicals on the tannin is so much more favorable than on the substrate that it is unlikely to occur too often.

A typical example of the radical concentration curves as a function of time obtained by ESR for tannins alone is shown in Figure 1. Figure 1 shows an example of the intensity increase and decrease of the average of the two opposite symmetrical phenoxyl radical peaks representing the ESR signal during UV-irradiation experiments. This is for quebracho flavonoid tannin extract powder in air and a quartz cell. The initial part of the curve in Figure 1, up to the maximum of intensity, describes the increase in the radical concentration as a function of time during irradiation. The decreasing intensity phase of the curve in Figure 1 describes the radical decay reaction from the moment the UV lamp has been switched off.

Thus, from the result of the values of k' and $t_{1/2}$ in Table II, the two effects of importance indicate that, as regards effect 1 radical formation, the faster the better, and in decreasing order of the formation rate, the trend is

$$mimosa \geq quebracho \gg chestnut$$

As regards effect 3, equally from the values of k';and $t_{1/2}$ in Table II and from the rate of radical decay, the slower the better, and the scale from slowest to less slow is

$$chestnut \gg quebracho > mimosa$$

In comparing the values of $t_{1/2}$ in Table II of the two effects for the three tannins, one notices that radical decay (effect 3) is the dominant one. Thus, in ESR testing of tannins alone, the total trend in antioxidant effectiveness of the three tannins should indeed be

$$chestnut \gg quebracho \geqslant mimosa$$

(with $>$ indicating here "better than").

The work done with a stopped-flow apparatus on the antioxidant capability of a number of different tannins alone by radical transfer from DPPH gave a scale similar to what was obtained by ESR (see Table II) for the first reaction phase, namely, radical formation/transfer. The scale here also was in decreasing order of the radical assumption rate, namely, *Mimosa* $\geq$ *Quebracho* $\gg$ *Chestnut*. In such stopped-flow experiments, the antioxidant capability of the different tannins was equated, incorrectly, only to the first part of the reaction,[12] while it was shown above that this is, in reality, only one of the two causes contributing to it.

Colorimetry of vegetable tannin-treated leather

The shape of the curves of ΔL and ΔE obtained on 800 h of UV-irradiation of leather prepared using the same vegetable tannins are shown in Figure 2(a,b). These curves present a very similar trend as shown by the ESR curves of tannins alone in Figure 1, with the ΔE curve following the same trend and the ΔL pre-

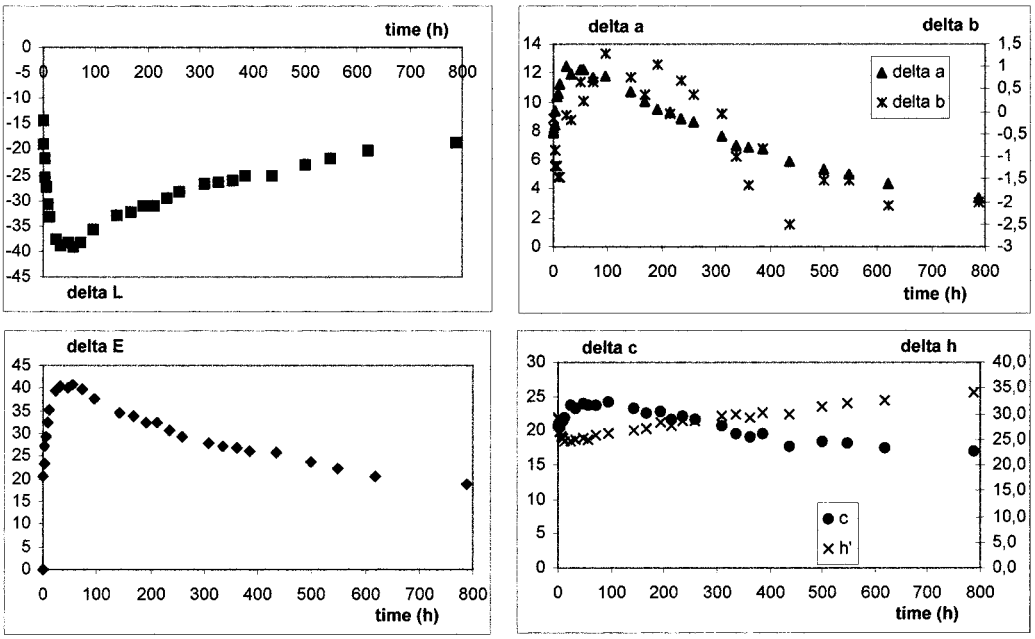


Figure 2 Typical example of parameters (a) ΔL, (b) ΔE, (c) Δa and Δb, and (d) ΔC and Δh, of CIELab color-evaluation system as a function of UV-irradiation time in hours for one type of vegetable tannin leather (a mimosa-tanned leather case).

senting an almost mirror image of the ESR curves in Figure 1. This trend is characterized by initial leather darkening caused by quinone formation on the phenolic structure of the tannins, followed by partial discoloration due to degradation caused by radical decay reactions. A typical example of the variation of the parameters important to evaluate color stability to UV-irradiation of the series of leather samples tanned with VegTan/MUF is shown in Table III. The same variation is illustrated by the shape of the kinetic curves of ΔL, ΔE, and ΔC and of Δa, Δb, and Δh obtained, also shown in Figure 2(a–d). The exact numerical values and the corresponding curves for all the cases of leather treatments used were reported elsewhere.[2,5]

These colorimetry curves were modeled in order to be able to forecast the trend of ΔE and ΔL as a function of time. The shape of the ΔE and ΔL curves (and the curves of other parameters) is composed of two effects, the same two effects observed by ESR on tannins alone. These are the oxidation reaction, which darkens the leather by formation of quinones, and the color-degradation reaction, which makes the leather lighter. It is the combination of these two trends and of the two curves representing them that yield the ΔE and ΔL peak composite curves observed in Figure 2(a–d). It is possible to model the influence of the two effects and to obtain an equation describing the trend of the experimental data. The model that has been applied is of the type

$$L = Ae^{-k_1 t} + B\left[1 - \left(\frac{k_2}{k_2 - k_1}\right)e^{-k_1 t} + \left(\frac{k_1}{k_2 - k_1}\right)e^{-k_2 t}\right] \quad (4)$$

TABLE III
Values of Coefficients A, A', and B and of Parameters k_1 and k_2 of Eq. (4) in the Modeling of ΔL and ΔE in Light and Colorfastness of Experimental Leathers

	ΔL			ΔE		
Tannin type	Chestnut	Quebracho	Mimosa	Chestnut	Quebracho	Mimosa
A	43.971	54.136	43.830	7.7815	6.8800	3.4634
k_1	0.0026	0.0047	0.0026	0.0371	0.1136	0.0047
B	70.980	69.785	61.972	−24.519	−26.19	−430.13
k_2	0.0378	0.0253	0.0226	0.0165	0.0059	0.0787
A'	—	—	—	35.843	31.909	435.13
min.err.	9.9104	492.21	555.35	116.70	102.73	95.91

Variable modeling: approach 2. Minimized error (min.err.)=minimized $\Sigma[(L_{\text{experimental}} - L_{\text{modeled}})^2 \sqrt{t}]$.

where L is the clarity as defined by the CIELab system; t, the time in hours; and A, B, k_1, and k_2, the parameters to be determined in the different cases. The first term in eq. (4), namely, $Ae^{-k1}t$, models the first decrease as a function of time of the value of L, a decrease due to phenolic oxidation and quinone formation, and, hence, leather darkening. The second term, with coefficient B, models, instead, the increasing part of the L curve which follows and which describes the leather color degradation—hence, leather lightening.

The parameters A, B, k_1, and k_2 can be determined according to two different approaches. In both cases, both k_1 and k_2 are set to be positive.

1. The initial value of L obtained at $t = 0$ is fixed and the other parameters are left free to vary until the error $\Sigma[(L_{\text{experimental}} - L_{\text{modeled}})^2 \sqrt{t}]$ is minimized (the multiplication by $\sqrt{t}$ is done to minimize the influence of the first values obtained during the initial L-decreasing phase).
2. No parameter is fixed at the start, the initial L-decreasing phase being minimized in relation to what was obtained first with the first method. In this method also, the parameters are left free to vary until the error $\Sigma[(L_{\text{experimental}} - L_{\text{modeled}})^2 \sqrt{t}]$ is minimized (and the minimum of this is indicated at the bottom of each case in Table III). This approach gave, by far, the best results. The results for this model are reported in Table III.

As regards the modeling of ΔE as a function of UV-irradiation time, a modification on the model represented by eq. (4) had to be implemented. This is so due to the initial, much more marked and sudden variation of E in relation to L in the initial phase of radical formation. This required the introduction in eq. (4) of a further term, namely, an A' term, to give eq. (5) below. The model that was best suited to represent ΔE as a function of UV-irradiation time was then as follows:

$$E = Ae^{-k_1 t} + A'[1 - e^{-k_1 t}] + B\left[1 - \left(\frac{k_2}{k_2 - k_1}\right)e^{-k_1 t} + \left(\frac{k_1}{k_2 - k_1}\right)e^{-k_2 t}\right] \quad (5)$$

For the model described by eq. (5), the same two approaches described above for eq. (4) were used as regards minimization of the error $\Sigma[(E_{\text{experimental}} - E_{\text{modeled}})^2 \sqrt{t}]$. The results for the second approach of the modeling of ΔE are shown in Table III. The minimized values of the error for ΔL and ΔE are shown for all the cases in Table III. All the experimental leather samples were modeled according to these two approaches.

A typical example of the fitting of the models obtained to the experimental points for ΔE, according to the best, the second, of these two approaches, is shown in Figure 3(a,b). The curve in Figure 3(a) is the total curve over the full 800-h irradiation period, while the curve in Figure 3(b) shows the details of the coincidence of the experimental points and the model during the first 100 h of UV-irradiation only.

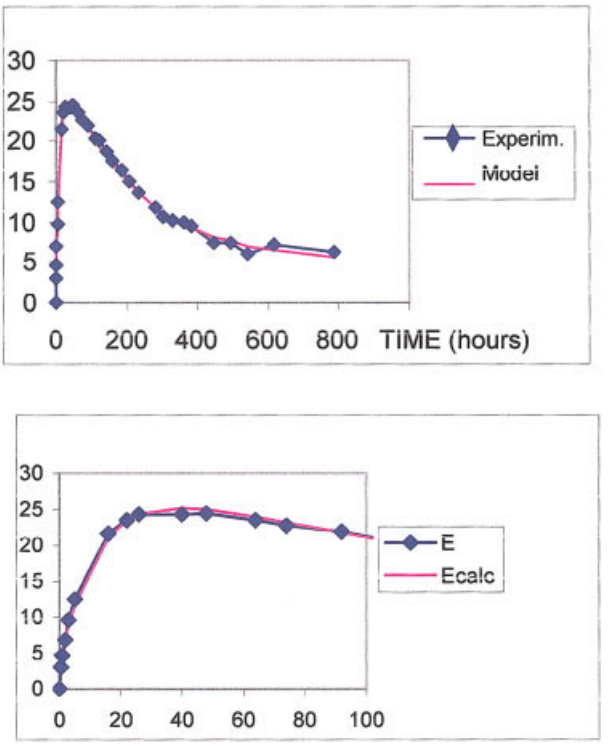


Figure 3 Typical example of model curve fitting for ΔE as a function of of UV-irradiation time for one type of vegetable tannin leather showing the better fit between model and experimental points obtained by approach 2: (a) model fit for approach 2 {eq. (5)] over the total 800 h of irradiation and (b) detail of the fit in (a) over the initial period of 100 h irradiation (case shown mimosa-tanned leather).

In all the cases studied, the second modeling approach yields a much closer fit with the experimental points than in the case of the first modeling approach, especially in the first section of the curve. It is for this reason that the values of A, B, A', k_1, and k_2 for the variation of L (hence, ΔL) and E (hence, ΔE) are only reported here for all the cases of leather made with the different tannins. Their values are shown in Table III. The model fit was particularly good, and the error small, in all the cases in which the hydrolyzable tannin, chestnut, was used, while the error was at its maximum in all the cases in which mimosa polyflavonoid tannin was used.

The curves obtained by colorimetry present a clear similarity of the trend to the curves obtained by ESR describing the antiradical effectiveness of tannin alone.[5] This correlation appears valid in the case of antiradical scales of effectiveness of tannins obtained when the role of the singlet oxygen is not minimized,[5]

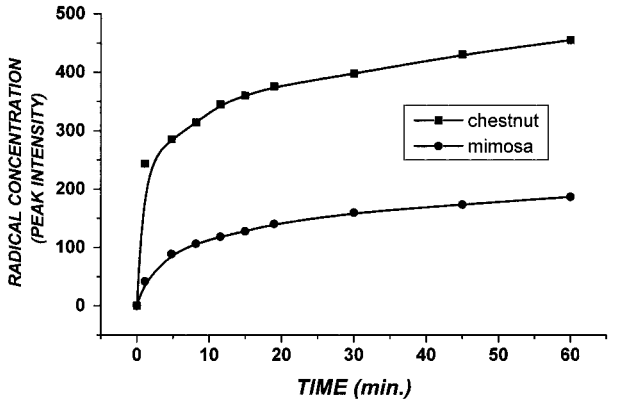


Figure 4 Typical examples of the intensity increase of the average phenoxyl radical ESR signal during UV-irradiation experiments of leather tanned with two vegetable tannins. The curves describe *in situ*, in the leather, the increase in radical concentration as a function of leather-irradiation time due to the tannin and tanning formulation. The treatments are identical—only the type of tannin used is different, namely, chestnut and mimosa. The curves describe the two phases of radical formation and radical decay occurring simultaneously: (■) ESR curve of chestnut tannin-treated leather; (○) ESR curve of mimosa tannin-treated leather.

as in the case of leather in air, but this similarity extends to just a qualitative shape trend and no more. Thus, correspondence does exist between the antioxidant activity of tannin by itself and the color fastness of the leather made using the same tannins.

ESR of vegetable tannin-treated leather

As regards the ESR study of the effectiveness of the same tannins, *in situ*, once they have reacted with collagen to form leather, the situation is more complex. In Table I, the value of the time constant τ allows the comparison of the effectiveness of the different polymers in leather: (i) as regards their stability to radical formation, and (ii) in rendering the leather treated with them also resistant to the formation of light-induced radicals. It could then be used as a measure of the lightfastness of a material, measured directly at the molecular level and by molecular level analytical means, rather than by eye chromatic perception methods. The higher the value of τ in Table I, the slower is the radical formation. This means that, in treated leather, the trend in a scale of antioxidant effectiveness is

$$chestnut > quebracho > mimosa$$

This means that the results shown in Table I represent what occurs in the totality of the two reaction phases of the tannin alone, namely, simultaneously, both the radical formation and decay phases. The two effects occur then at the same time and are in competition with each other. The higher the value of τ in Table I, which also corresponds to that the higher is the value of $t_{1/2}$ in Table II the slower is the radical formation. Thus, the ESR of the leathers treated with the three tannins give a cumulative curve of the two effects, namely, radical formation and decay, tending asymptotically toward an equilibrium. Curves of this type can be observed in Figure 4. The difference in appearance of the ESR curves in leather (Fig. 4) and for the tannin alone is due to the different design of the two types of experiments. Leather was UV-irradiated continuously. For the tannins alone, UV-irradiation was stopped after a certain time. This was done to observe the pure radical decay kinetics and model them (Table II, Fig. 1).

The trend of the ESR curves shown in Figure 4, which appear different from what was shown in Figures 1–3, can then be explained on the basis of the simultaneous occurrence of the two reactions. The order of the antioxidant effectiveness of different tannins, *in situ* in the leather, can also be explained on the basis of the simultaneous occurrence of the two reactions. Thus, it can be explained by the combination of radical formation and decay curves observed for the tannins only (Fig. 1). Figure 5 shows this schematically: A marked variation in the radical decay rate yields leather ESR curves that are the composition of the two effects. This is so for two tannins having the same radical formation rate and curve (Fig. 5). Hence,

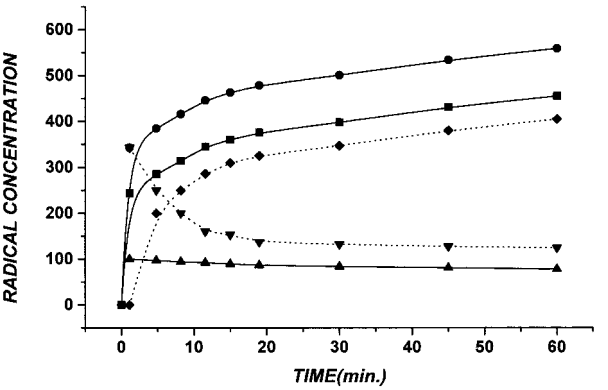


Figure 5 Schematic representation and explanation of the simultaneous occurrence of radical formation and radical decay in ESR kinetics of treated leather explaining the trend of the experimental curves shown in Figure 4. Compare with the different shapes of the ΔE curves in Figure 3: (■) ESR curve of chestnut tannin-treated leather composed of the simultaneous occurrence and combination of the curves (●) of the radical formation of chestnut-treated leather and (▲) of the radical decay of chestnut-treated leather; (◆) ESR curve of mimosa tannin-treated leather composed of the simultaneous occurrence and combination of the curves (●) of the radical formation of mimosa-treated leather and (▼) of the radical decay of mimosa-treated leather. Note that the radical-formation curves for the two tannins are shown as coincidental in the scheme to facilitate understanding.

this yields a real, macroscopic, single curve proportional to the effectiveness of the tannin both as an antioxidant *in situ* in the leather and of its intensity as an agent of leather color variation. Thus, good correlation exists between the combination of the tannins' antioxidant effectiveness scales with the results obtained on leather by colorimetry. The effectiveness scales were obtained for the tannins alone and *in situ* in the leather.

The relationship between τ and ΔL and ΔE is, however, rather complex. The parameter τ is a composite of two causes occurring in "parallel." For ΔL and ΔE instead, the two causes of the curve are mainly in "series." The two values (τ and ΔL or ΔE), issued from different analytical techniques, namely, ESR and colorimetry, describe in a different manner a similar set of properties. τ only represents, through a single parameter, a mix of effects, while the kinetics of ΔL and ΔE obtained by colorimetry represent separately the two effects. Thus, by following ΔL and ΔE, the relative kinetics of each contributing reaction can be clearly distinguished. This is not the case for τ. By using τ, however, a single parameter can describe the total visual effects occurring in leather. In principle, the lower the value of τ, the faster should be the shift toward radical uptake and the slower the simultaneous radical decay to reach a *radical uptake* $\leftrightharpoons$ *radical decay* equilibrium; hence, the material should be more stable to light. Figure 5 indicates that the slower the radical decay is, the higher is the accumulation of radicals on the tannin and the lower is its accumulation on the substrate. This means that the lower the concentration of radicals in the substrate, the better is the substrate protection. It is, again, the radical decay that is proven to be the more influential of the two effects as regards the antioxidant capability of the vegetable tannins by themselves and within leather. Where the ESR curves of pure tannin are represented, such as in Figure 1, correlation with the ΔL and ΔE curves of colorimetry (Fig. 1) is, indeed, much clearer. The relationship of the values of just τ with ΔL is, instead, very complex. Last, to further confirm that the correlation, however complex, does indeed exist, halving the amount of material used for the hide treatment does also decrease markedly the value of τ. This indicates that it is, indeed, the tannin which is able to absorb and stabilize the free radicals formed.

The results of ΔL and ΔE already obtained by colorimetry[1] indicate the same trend as that of the ESR results, although the differences in proportion are not quantitatively equal. This solves the uncertainty that has existed in the interpretation of what are the parameters from which the antioxidant effectiveness of tannins depends for different applications.[5]

CONCLUSIONS

The kinetic results obtained by colorimetry indicated that this technique appears to describe well the overall phenomenon of oxidation and color change *in situ* observable in vegetable-tanned leathers. The variation of the leather color as a function of aging time on prolonged irradiation with UV light is composed of two main effects: The first is the darkening reaction of the leather. This is due to the formation of quinones on the phenolic structure of the vegetable tannin. The second is the lightening reaction due to the photodegradation of the system. These two phases were equated and correlated with the radical uptake reaction (first phase) and radical stabilization/decay reaction (second phase) observed by ESR for UV-irradiation of pure tannin in solid form. The equal trend of the two sets of curves shows that the two analytical techniques describe similar, if not completely coincident, phenomena as regards light fastness of vegetable-tanned leather. It was also shown that the ESR results describing the radical uptake and decay vegetable-tanned leathers presented a differently shaped curve. This was due to the combination of the simultaneous occurrence of radical uptake and decay, the two effects reaching an equilibrium. Thus, correlation between the antioxidant capability of tannins in solid form, their antioxidant capability once included in the leather, and the color variation (darkening and lightening) of leather by colorimetry was established. A predictive model and two equations for the variation of leather color as a function of UV-irradiation time and as a function of the different vegetable tannins used was also established.

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