

# Ionic Polycondensation Effects on the Radical Autocondensation of Polyflavonoid Tannins: An ESR Study

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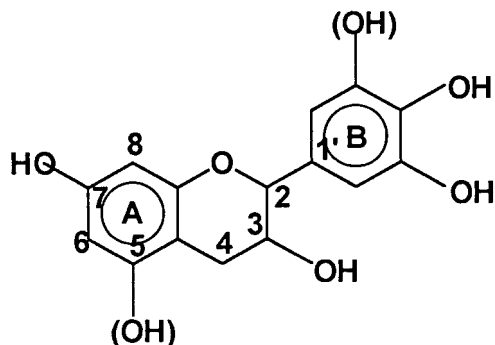
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**ABSTRACT:** An electron spin resonance (ESR) study of the presence or lack of interference by ionic hardening mechanisms and ionic coreactants on the polyflavonoid tannin radical autocondensation reaction indicated that in certain cases hardening by ionic coreactants can be coupled with the simultaneous hardening of the tannin by radical autocondensation. Some coreactants tend to depress the tannin radical autocondensation while still leaving a small contribution of this reaction to the formation of the final crosslinked network. Other coreactants instead appear to enhance formation of the final network by synergy between ionic and radical mechanisms, while still others do not show any interference between the two types of reaction. Mechanisms describing the interaction between the two reactions are proposed and discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2623–2633, 1997

## INTRODUCTION

Polyflavonoid tannins are natural polyphenolic materials which can be hardened by reaction with formaldehyde.<sup>1</sup> They have now been used for over 20 years as industrial thermosetting tannin–formaldehyde adhesives for wood products.<sup>1</sup> Industrial polyflavonoid tannin extracts are mostly composed of flavan-3-ols repeating units and smaller fractions of polysaccharides and simple sugars. Two types of phenolic rings having different reactivities with formaldehyde are present on each flavan-3-ol repeating unit, namely, A-rings and B-rings:



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Recently, the radical mechanisms of the reaction of autocondensation and networking to hardened resins of polyflavonoid tannins induced by bases and by weak Lewis acids were described.<sup>2–8</sup> The application of such a reaction for the application to wood adhesives of tannins hardened without the use of an aldehyde was also examined.<sup>9</sup> The results of this latter investigation revealed that, notwithstanding the differences in structure and behavior of different polyflavonoid tannins, effective wood particleboard bonding could be obtained based just on the autocondensation reaction of tannins. The results showed, however, that tannins hardened in this manner only yielded bonds of interior-grade quality,<sup>9</sup> while the reaction of tannins as phenolic materials with formaldehyde has always traditionally yielded weather- and boil-proof networks—hence, exterior-grade bonds.<sup>1</sup> The reasons for such behavior have been ascribed mainly to the low crosslinking density of tannin networks obtained exclusively through their reaction of autocondensation.<sup>9,10</sup>

The autocondensation reaction of tannins to yield resins, however, still holds great interest as bonded wood products which do not emit formaldehyde (as none has been added) can be produced.<sup>9,10</sup> To examine, then, if exterior-grade

hardened tannin networks still conserving the property of yielding no or very low formaldehyde emission can be obtained, it is necessary to examine if the use of much reduced amounts of the traditional coreactants and hardeners for polyflavonoid tannins, which react by two-electron, ionic mechanisms<sup>1,10</sup> to form polycondensates, could be used coupled to the mainly, but not only, radical autocondensation reaction.

This article investigated the influence and effects caused on polyflavonoid tannin radical autocondensation by the presence of the most common tannin resin coreactants and hardeners such as paraformaldehyde,<sup>1</sup> formalin,<sup>1</sup> urea,<sup>11–13</sup> paraformaldehyde + urea,<sup>14</sup> hexamethylenetetramine (hexamine),<sup>16,17</sup> furfuryl alcohol,<sup>18,19</sup> and polymeric 4,4'-diphenylmethane diisocyanate (MDI).<sup>20,21</sup>

## EXPERIMENTAL

### Tannin Types

Four types of commercial flavonoid tannin extracts were used, namely, (1) pecan (*Carya illinoensis*) nut membrane tannin extract, from the United States, (2) pine (*Pinus radiata*) bark tannin extract, from Chile, (3) natural quebracho (*Schinopsis balansae*) wood tannin extract, from Argentina, and (4) quebracho tannin extract modified for use in wood adhesives according to procedures already reported.<sup>22</sup>

### Coreactants

Seven different coreactants known to react in different manners with flavonoid tannin extracts were used. These were (1) paraformaldehyde 96% fine powder; (2) 39% formalin solution stabilized with 9% methanol; (3) urea, analytical grade; (4) hexamethylenetetramine (hexamine), 99% purity grade; (5) furfuryl alcohol, 99% purity grade; (6) polymeric 4,4'-diphenylmethane diisocyanate (MDI, Bayer 44V20); and (7) fine Aerosyl silica smoke (pure SiO<sub>2</sub>).

### Tannin Extracts Solutions and Electron Spin Resonance (ESR) Spectroscopy

Tannin extract water solutions of 10% concentration were prepared by dissolving a spray-dried powder of each tannin extract in water and adjusting to pH 13 with a 33% solution of sodium hydroxide. To these solutions were added 10% of each coreactant by weight of dry tannin extract.

A combination of two of the coreactants, namely, paraformaldehyde and urea, was also tested.

ESR spectra of all the solutions were done at 293 K on a Brüker ER 200 D spectrometer (X-band) equipped with a TE<sub>102</sub> sample cavity. Fine structures of the phenoxyl radical signals in the range 3465–3495 Gauss, centered on the signal of DPPH as the standard<sup>23</sup> at 3843 Gauss, were studied with a field modulation intensity of 0.5 Gpp and scan times of 60 s. The decay of each radical concentration was followed by scanning the material after an initial coreactant addition at 60 s for a period of 1 h or more. Thus, on the same material, an ESR spectrum was done on average every 120 s for a period of 1 h or more. Each experiment was duplicated and each of the points given in the figures is the average of the two measurements. The method used to fit the data into equations was an iterative method.<sup>24</sup> The program iterates until the expression

$$|(\chi_i^2 - \chi_{i-1}^2)/(\chi_i^2 + \chi_{i-1}^2)|$$

where

$$\chi^2 = \left\{ \sum_{i=1}^n \left[ f(x_i) - y_i \right]^2 \right\} / [N - n]$$

is less than a given tolerance value, which in the present calculations was taken as 0.05;  $N$  is the number of observations;  $n$ , the number of fitting parameters;  $f()$ , the fitting function,  $x_i$  and  $y_i$ , data points; and  $N - n$ , the degrees of freedom.

## DISCUSSION

The radical decay reaction of the phenoxyl radicals was followed by the variation as a function of time of the peak intensities of the resolved fine structure of the phenoxyl signal in the presence of the different coreactants. In general, between 8 and 10 peaks appeared, in reality representing only four to five radical-anion species, as each peak is the mirror image around the symmetry center of the spectrum of another peak representing the same species.<sup>5–8</sup> Of these, the four mirror image peaks closer to the symmetry center of the spectrum are representing radical anions on the tannin B-rings while the four or six further away from the spectrum center of symmetry represent the radical anions on the tannin A-rings. The curve of the rate of decrease of each peak intensity, for each peak, for each of the four tannins,

and for each of the eight cases (one control and seven coreactant) for each tannin was modeled by double exponential equations of the type

$$Y = Y_0 + A_1e^{-x/T_1} + A_2e^{-x/T_2} \quad (1)$$

where  $x$  is the reaction time,  $Y$  and  $Y_0$  are, respectively, the total peak intensity of the peaks at a time  $t$  and the residual intensity (time  $\rightarrow \infty$ ),  $A_1$  and  $A_2$  are the preexponential factors, and  $1/T_1$  and  $1/T_2$  are the two rate constants ( $s^{-1}$ ). Considering the number of peaks which could be followed for all the different cases, this gave rise to 205 equations of this type for which  $Y_0, A_1, A_2, T_1, T_2$ , the coefficient of correlation between model and experimental data, and the value of  $Y$  at time = 0 were determined and recorded. A few examples of these equations are shown in Table I, but as there is clearly not the space in an article of this kind to report all the 205 equations obtained, these are accessible to

the reader elsewhere.<sup>25</sup> Previous research on the radical-induced autocondensation of tannins was generally modeled by single exponential expressions with the exception of pine tannin (which could not be easily modeled) and pecan tannin for which a double-exponential expression was always used.<sup>6-8</sup> In the experiments presented here, the double-exponential expression was used in all cases because the double-radical decay curves became much more evident. This indicates that the presence of ionic coreactants enhance this effect far beyond what is generally observed with only the tannins by influencing somehow the radical mechanism of autocondensation.

The relative proportions of the initial radical concentration intensity for different tannins and different coreactants—hence, the rate of radical decay describing the radical component of the autocondensation, is generally in the order (from higher and faster to lower and slower)

Pine tannin

$SiO_2 \sim isocyanate \geq urea > hexamine \sim furfuryl alc. > \underline{tannin alone} > paraf. \sim formalin \sim paraf./urea$   
 radical reaction increases  $\Leftarrow| \Rightarrow$  radical reaction decreases

Pecan tannin

$isocyanate > SiO_2 \sim urea > formalin > furfuryl alc. > \underline{tannin alone} > paraf./urea \sim paraf. > hexamine$   
 $\Leftarrow| \Rightarrow$

Natural quebracho tannin

$SiO_2 \gg urea \geq \underline{tannin alone} \geq isocyanate > furfuryl alc. \sim hexamine > formalin \sim paraf./urea > paraf.$   
 $\Leftarrow| \Rightarrow$

Modified quebracho tannin

$isocyanate > formalin > urea > paraf./urea > hexamine > furfuryl alc. \sim \underline{tannin alone} \sim paraf. > SiO_2$   
 $\Leftarrow| \Rightarrow$

In tannins in which the colloidal level is high (the first three above), silica, isocyanate, and urea, in general, cause an increase in the radical response of the system, increasing the relative proportion of radical autocondensation mechanisms in relation to ionic ones. Paraformaldehyde, and most often also formalin and paraformaldehyde + urea, instead favor polycondensation through ionic mechanisms: They work then as proper polycondensation hardeners and minimize the relative importance of the radical reactions of the system. Hexamine and furfuryl alcohol change behavior according to

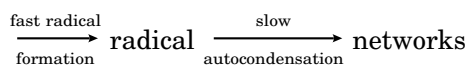
the type of tannin in a manner which is difficult to explain.

In Table II are given all the relative intensity values of the two A-ring and of the two B-ring ESR peaks (hence, of only one each of the mirror images) and of the total intensity of these four peaks for all the cases studied. Only  $SiO_2$ , paraformaldehyde, urea, and isocyanate give a consistent increase or decrease in the radical surge for all the tannins.  $SiO_2$  achieves this by the already-described<sup>2,5,6</sup> Lewis acid-induced mechanism of heterocyclic ring opening of flavonoid units. The effect of urea may be related to

**Table I An Example of the  $Y_0$ ,  $A_1$ ,  $A_2$ , and  $Yt = 0$  Coefficients (Values Presented Are by  $10^{-7}$ ) Obtained in the Pine Tannin + Paraformaldehyde Case Modeled by the Equation  $Y = Y_0 + A_1 e^{-x/T_1} + A_2 e^{-x/T_2}$**

Peak (Gauss)	3395.7	3396.7	3397.6	3398.5	3399.3	3400.5
$Y_0$	1281.87	1147.22	520.87	281.03	1432.69	1674.98
$A_1$	2228.90	790.20	458.46	1038.75	1768.88	3244.90
$T_1$	150.58	690.77	1395.20	5337.32	1976.52	263.08
$A_2$	1339.41	722.08	634.70	1232.82	1960.69	1388.55
$T_2$	1480.60	3406.67	13536.94	669.67	204.65	1902.80
$r$ (coefficient correlation)	0.998	0.991	0.967	0.995	0.997	0.998
$Yt = 0$	4850.18	2659.51	1614.03	2552.61	5162.26	6308.43

(1) its well-known capacity of disruption of the association of the tannin colloidal particles in solution<sup>11-13</sup>: That this is the case is shown by its effect being stronger the more colloidal<sup>22</sup> is the tannin, namely, in the order natural quebracho  $\gg$  pine  $>$  pecan  $\gg$  modified quebracho adhesive. (2) While urea is also known to block or retard tannin autocondensation,<sup>11</sup> mainly by an ionic mechanism, an important contribution by a similar effect on the radical mechanism cannot be excluded as a retardation of the autocondensation:



which will increase the radical autocondensation in the intermediate stage and, hence, initial peak intensity.

Why isocyanate should have a strong influence on the increase in the initial peak intensity (thus on the radical surge) is not immediately evident. A  $-\text{N}=\text{C}$  group in isocyanate and an amido group in urea might behave as an additional base shifting to higher values of the system pH and thus cause an increase in radical-anion generation by an additional attack on the B-rings of the flavonoids. However, their contribution to the alkalinity of the system is small in relation to the already high level of base present, and although some effect could be expected, this would not be as noticeable, as shown in Table II.

The reasons and mechanism for the paraformaldehyde depression of the initial radical concentration surge are, in short, as follows: As the radicals are formed, a rapid reaction and crosslinking through ionic reactions with formaldehyde subtract radicals very rapidly from the system. Such an effect occurs also for formalin on pine tannins and modified quebracho tannin, while for pecan tannin and particularly for modified quebracho tannin, formalin enhances instead the initial radi-

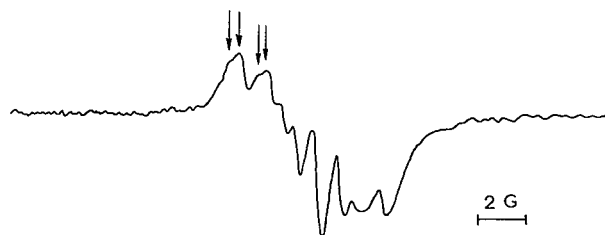
cal concentration. This means that other effects might also be at play according to the polymerized or depolymerized form the formaldehyde is presented in. It is not possible to advance an opinion on this based on the present data. The paraformaldehyde + urea case yields a combination of the two separate effects (Table II). This can also be observed in Figure 1 for the natural quebracho tannin case: There are double peaks in the ESR spectrum. In general, it is mostly the paraformaldehyde effect which predominates.

In the case of hexamine, it must be remembered that hexamine starts to decompose at about 65°C,<sup>26</sup> while the tests reported were carried out at ambient temperature (25°C), and, consequently, hexamine under these conditions cannot behave as does formaldehyde as it cannot decompose. It behaves instead as a monoprotic nitrogen base,<sup>26-28</sup> as any amine or amide might behave. There are some important differences, however, when comparing hexamine behavior to that of urea: While the hexamine effect is less intense than that of urea, undissociated hexamine being after all a monoprotic weak base, in the case of pine tannin, its action is not at all on the B-ring but definitely on the flavonoid A-rings, confirming previous findings<sup>27,28</sup> that monoprotic hexamine leads an attack directly on fast-reacting phenolic rings before its decomposition to formaldehyde.<sup>27,28</sup> Recent findings<sup>16,29</sup> on its decomposition at higher temperatures in the presence of fast-reacting phenolic rings, or other fast reacting species, confirm such findings.

As regards the hexamine case, it is possible to also start to see the relative variations of the intensities of the A-rings in relation to the B-ring peaks. In pine tannin, its action on the A-ring peaks is evident by the consistently higher radical concentration increase on these rings: If A-ring peaks are not observed as separate peaks, then a single taller peak is the resultant effect. Equally,

**Table II Relative Maximum Intensities Compared to the Tannin + Base Alone Controls and Percentage Changes for A-ring and B-ring Peaks of Polyflavonoid Tannin Extracts in of Different Ionic Coreactants of Different Tannin Extract Types**

Gauss from Spectra Center of Symmetry	A-rings				B-rings				A-rings				B-rings							
	% Change		% Change		% Change		% Change		Total	% Change	% Change		% Change		Total	% Change				
	2.3	1.5	2.3	1.5	1.1	0.5	2.3	1.5	1.1	0.5	1.1	0.5	1.1	0.5	1.1	0.5				
	Pine Tannin								Pecan Tannin											
Base alone	5.4	—	7.3	—	5.4	—	4.8	—	22.7	—	5.2	—	5.0	—	3.4	—	4.0	—	17.6	—
+ SiO <sub>2</sub>	8.4	+56	11.2	+53	10.8	+100	7.0	+46	37.4	+65	6.0	+15	6.4	+28	6.0	+76	6.8	+70	25.2	+43
+ hexamine	6.4	+19	9.2	+26	5.6	+4	4.9	+2	26.1	+15	2.4	-54	2.4	-52	1.8	-47	2.0	-50	8.6	-51
+ furfuryl alcohol	5.8	+7	8.0	+10	5.9	+9	5.0	+4	24.7	+9	5.4		5.4		3.6		5.4	+35	19.8	+13
+ paraformaldehyde	3.5	-35	4.8	-34	4.3	-20	3.5	-27	16.1	-29	3.8	-27	4.1	-18	4.2	+24	4.1	+3	16.2	-8
+ urea	8.3	+54	9.9	+36	9.3	+72	6.7	+40	34.2	+51	7.6	+46	7.2	+44	4.4	+29	5.6	+40	24.8	+41
+ urea + paraformaldehy.	2.6	-52	3.1	-58	3.8	-60	3.1	-35	12.6	-45	—		5.4		5.4		5.4		(16.2)	(-8)
+ formalin	3.6	-33	4.0	-45	4.4	-19	3.8	-21	15.8	-30	5.6	+8	6.8	+36	5.2	+53	5.6	+40	23.2	+32
+ isocyanate	7.2	+33	8.8	+21	11.6	+115	9.6	+100	37.2	+64	22.1	+325	20.7	+314	11.7	+244	18.0	+350	72.5	+312
	Natural Quebracho Tannin								Modified Quebracho Tannin											
Base alone	12.8	—	7.6	—	-0.4	—	—	—	20.0	—	3.2	—	1.6	—	0.9	—	0.8	—	6.5	
+ SiO <sub>2</sub>	20.0	+56	11.5	+51	1.5	—	—	—	33.0	+65										
+ hexamine	10.0	-21	5.2	-32	0.0	—	—	—	15.2	-24	3.6	+13	2.4	+50	2.8	+211	3.6	—	12.4	+91
+ furfuryl alcohol	9.4	-27	5.6	-26	0.8	—	—	—	15.8	-21	1.6		1.2		1.8		2.0		6.6	+2
+ paraformaldehyde	2.9	-77	—	—	—	—	—	—	2.9	-86	1.8		1.6		1.8		1.1		6.3	-3
+ urea	13.6	+67.2	—	—	0.4	—	—	—	21.2	+6	6.3		5.6		4.2		2.8		18.9	+191
+ urea + parformaldehy.	8.1	-37	4.3	-43	—	—	—	—	12.4	-38	4.8		4.1		2.2		2.0		13.1	+102
+ formalin	8.2	-36	4.6	-39	-0.3	—	—	—	12.5	-38	7.0		8.6		6.6		5.8		28.0	+331
+ isocyanate	10.5	-18	6.3	-17	1.2	—	—	—	18.0	-10	6.4		9.2		10.2		7.7		33.5	+415



**Figure 1** Presence of a double-peak system for the combined action of paraformaldehyde and urea on modified quebracho tannin extract.

the reaction of paraformaldehyde is always by ionic reaction with the A-rings.<sup>1</sup> In isocyanates, the influence of the coreactant is on the B-rings. In urea, it is on both the B-rings and A-rings, indicating that for urea both causes described are at work. In the case of silica, the effect is strong on all the peaks, but unusually also on the B-rings, it being a consequence of the presence of the equilibrium between the different radical-anions or a consequence of the reaction of  $\text{SiO}_2$  on the A-rings in the already reported manner<sup>2,5,6,10</sup> and on the B-rings in some other manner. In Tables II and III is shown the relative importance of the different additives on the different tannin aromatic rings. Furfuryl alcohol, as noticeable in the scales reported above and from Tables II and III, appears to have little or no influence on the tannin autocondensation reaction, i.e., it can only react ionically at acid pHs while the tests were mainly done at alkaline pH and, hence, paraformaldehydelike interference with tannin autocondensation does not appear to occur.

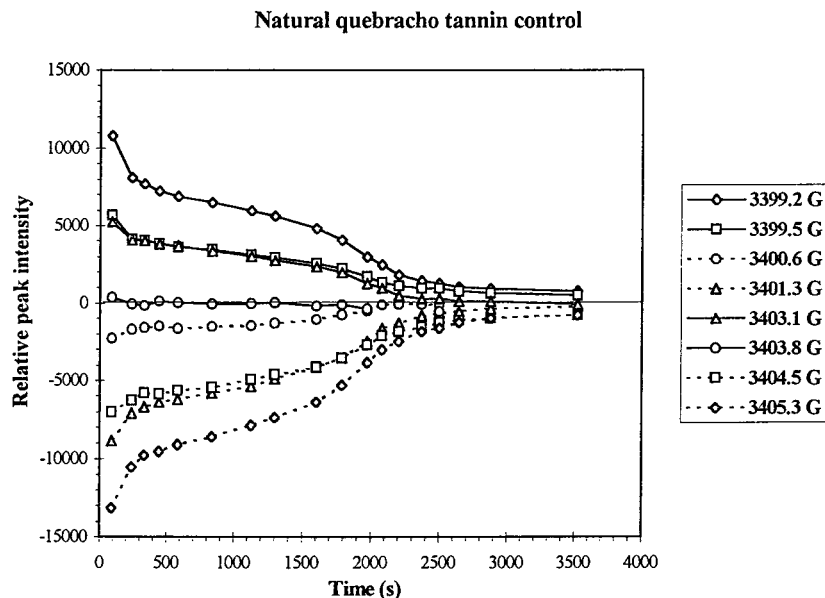
While the kinetic equations presented describe at acceptable level, with coefficients of correlation

of between .92 and .999, the decrease of the phenoxyl radical concentration, a few other interesting observations were possible: What meaning can be attributed to a two-component decay as represented by the equations? Deviation of the position of the experimental points from the regression curve of the model indicates that reactions other than simple radical decay appear to be present. Thus, as the rate of rapid radical decay indicated by the sharp slope of the initial part of the curves starts to slow down, the reestablishing of the concentration of the B-ring radical by a shift in the  $A = B$  equilibrium becomes so noticeable as to cause an upsurge, a "bump" in the curve, in radical concentration. Equilibria between the different radical-anions are then important and rapidly shifting, influencing the relative concentration of each radical-anion during radical decay reactions.

In this context, the graphs depicting the decrease in radical concentration as a function of reaction time for each peak (for each radical-anion), in the presence or absence of ionic coreactants, are also of interest. Four types of graphs occur, as shown in Figures 2 and 3 and in the examples which are subsets of Figure 2 such as in Figures 4 and 5. The graphs of the type shown in Figure 3 show the usual rapid radical concentration decay curve modeled by eq. (1). The situation is more complex for the cases in which the graph appears as in Figure 2 or even as in Figures 4 and 5. In these, after an initial decrease (Fig. 2) or even increase (Figs. 4 and 5) in the radical concentration with the progress of the reaction, the radical decay slows down to form a plateau which can be quite flat, or of slightly

**Table III** Indication of the Main Action That Each Ionic Coreactant Has on the Radical Response of the A-ring and B-ring Structures of Different Tannins

Coreactant	Main Action (*) on							
	Pine		Pecan		Modified Quebracho		Natural Quebracho	
	A	B	A	B	A	B	A	B
$\text{SiO}_2$	*	*		*	*	*	*	
Hexamine	*		*	*		*		*
Furfuryl alcohol								
Paraformaldehyde	*		*		*			*
Urea	*	*	*	*	*	*		
Urea + paraformaldehyde	*				*	*		*
Formalin	*		*	*	*	*		*
Isocyanate		*	*	*	*	*		*



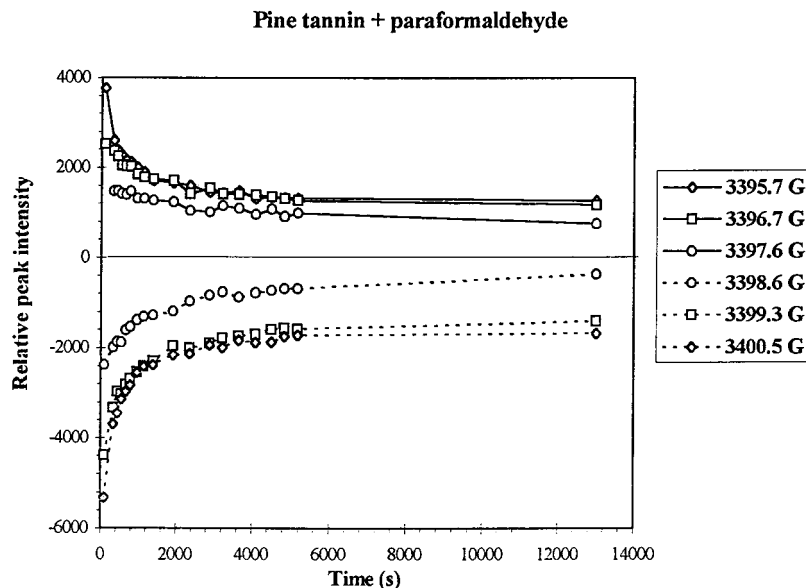
**Figure 2** Trend in the variation of intensity as a function of reaction time of all the peaks in the series of ESR spectra of natural quebracho tannin + base alone. Note the mirror image aspect of the curves in relation to the center of symmetry of the ESR spectra (Y axis = 0 line) and the presence of the plateau effect in the range of 500–1700 s reaction time.

descending slope, followed by a final radical decay reaction.

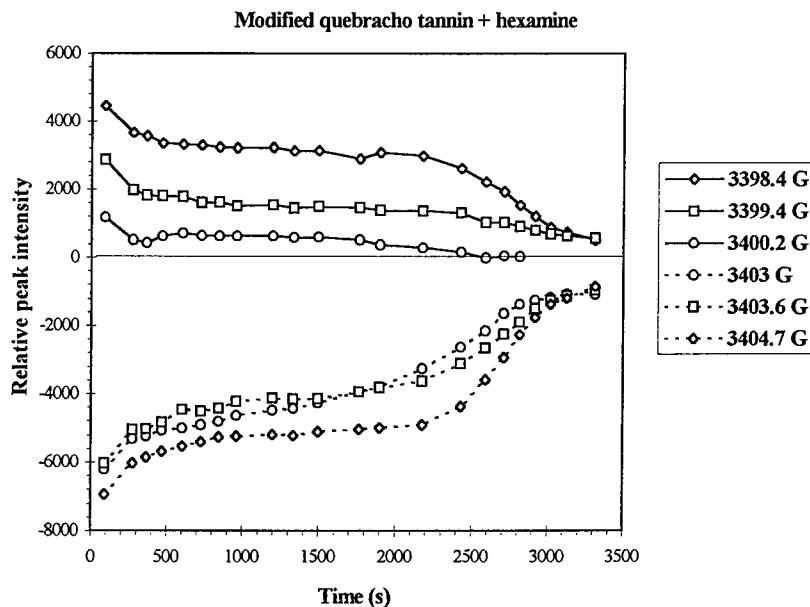
These peculiar shapes of the radical decay curves indicate that several complex reactions are at play, especially when ionic coreactants are

present. Three initial hypotheses could be advanced for this behavior:

1. The presence by transfer or other reactions of radical species different from the phe-



**Figure 3** Trend in the variation of intensity as a function of reaction time of all the peaks in the series of ESR spectra of the pine tannin + paraformaldehyde case. Note the absence of the plateau effect.

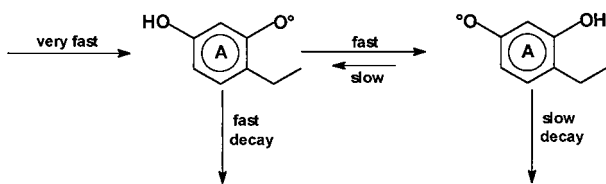


**Figure 4** Trend in the variation of intensity as a function of reaction time of all the peaks in the series of ESR spectra of modified quebracho tannin + hexamine. Note the presence of the plateau effect in the range of 500–2300 s reaction time.

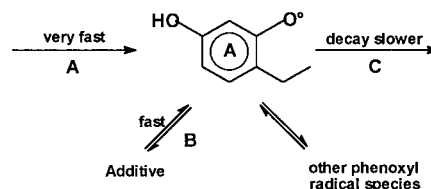
noxylys, a possibility which is unlikely because no other types of radical species are shown in the ESR spectra.

2. The presence of ionic equilibria with the added coreactants on top of the known equilibrium between the flavonoid radical-anions.
3. The presence of ionic reactions with the added coreactants which would subtract radicals to the main equilibrium between the flavonoid radical-anion species.

The existence of (2) and (3) above are rather likely. Mechanisms to explain the radical decay curve behavior for the A-rings radicals can be advanced:

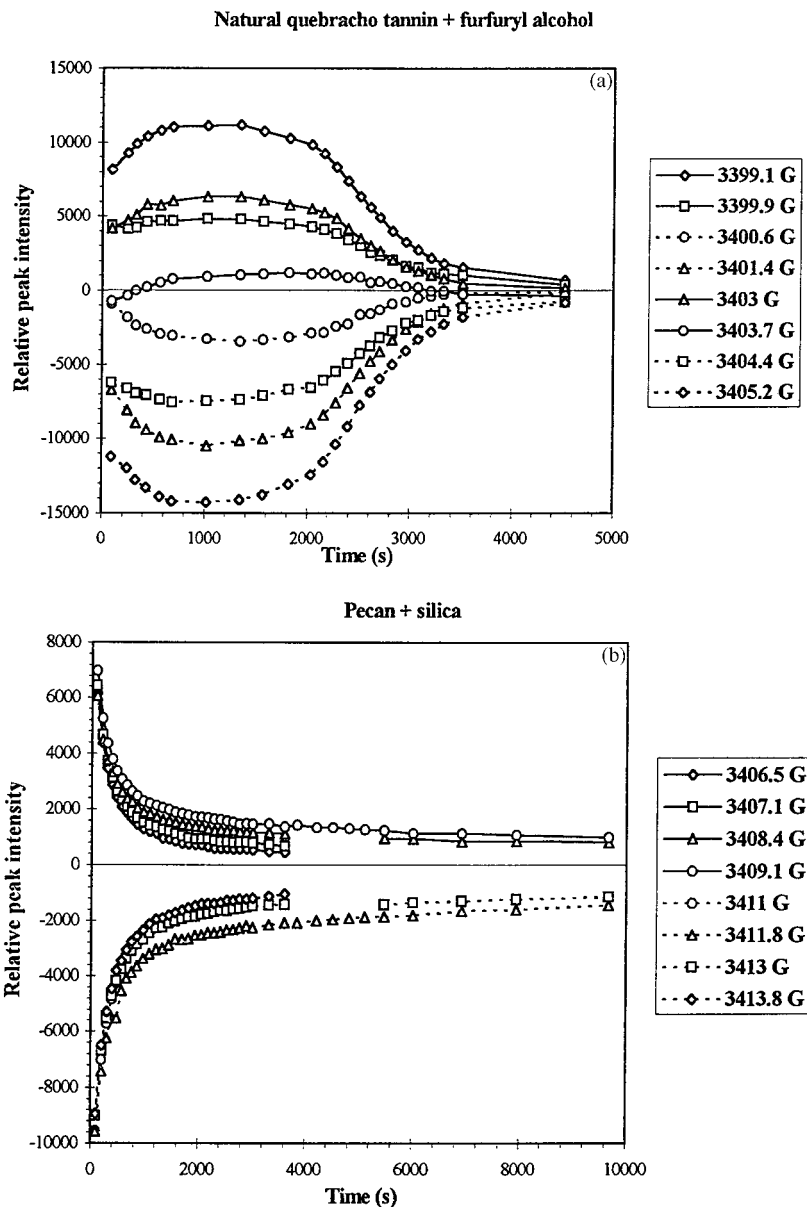


However, this proposed mechanism should mean that the relative intensity of one of A-rings peaks should increase/decrease at a different rate. This indeed occurs, but what is not easily explainable with this mechanism is the fact that the trend (but not the intensity) for all the peaks is the same. A more acceptable mechanism would then be



Thus, after, at first, a fast radical surge, then the radicals start to decay at a slightly slower rate, but transfer to or quenching by the coreactants of the phenoxyl radicals will give, at first, a diminishing radical concentration (Fig. 3). As the phenoxyl radical concentration becomes lower due to the slower decay rate, the coreactant = phenoxyl equilibrium shifts and tends to reestablish the concentration of the phenoxyl radicals: If reaction B is fast and reaction C is slower, then, at first, an increase followed by a plateau in phenoxyl radical concentration is obtained (Figs. 4 and 5). If the radical decay reaction and the reaction of the equilibrium have similar rates, then a plateau is again reached. As the store of radicals entrapped in whatever manner in the additive becomes exhausted, then, again, only the radical decay reaction will again be visible and the curve of radical concentration as a function of time will assume the descending slope appearance noticeable in the end parts of the graphs (Figs. 4 and 5). Such a mechanism would explain well the effect of the coreactants, but as no coreactant radicals are observed, the equilibrium can only be based on





**Figure 5** (a) Trend in the variation of intensity as a function of reaction time of all the peaks in the series of ESR spectra of natural quebracho tannin + furfuryl alcohol. Note the presence of the plateau effect in the range of 500–2300 s reaction time. (b) Trend in the variation of intensity as a function of reaction time of all the peaks in the series of ESR spectra of the pecan tannin + silica case. Note the absence of the plateau effect.

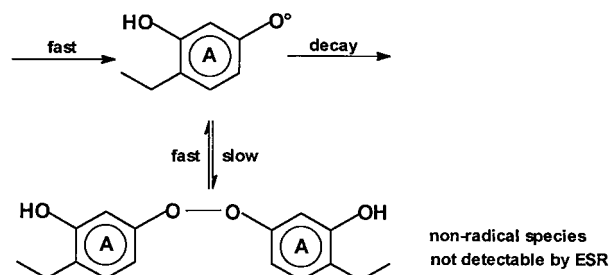
ionic reactions. The problem of such an approach is that, on reversing the equilibrium, phenoxyl radicals must again be produced, a difficult occurrence to explain. The concept which needs to be introduced in the mechanism proposed is then that of an unknown species not detectable by ESR, not detectable or because it is not a radical, or because it is a diradical (hence, the two unpaired

electrons spins would cancel each other and the species would also not be paramagnetic). While phenoxyl radicals are well known to be rather stable and, hence, very slow to undertake transfer and termination reactions, they nonetheless can yield these types of reactions. As a consequence and just as an example, to form unstable peroxides by termination could be thought (the forma-

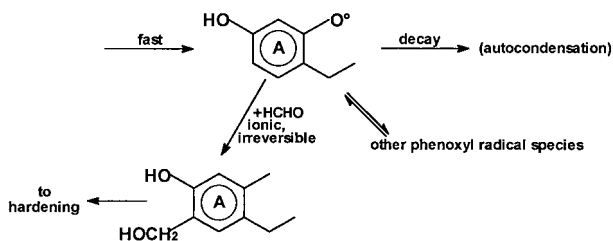
**Table IV Slope Trends of the Variation of Phenoxy Radical Peaks**

	Pine Tannin	Pecan Tannin
Base alone	Normal exponential with very slight plateau effect	Normal exponential
+ SiO <sub>2</sub>	Normal exponential	Normal exponential
+ hexamine	Mainly normal exponential with weak plateau effect	Normal exponential
+ furfuryl alcohol		Normal exponential
+ paraformaldehyde	Normal exponential	Normal exponential
+ urea	Normal exponential	Normal exponential
+ urea + paraformaldh.	Normal exponential	Normal exponential
+ formalin	Normal exponential	Normal exponential
+ isocyanate	Normal exponential	Normal exponential
	Modified Quebracho Tannin	Natural Quebracho Tannin
Base alone	Plateau effect	Plateau effect
+ SiO <sub>2</sub>	Normal exponential	Strong plateau effect
+ hexamine	Plateau effect	Strong plateau effect
+ furfuryl alcohol	Strong plateau effect	Strong plateau effect
+ paraformaldehyde	Normal exponential	Almost normal exponential
+ urea	Plateau effect	Strong plateau effect
+ urea + paraformaldh.	Normal exponential	Normal exponential
+ formalin	Mostly normal exponential	Normal exponential
+ isocyanate	Weak plateau effect	Strong plateau effect

tion of peroxide is not proposed here: it is presented only as an example of a nonradical species which can easily decompose to form radicals):



The situation is simpler as regards the initial interference between tannin radical autocondensation and formaldehyde both in the form of paraformaldehyde and of a formalin solution. In these cases,



In these cases, the radical decay curves should not present the plateau effect, and this is what is always observed. Thus, the case in Figure 4 can be explained by the noninterference of the ionic species in the radical mechanism or by the mechanism presented above. Most of the pine tannin cases and all of the pecan tannin cases present this trend in the radical decay curve shape, with only two cases, namely, pine tannin + base only and pine tannin + base + hexamine showing for only some of the peaks a very short, little noticeable plateau effect (Table IV). The fact that the plateau effect is observed mostly with the two quebracho tannin species (Table IV) is consistent with the reactions and equilibria involved proceeding at different rates for different flavonoid structures, as already shown by kinetic experiments reported previously.<sup>5-8</sup> It is also clear that the existence of a plateau effect, in three of four cases for the tannins + base only controls, might well depend more on the structure of the tannin and the conditions used rather than on the presence or not of ionic coreactants. In short, the existence or not of a plateau effect does not allow by itself to say if there is or there is not interference by the ionic coreactant involved on the tannin autocondensation. Furthermore, in principle, the existence of a normal exponential shape of the radi-

cal decay curve, as in the case of formaldehyde, also does not allow one to say if interference by the ionic coreactant occurs: It may or it may not.

In conclusion, can the different coreactants be used in combination with tannin autocondensation? The data from the ESR study give only partial results but it appears that paraformaldehyde and formalin do clearly depress the autocondensation reaction; thus, while autocondensation is still likely to present a small contribution to the formation of the final hardened network, the combination of the two effects clearly does not offer great synergistic advantages, and, thus, the two systems should not be used together. Urea, however, improves the radical autocondensation but such an improvement is not translated in the main to its combination with paraformaldehyde, the effect of paraformaldehyde clearly predominating, denying the potential utility of urea (other than for other purposes<sup>11</sup>). Isocyanate instead appears to be usable as a coreactant in combination with tannin autocondensation, if the radical surge it causes is not due to a slowing down of the radical decay reaction. Furfuryl alcohol can also be used in combination with tannin autocondensation but its application might become more exciting in an acid environment as its rate of condensation with tannins is not very exciting in alkaline environments.<sup>18,26</sup> Hexamine can also present some synergy effect with some tannin autocondensation, while in others, instead, it can function as a depressant of the initial radical surge. However, at higher temperatures, one will have to observe, as hexamine decomposes, what its interference is with autocondensation (this will be done by different means, namely, by thermomechanical analysis<sup>30-32</sup> methods).

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