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Polyflavonoid tannins – a main cause of soft-rot failure in CCA-treated timber

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Summary. Polyflavonoid tannins are proven to be fast-reacting with CCA solutions and hence, to be strong competitors of the structural wood constituents for fixation of CCA preservatives. The consequence of this effect is that even relatively small amounts of tannin cause severe undertreatment of the structural wood constituents which in turn badly affects the long term durability of CCA treated timber. The effect is compounded by heavy disproportionation between tannins and structural wood constituents of Cu, Cr and As. This leads to the well-known high susceptibility to soft-rot attack in eucalyptus species and in vineyard posts even experienced with some susceptible softwoods. Relationships found by other authors between soft-rot incidence and lignin content in CCA-treated timber are proven here to be only part of the total failure mechanism. The total mechanisms of resistance and failure are due to the balance of distribution of reactions among the various proportions of highly reactive tannins and more abundant but less reactive lignin and carbohydrates present in any wood. As a consequence of the clarification of these mechanisms the liability of different woods to soft-rot attack can then be accurately determined. Solutions to the problem are presented and discussed.

Introduction

Polyflavonoid tannins are wellknown to complex heavy metal ions. Easily and rapidly-forming complexes of catechin and of natural polyflavonoid tannin extracts with copper, arsenic and chrome have been reported in the literature (Slabbert, 1972; Pizzi, 1983). Copper, for instance, form stable complexes by coordinating with flavonoid molecules in the ratios 1 : 1, 1 : 2 and 1 : 3 copper : flavonoids at approximate pH ranges 3–4; 5.4–5.6; 6.0–6.3; in addition precipitates form after the complete formation of the first complex species (1 : 1 metal : flavonoid). This complexing capability is wellknown for all ortho-diphenols, such as the catechol and pyrogallol B-rings of flavonoid tannins.

The tannin content of timber varies according to the species. Generally hardwood timber has a much higher tannin content than softwoods. Thus the timber of many pine species contains, generally, little or no tannins. The tannin content of hardwoods varies. In *Eucalyptus grandis* the tannin content of the timber is of the order of 3% to 5% (Garbutt 1985). In other eucalyptus species the tannin content is higher (Garbutt 1985). A flavonoid molecule is capable of complexing one or two metallic ions: one when it contains a catechol B-ring and two when it

contains a pyrogallol one. CCA preservatives and copper, chromium and arsenic ionic species complex more readily with flavonoid tannins than with other wood constituents, including the phenolic groups of lignin as indicated by the higher stability of their complexes with tannin than with lignin. The presence of tannins in the treated timber, then, will considerably interfere with the fixation of CCA preservatives to wood, and by inference, with the long-term durability of CCA-treated timber. A 5% content of flavonoid tannins in timber sapwood will complex approximately 14.4 kg/m³ of CCA salts in the same timber. Higher tannin content will complex more. This means that if eucalyptus timber is treated to a CCA retention of 16 kg/m³ most of the preservative could well be fixed to the tannin rather than to the wood. As in *Eucalyptus grandis* ± 50% by volume of the timber is untreatable heartwood, a retention of 16 kg/m³ on the whole timber volume is equivalent to ± 32 kg/m³ on the sapwood; if ± 15 kg/m³ is fixed by the tannin only 17 kg/m³ is fixed in the wood. It is amazing to find that also by empirical experimentation 32 kg/m³ sapwood has been found to be the best treatment for *Eucalyptus grandis* sapwood. Exotic eucalyptus species of higher tannin content should fare even worse, explaining why soft-rot is particularly rife in CCA-treated eucalyptus species. Thus, as a consequence of their tannin content, eucalyptus species are likely to be, even at high retentions, badly undertreated. We do not want to advance the hypothesis that tannin content is the only cause of susceptibility to soft-rot of CCA-treated eucalyptus species, but that it is definitely a very strong contributory factor. Pine wood, with perhaps a few exceptions where the tannin content is low or non-existant, is much less or not susceptible to severe soft-rot attack when CCA-treated.

Why and how does tannin render. CCA ineffective? What are the consequences? This is the theme of this article.

Experimental

Three *Pinus patula* matched blocks 95 mm × 95 mm × 105 mm of low tannin content (0.15% to 0.20%) with end-grain well-sealed with sanding sealer were treated as follows:

One block pretreated under vacuum/pressure with a 7.5% solution of wattle (*Acacia mearnsii* formerly mollissima) tannin (tannin content of tannin extract used = 80% ± 1), dried in oven at 95 °C for 16 hours then retreated with a 4% solution of CCA type I (Vogel et al., 1983; SABS specification, 1976) (type C (AWPA specification, 1971; AWPA specification, 1971)) powder under a standard industrial-type vacuum/pressure/vacuum treatment schedule.

One block treated as above but with a 2.5% tannin extract solution.

One block treated with water only as for the tannin extract in the previous two blocks, dried as previous two blocks, and then treated with CCA solution as previous two blocks, as a control.

The three blocks were treated with CCA, in different containers, but the same autoclave, all at the same time. The treatment was repeated for duplicate blocks.

Retentions in tannin solids and CCA were calculated by normal industrial practice mass/volume/concentration methods and by atomic absorption analysis of depleted solutions used for treatment.

Amounts of CCA solutions extracted after treatment, amount of sludging of the solutions after 48 hours were also determined.

The blocks were then sliced in the tangential and radial directions in slices of the following subsequent thickness: 5 mm/5 mm/8 mm/core. CCA gradients in the blocks were obtained with a method already reported (Jansen et al. 1984). Both leached and unleached results were obtained. The results obtained are reported in Table 1 and Fig. 1. The CCA gradient profiles in the blocks have been reported in a previous article (Jansen et al. 1984), and do not contribute to the hypothesis advanced.

The curves presented in Fig. 1 are obtained, by non-linear regression analysis from the solution depletion results shown in Table 1. It must be pointed out that while Cr and Cu curves by extrapolation confirmed that the tannin content of the blocks was of 0.16% (0.16% obtained by extrapolation; 0.15% to 0.20% obtained by analysis) extrapolation of the As curve gave a tannin content of 0.67%. As this causes a problem in the presentation and calculation of the curve of As depletion from the solution absorption by the block) both, the curve of As with 0.16% original tannin content and the curve with 0.67% tannin content are reported

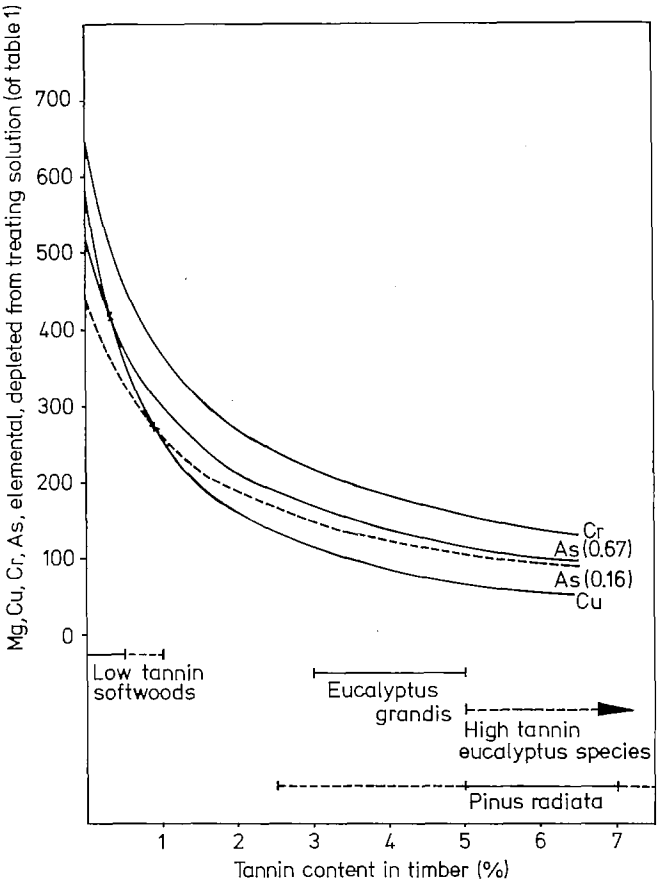


Fig. 1. Tannin content in timber versus elemental concentration in the depleted solution

Table 1. Effect of tannin retention on the absorption, fixation and leaching of CCA in timber (CCA solution = 4%). Cu, Cr and As in treating solution before and after treatment

	Pretreatment tannin solution Concentration	Tannin content by mass on wood	Tannin retention in timber	Metal ions in treatment solution			Mass of sludges formed	Timber density	Mass-volumetric final CCA retention in wood	Effective CCA retention in wood by AA	Over fixation of CCA	CCA fixed on tannin	CCA fixed on wood	Molar proportions of metal ions in treated wood (fixed on wood + fixed on tannin)			Percentage of CCA active elements leached on total CCA active elements retained in wood and tannin
				Cu	Cr	As								Cu	Cr	As	
	%	%	kg/m³	mg/l	mg/l	mg/l	g	g/cm³	kg/m³	kg/m³	kg/m³	kg/m³	kg/m³				%
CCA solution before treatment	–	–	–	587.8	649.1	568.7	0.10	–	–	–	–	–	–	4.4*	6*	3.7*	
CCA solution after treatment	0.0	0.0	0.0	519.9	552.6	314.5	0.34	0.577	15.7	16.8	1.1	0.0 (0%)	16.8 (100%)	4.3	6	4.6	0.47
CCA solution after treatment	2.5	1.5	8.8	151.6	323.8	196.1	0.20	0.575	12.2	15.8	3.6	4.3 (27.2%)	11.5 (72.8%)	5.2	6	4.0	0.77
CCA solution after treatment	7.5	3.4	19.3	108.3	184.2	144.2	0.12	0.566	15.8	20.1	4.3	9.8 (48.7%)	10.3 (51.3%)	4.7	6	3.7	1.40

* The proportions of normal CCA type C are 3:6:4 Cu:Cr:As. The proportions indicated were the effective ones obtained for a particular industrial batch supplied for the experiment

in Fig. 1. While the general conclusions are the same whatever of the two As curves is taken into consideration, the intersection point between the Cu curve and the As curve are slightly different (0.3% in one case and 0.9% in the other).

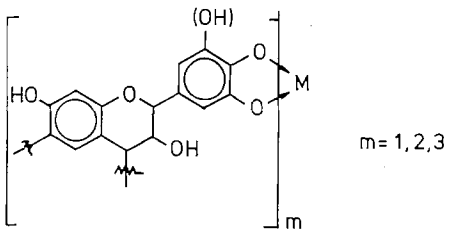
[For calculation purposes the flavonoid units average molecular weight used was 273. Thus, at 5% tannin content and 450 kg/m³ of timber 0.0824 kilomoles are present. The Cu, Cr, As elements present can coordinate, for a 16 kg/m³ CCA retention 0.0964 kilomoles of catechol B-ring flavonoids. Hence, $\frac{0.0824}{0.0964} \times 16 \approx$ 13.7 kg/m³ CCA active elements coordinated by the tannin (phenolic material) present. However, as ±5% if flavonoid units in the tannins used have pyrogallol rather than catechol B-rings 13.7 kg/m³ + 5% of 13.7 = 14.4 kg/m³ of CCA active elements absorbed by the tannin (cf. introduction).]

The regression equations for the curves in Fig. 1 are:

Cu $y = 582.04\,(x+1)^{-1.18}\ r^2 = 0.98$
Cr $y = 646.14\,(x+1)^{-0.79}\ r^2 = 0.99$
As [0.67]: $y = 528.84\,(x+1)^{-0.83}\ r^2 = 0.98$
As [0.16]: $y = 449.08\,(x+1)^{-0.79}\ r^2 = 0.89$

Discussion

Complexes of heavy metals with flavonoid tannins are of the type (Slabbert 1972):



Thus, very similar to the type of complexes formed by copper and particularly chrome with the guajacyl nuclei in lignin (Pizzi 1979). As the tannin complexes are formed by two phenolic hydroxy groups rather than an hydroxy and a methoxy group or by two methoxy groups, as in guajacyl and other lignin units, their rate of formation and their stability are higher. These are a good indication that in competitive reactions, for the CCA active elements, between the tannins and the structural wood constituents, the CCA will react preferentially with the tannins rather than with lignin and holocellulose. Flavonoid tannins/CCA insoluble complexes form and precipitate practically instantaneously, at ambient temperature, by simply adding some CCA solution to a tannin solution (Pizzi et al. 1984). The equivalent wood lignin/CCA complexes, under similar conditions, take as much as a few hours to precipitate completely. All this only indicates that there is already a considerable amount of circumstantial evidence as regards a possible strong interference from the tannins on the CCA fixation mechanism onto wood.

The results in Table 1 confirm our hypothesis and indicate clearly the mechanisms involved, namely:

Increasing tannin content in the timber (Table 1, columns 2, 3, 4) causes increased absorption and fixation of CCA at equal treatment times. This is shown in Table 1 by the progressively higher depletion of the CCA treating solutions in Cu, Cr and As with increased tannin content (columns 5, 6, 7) which indicates progressively higher CCA absorptions and fixation. It is further confirmed by the progressively higher discrepancy between the apparent CCA retention values in the treated timber calculated by the ordinary mass/volume/concentration method and the effective CCA retention calculated by atomic absorption spectroscopy of the solutions. The higher the tannin content, the higher the effective CCA retention and the greater the amount of CCA overtreatment of the timber.

Thus, that the tannins are strong competitors of lignin and carbohydrates for the available CCA is a proven point.

More interesting is the fact that if we have, for instance, 3.4% tannin content in the timber, as shown in Table 1, and we try to treat timber at 16 kg/m^3 CCA, we will not obtain, as presupposed in the introduction of this article, 9.8 kg/m^3 of CCA fixed onto the tannin and 6.2 kg/m^3 fixed onto the wood. Rather, we obtain, as a consequence of the increased "pull" of the tannin and of the consequent overtreatment, 9.8 kg/m^3 of CCA fixed to the tannin and 10.3 kg/m^3 fixed onto the wood (Table 1). This effect is compounded and progressive with increasing tannin contents. The tannin available will fix all the CCA it possibly can but, as a consequence of the "pull" overtreatment, the lignin and holocellulose in wood will end better treated than what is expected. Better treated, but still badly undertreated. This should not decrease the long term resistance of the treated timber to insect attack, possibly termites included, as insects probably feed on wood without discerning the different wood constituents and extractives they chew. If the timber contains arsenic in any form, whatever it is fixed to, even tannin, this should provide protection against insect attack.

The situation, however, is very different for fungal attack. Fungi absorb only depolymerised carbohydrates. Their enzymes may even attack lignin or other constituents to liberate the carbohydrates, but effectively they will only absorb the carbohydrates. The severe undertreatment of the timber caused by the presence of the tannins will then badly and surely affect the resistance of the timber to fungal attack. In short, timber that we think is industrially treated to 16 kg/m^3 CCA salts retention is in effect only treated, as regards protection against fungal attack, to 10.3 kg/m^3 if the timber sapwood contains only 3.4% tannins. *Eucalyptus grandis* tannin content is in the 3% to 5% range. More exotic eucalyptus species contain considerably more. This is probably the cause why very high CCA retentions are needed for the protection of eucalyptus species. In South Africa *Eucalyptus grandis* sapwood is treated at 30 to 32 kg/m^3 CCA salts retention: as $\pm$ 14.4 kg/m^3 maximum fixes on the tannin, this leaves between 15.6 and 17.6 kg/m^3 minimum CCA retention on the wood. It has been practically demonstrated that retentions lower than 30 to 32 kg/m^3 will not ensure protection against soft-rot for *Eucalyptus grandis* sapwood in ground contact applications. In Queensland, Australia, it is reported (Leightley 1983) that retentions as high as 40 to 50 kg/m^3 for exotic, and very high tannin content, eucalyptus species are barely or scarcely enough for soft-

rot control for ground contact applications. Both these practically obtained retention ranges further strengthen the "tannin interference" hypothesis.

The compounded mechanism is however more complex as, in the competitive complexation of CCA, lignin and carbohydrates also exercise an important role. Softwoods have, generally, higher lignin content and low or very low tannin content. Hardwoods instead have lower lignin content and much higher tannin content. From chemical kinetic laws it is well known that relative amounts of products formed by two competitive reactions are not only directly proportional to the relative rates at which the reactions occur, but also directly proportional to the relative amounts of the initial reagents. Thus, a softwood will fix more CCA on lignin, hence on wood, than a hardwood is generally capable of fixing. The reverse applies to hardwoods. A hardwood, conversely, will fix more CCA on tannins than a softwood.

These observations explain why Butcher and Nilsson (1982) (Nilsson 1982) found that timber species treated with CCA present better soft-rot resistance the higher their lignin content is. They found, correctly, half of the mechanism determining CCA-treated timber resistance or failure to soft-rot attack. The real mechanism, however, is not due to a simple linear dependance of soft-rot resistance from the lignin as they advocate (Butcher et al. 1982). It is, rather, the more complex competitive interaction for the CCA of the lignin, tannin and also of the wood carbohydrates which we are presenting in this article. Thus, to the parallel reactions of CCA with lignin and carbohydrates, which we have already explained (Pizzi 1982), a third parallel reaction can be added, namely the much faster reaction of CCA with tannins. The distribution of CCA through these three reaction routes will then determine the resistance of the treated timber to soft-rot and other fungal attack. Admitting a simple thermodinamic control of the reactions, and we have proof already that both kinetic and thermodinamic controls exist (Pizzi, 1982) in these three competitive reactions, the stability pK's of Cu^{II}/tannin, Cr^{III}/tannin and Cr^{VI}/tannin complexes are of the order of approximately 14.7, 17.1 and 5.4 respectively (Slabbert 1972). This means that the order of priority with which copper and chrome should react with the tannin is:

$$Cr^{III} > Cu^{II} \gg Cr^{VI}.$$

However, at the beginning of the treatment, Cr^{III} is not present, as it must be produced by reduction of Cr^{VI} from the carbohydrates. This reduction is the determining step of Cr reaction with tannin. Thus, the effective order, in which Cu and Cr will reach with the tannin at the beginning of the timber treatment, is:

$$Cu^{II} > Cr^{III} \gg Cr^{VI}.$$

This is indeed the case, as can be seen from the graphs in Figure 1. In Fig. 1 the initial solution depletion of copper is more rapid than that of chrome, hence the initial molar absorption and fixation of copper is also more rapid than that of chrome. A situation quite different from tannin-free timber species. As Cr^{III} becomes available the situation changes and chrome fixes more rapidly than copper. By then the pH is higher and also the fast-fixing Cr^{VI} species ($HCrO_4^-$ on lignin) appear (Pizzi 1982; Pizzi 1981). The inference is that both Cr^{III}/tannin and Cr^{VI}/tannin complexes are formed. Also, by inference, the presence of both

thermodinamic as well as kinetic control of the reactions, with kinetic control appearing to be dominant, are again proved.

Arsenic complexes with ortho-diphenol, such as tannins, much more weakly and although approximate pK's stability constants of its tannin complexes are not available, this fact is shown by the As slower depletion curves in Fig. 1. Again, we can say that the arsenic fixation is mainly obtained by the "pull" through the chromium (Pizzi 1982).

In general term it is then possible to say that when:

Lignin content	Tannin content	Holocellulose content	Soft-rot resistance
high	low	low	good (softwood case)
low	high	high	very poor (hardwood case)
high	high	low	poor (some softwoods)
low	low	high	from acceptable to good (rare examples, i.e. ironwood)

and that it is probably necessary to know the balance of all materials capable of reacting with CCA, possibly including extractives other than tannins, to determine susceptibility to soft-rot.

The soft-rot susceptibility of eucalyptus species caused by this mechanism has already been discussed above. This mechanism however, also explains the failure of CCA-treated vineyards and kiwi-fruit orchard poles. In South Africa these are undertreated Eucalyptuses. In New Zealand they are *Pinus radiata.* It is not a coincidence that, among softwoods, radiata pine from New Zealand has a tannin content higher than other common pine species. This is reflected in the high tannin content in its bark, allowing use of its tannin extract for the commercial production of adhesives (Swann et al. 1976; Jenkin 1984). *Pinus radiata* bark has a tannin content of up to 25%. By comparison South African *Acacia mearnsii* bark (wattle), another commercial source of tannin extract, contains 38% tannin while the wood tannin content is in the 8% to 11% range. By simple proportions, *Pinus radiata* timber is then likely to contain at least between 3% and 7½% of tannin, probably 5% to 7%. Thus, the same disruptive mechanism applies to softwoods in the more rare cases when their tannin content is high.

There is, however, an additional cause also derived from this same mechanism, for these failures. This is evident in Fig. 1. The relative proportions of Cu, Cr and As absorbed by tannin-rich wood vary considerably, according to the tannin content, when treating with the same CCA formulation.

The proportional arsenic and chrome contents are depressed by the over-absorption of copper. In particular the proportional arsenic content is depressed drastically after the point of intersection between the arsenic and copper absorption curve in Fig. 1. This point of intersection is in the 0.3% to 0.9% tannin content range according to the calculation system used, but quite likely around 0.7% tannin content (cf. experimental). This contributes to explain the unusual and unexpected finding (Butcher 1983) that after a few years in service New Zealand vineyard and kiwi fruit orchard poles present high copper content and depleted chrome and

arsenic content. It fits in with Hedley's (1983) finding that in this situation the Cr/As ratio is important to the performance as it appears that soft rot fungi are copper-tolerant (Richardson 1978). It indicates also that chrome is partially responsible for some soft-rot control as inferred by other authors (Hedley 1983): this may also be attributed to the higher water repellancy caused by chrome in softwoods where the lignin content is higher (Pizzi 1979; Kubel et al. 1981). It is then possible to establish approximate danger limits according to the tannin content of the timber species to be treated. Over 2% to 3% tannin content the CCA-treated timber becomes prone to attack from copper-tolerant organisms as the arsenic (and also the chrome) content on carbohydrates is not only already low due to a high amount of it being fixed by the tannin rather than the wood, but it is furthermore depressed by the copper disproportional over-absorption that already manifests itself at ± 1%.

The small increasing amount of CCA leached with increasing tannin content shown in the last column of Table 1 can be ascribed to the presence of monoflavonoids complexes with the CCA constituents. Monoflavonoids, a small percentage of tannin extracts, are very soluble in water and thus some of their complexes, still monomeric, with Cu, Cr and As will tend to leach easily.

Remedial actions

Having identified the tannin interference effect, a few suggestions can be advanced to improve the situation or maybe to eliminate the problem:

1. Preleaching. By placing logs prior to treatment in a water, possibly hot water, pit, or even by pre-steaming them, as it is for instance done with logs prior to rotary veneer peeling, a considerable amount of tannins can be leached, both achieving a decrease in the tannin content with reduced interference and better CCA fixation to wood (particularly for timber with tannin content at critical levels), and improved durability and opening of the wood flow paths, allowing better penetration and distribution of the preservative. Coupled with post steam-treatment (Peek et al. 1981) to improve and accelerate CCA fixation after treatment the installation of a heating plant onto treatment cylinders may well be a very economical proposition.

2. Preleaching with solvents. This would be expensive but also effective. It may be needed only when the high tannin content in the timber is coupled with a very high percentage of high molecular weight tannins of low solubility in water.

3. Higher CCA content. This has been the solution which has been unconsciously and empirically applied for exotic eucalyptuses with high tannin content. However, the considerable excess of CCA to be used must be linked to a real knowledge of the effective tannin content, thus should vary from species to species, maybe from pole to pole for this remedy to be really effective. This solution is indeed very expensive if one considers the considerable amount of CCA which is wasted in just "neutralising" the tannin effect, before CCA uncomplexed from the tannins can fix to the timber in a quantity high enough to contribute to its long term durability.

4. The presence of tannin disproportionates the relative ratios of Cu : Cr : As with increasing tannin content of the timber. As shown in Fig. 1, there are certain zones in which the As proportion to Cr and Cu or the Cu and As proportion to Cr

are much lower than what was obtained by CCA type C in absence of tannin. Thus it would be advisable to change the CCA formulation (namely the Cu : Cr : As ratio) according to the tannin content of the timber to "re-balance" the proportions of active elements in the timber. This approach could be simple, practical and effective but can really be applied only in the case of: (i) a very abundant and very used species such as *Eucalyptus grandis* or *Pinus radiata* in which the tannin content range is fairly narrow and an average modified CCA formulation can be used for the majority of the timber of that species, or (ii) for well-defined high tannin content species for particular types of applications, such as some of the more exotic eucalyptus species. This solution is in a similar mould to that presented in solution number 3 above, but could decrease CCA wastage and improve CCA durability by trying to maintain the most effective Cu, Cr and As relative proportions. The tannins, however, will still absorb a part of the material and considerable CCA wastage would still ensue. This does not mean that CCA type B would be suitable for vineyard because As in this formulation is still free to leach (Pizzi 1982; Vogel et al. 1983). It would entail among others a decrease in copper and an increase in the chrome and arsenic content (but with Cr and As in proportions similar to CCA type C), thus a formulation in between CCA type C and CCA type A. All the same an arsenical creosote in which arsenic is effectively fixed may also be helpful against the soft-rot problem.

The fact that the soft-rot problem was not identified in the time in which CCA type A was used may be a confirming point. To decrease the copper content excessively however, should cause other, just as deleterious, types of fungal attack. It must be pointed out, to add to the difficulty of solving this problem, that while there are major differences in tannin contents between different timber species, there are also minor differences in tannin content within the same species according to the age of the three, the zone of provenience, the climatic conditions during growth, etc. For instance, *Pinus patula* reaches its maximum water soluble tannin content at 30 to 35 years of age, while *Acacia mearnsii* at 9 to 12 years.

Fast pre-leaching and change of Cu : Cr : As ratio to minimize the problem are already under investigation in our laboratories.

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