REVIEW OF LABORATORY AND OUTDOOR EXPOSURE EFFICACY RESULTS OF ORGANIC BIOCIDE: ANTIOXIDANT COMBINATIONS, AN INITIAL ECONOMIC ANALYSIS AND DISCUSSION OF A PROPOSED MECHANISM

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ABSTRACT

As previously reported, the combination of various organic biocides with relatively high levels of commercial antioxidants always increased the biocides' efficacies against wood-destroying fungi in short-term laboratory decay tests. The two principal antioxidants examined, propyl gallate (PG) and butylated hydroxytoluene (BHT), are low cost and benign. In reviewing ground-contact outdoor exposure results, samples treated with the biocide chlorothalonil and the antioxidant BHT had 2–3-fold enhanced efficacy after four years of exposure against decay and termite degradation compared to stakes treated with only the biocide. In above-ground outdoor exposure tests after three years of exposure, lap-joint samples treated with only BHT at the relatively low retention of 0.94 kgm⁻³ had significantly less fungal decay than untreated samples. In addition, mini lap-joint samples treated with a quaternary formulation and 2.56 kgm⁻³ BHT and exposed in Hilo, HI, for two years, had more than 3-fold greater decay resistance than samples without BHT. However, relatively poor results were observed for both ground-contact and above-ground samples treated with various biocides and the antioxidant PG. Less BHT may be required to protect wood outdoors than the initial laboratory decay tests indicated. The antioxidant concept appears to be an economical option for totally organic systems. A mechanism by which BHT protects wood against fungal degradation is proposed.

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INTRODUCTION

Many solid and composite wood products are
treated with a biocide to prevent degradation by
various wood-attacking organisms. The major
wood preservative has been chromated copper
arsenate (CCA), accounting for about 80% of all
wood treated in the United States in 1998. How-
ever, a voluntary withdrawal of CCA from the
residential market by the suppliers limited CCA
to industrial applications effective January 2004.
The "new" copper-rich 2nd generation systems
for U.S. residential applications are based on
combining copper(II) with various organic co-
biocides (Schultz and Nicholas 2003). While
copper is not as acutely toxic or mutagenic as the
arsenic and chromium in CCA, some environ-
mental concerns exist. These include relatively
high copper leaching in the newer systems com-
pared to CCA-treated wood and the impact of
copper on aquatic ecosystems. Also, disposal of
metal-containing wood products may someday
become relatively expensive and onerous. Thus,
the new 2nd generation copper-rich systems may
also face future restrictions. Indeed, several Eu-
ropean countries will shortly require totally or-
ganic 3rd generation systems, and non-metallic
preservatives for residential applications may
someday be mandated in the United States.

Several problems exist with developing a to-
tally organic wood preservative system, one of
which is cost. Many organic biocides have been
examined as potential wood preservatives
(Schultz and Nicholas 2003), but most are about
10–30-fold more expensive per kgm^{-3} than
copper(II). (While many of the newer organic
agrochemicals are extremely effective as wood
preservatives at much lower doses than
copper(II), a critical minimal organic biocide re-
tention is necessary. This is because leaching oc-
curs for both metallics and organics, but organics
also undergo biodegradation, chemical, and/or
photodegradation reactions that further reduce
the biocide's concentration over time.) Another

concern is the public's generally negative per-
ception of bioactive compounds (Goodell et al.
2003a). Furthermore, while satisfactory organic
systems suitable for protecting wood in residen-
tial applications are available for the relatively
mild above-ground deterioration conditions
found in some European regions, development
of effective totally organic above-ground and
ground-contact preservative systems for high de-
terioration hazard areas, such as exist in the
southeastern United States, will be a challenge.

One approach to the development of new or-
ganic systems is to understand why the heart-
wood of certain tree species has considerable
natural resistance to decay fungi and/or insects.
We previously examined the role which heart-
wood extractives, particularly stilbenes, play in
natural durability (Schultz et al. 1995). Later we
hypothesized that extractives may protect heart-
wood by a dual function; extractives have limited
fungicidal activity but are excellent antioxidants
(Schultz and Nicholas 2000a) and protect wood
against the fungal-generated free radicals (Good-
ell et al. 2003b, and references therein). In labo-
ratory decay tests, we found that an antioxidant
alone provided no protection against brown- and
white-rot fungal degradation. However, when
combined with different organic biocides, greater
efficacy was always obtained with an anti-
oxidant:organic biocide mixture than with the
biocide alone (Schultz and Nicholas 2000a and
2002); i.e., the mixtures were synergistic.

The main antioxidant examined in laboratory
tests, butylated hydroxytoluene (BHT), is rela-
tively low cost and benign (used in many food
and personal care products). We found that
adding this economical, nonbioactive, and safe
substance enhanced the efficacy of all organic
biocides examined, often by 2–3-fold. Since the
biocides' efficacies were increased, less biocide
was needed to protect wood. Consequently, the
biocide cost could be reduced along with poten-
tial disposal and environmental problems. We
felt that this concept may have some promise,

provided that: 1) it is economically viable in totally organic preservative systems [the savings from using less biocide is greater than the antioxidant cost]; and 2) long-term efficacy is demonstrated in outdoor above-ground and/or ground-contact exposure tests.

The purpose of this article is to: 1) briefly summarize our prior laboratory decay results; 2) discuss the results obtained to date from outdoor exposure tests, both above-ground and ground-contact; 3) discuss the differences between the laboratory decay test results and outdoor field exposure data; 4) conduct a preliminary economic analysis of the potential viability of this concept; and 5) propose a generalized mechanism by which antioxidants may protect wood.

EFFICACY STUDIES

Brief summary of laboratory decay results

Laboratory decay tests (Schultz and Nicholas 2000a and 2002) showed increased efficacy for biocide:antioxidant mixtures compared to the biocide alone for all seven organic biocides examined, using both gymnosperm and angiosperm woods, brown- and white-rot decay fungi, and various antioxidant:biocide mixtures. The biocides examined were all commercially available and have either been examined as potential wood preservatives or are used in wood preservative systems (Schultz and Nicholas 2003). Initial studies were conducted with the antioxidant BHT. We later also examined the antioxidant propyl gallate (PG), another economical food additive. Better results were obtained in lab decay tests with PG than BHT, possibly due to: 1) PG's tri-vicinal phenol hydroxyls which give PG good metal chelating ability, and the combination of biocide:antioxidant:metal chelator proved even more effective at protecting wood than a biocide:antioxidant mixture (Schultz and Nicholas 2002); 2) PG has a lower electrode potential than BHT, about 0.6 vs. 0.8 V, respectively (Ni et al. 2000) and, thus, might disrupt more fungal redox cycles than BHT (Schultz et al. 2004); 3) increased hydrophilicity of PG relative to BHT suggests that PG might

penetrate the cell wall unlike the highly hydrophobic BHT; 4) other possible properties of PG, as yet unknown; and 5) a combination of two or more of the above.

While these initial laboratory decay tests were promising, we had several concerns. First, we initially ran standard laboratory tests on wood samples treated with biocide alone and biocide:antioxidant combinations, but did not observe an enhanced effect. It was not until we ran a laboratory test for only a relatively short period that synergism was observed. Later experiments that showed synergism employed a very short incubation period of 4–6 weeks (Schultz and Nicholas 2000a, 2002). Secondly, relatively high BHT levels (5%) in the treating solution were used, which would likely be uneconomical in a commercial system.

The reason positive results were obtained only in short-term laboratory tests of 4–6 weeks' duration may be because BHT can only scavenge a limited number of radicals before being rendered inert (Dexter 1992). Laboratory decay tests are optimized so that decay fungi rapidly degrade small wood blocks. Therefore, decay fungi in the untreated wood feeder strips, or agar, endlessly produce many free radicals. These free radicals could quickly overwhelm the BHT in the wood block. Once the BHT is consumed, wood treated with a BHT:biocide combination would decay at about the same rate as blocks with the biocide alone. We emphasize that our concept works only with organic biocides. When an antioxidant is combined with a metal, such as BHT and Cu(II), a pro-oxidant (free radical generating) system is formed (e.g., Lee 1975; Nath et al. 1984). This was verified in a laboratory decay test using Cu(II), with no positive effect observed by co-adding BHT.

Outdoor ground-contact exposure results

Synergism in short-term laboratory decay tests does not ensure that a preservative will be effective for the many years expected from treated wood. Thus, early in this project an outdoor ground-contact study was installed at the MSU Dorman Lake and Saucier test plots using

stakes cut from defect-free southern yellow pine (SYP) (*Pinus* spp.) sapwood. Dorman Lake is located in northeast Mississippi and is in a high (AWPA Zone 4) deterioration zone. The Saucier plot is located in the Desoto National Forest near the Mississippi Gulf Coast, and is in a severe (AWPA Zone 5) deterioration zone. Further details on the soil type, climate, etc., are available (Schultz et al. 2002). BHT was employed in this first outdoor exposure study at 2% and 4% levels, and the biocide was chlorothalonil (CTN). The objective was to verify the antioxidant concept, rather than obtain efficacy data on a possible commercial formulation. After 52 months of exposure, we found that the combination of BHT and CTN was 2–3-fold more effective than CTN alone against both decay fungi and termites. These results are fully discussed elsewhere (Schultz et al. 2004).

The outdoor exposure results were more encouraging than we had anticipated. First, the antioxidant concept was based upon the well-known free-radical oxidative mechanisms by which decay fungi attack wood and the fact that heartwood extractives are excellent antioxidants. Thus, we expected greater efficacy against decay fungi. However, BHT's protective effect against termite degradation was unexpected. [Research conducted after this manuscript was submitted suggested a possible explanation for the unexpectedly good termite results. Specifically, we examined depletion of BHT and CTN after 54 months of exposure at both locations. Based on a preliminary analysis, it appears that less biocide depletion occurred for samples with BHT as compared to CTN depletion in stakes without co-added BHT. We suspect that the CTN depletion is due, at least in part, to microbial degradation. This possible BHT protective effect on reducing biocide depletion via microbial action would explain our good results against termites and provides a second mechanism by which an antioxidant:organic biocide combination might protect wood.] A second reason for the unexpectedly positive field exposure results was that the protective effect of BHT in laboratory decay tests was limited to a relatively short duration, as discussed above. We anticipated that

decay fungi would attack ground-contact stakes on an almost continuous basis. This suggested that BHT might only last for a relatively short period in outdoor ground-contact exposure. Further, smaller amounts of BHT were employed in this first outdoor exposure test (2% and 4%) than in the short-term laboratory decay tests (5%). Thus, it was a pleasant surprise to observe a large protective effect after 52 months of exposure, especially with the relatively low BHT levels employed. Also, when analyzing BHT depletion at the lower sections of selected stakes after 48 months of exposure we found that BHT depletion averaged 16–36% (Schultz et. al, 2004), a relatively low value. (A possible explanation for this relatively low depletion is given later.) Thus, we conclude that lower [more economical] BHT levels can be used in outdoor exposure than the initial laboratory decay tests indicted. Finally, many biocides initially show promise in short-term laboratory decay tests, but in lengthy outdoor exposures, these same biocides often give poorer results. In this instance outdoor exposure results with BHT:CTN-treated wood are more promising than data from the short-term laboratory decay tests.

Based on the encouraging results, additional ground-contact field stake samples, treated with the biocide didecyldimethylammonium chloride (DDAC) alone or DDAC combined with BHT or PG, were installed in 2003 at our Saucier and Dorman Lake test sites. Although the exposure time has been relatively short, it appears that the samples co-treated with PG are performing poorly.

Above-ground outdoor exposure results

Above-ground lap-joint samples (AWPA Standard E16-98), made using defect-free SYP sapwood, were installed in 2001 at the Saucier test plot. Twenty samples were treated with 0.13% BHT by a full-cell process to give a relatively low BHT retention of 0.94 kgm^{-3}, and a large number of untreated (control) samples were installed. After three years of exposure at Saucier, an average rating of 9.5 for the 20 replicates treated with 0.94 kgm^{-3} BHT was obtained,

compared to a significantly lower average rating of 6.9 for the 53 untreated samples using the AWPA Standard E7-01 decay rating system (10 = sound, 9 = trace up to 3% decay, etc., to 0 = failure).

Two sets of mini lap-joint samples [33 cm length × 4.45 cm width × 1.90 cm thick], made from defect-free spruce pine (*P. glabra* Walt.) sapwood, were installed in 2002. One set was treated with various levels of the biocide propiconazole with and without the antioxidant PG and installed at Saucier. The second set was treated with a quaternary formulation consisting of a mixture of DDAC and amine oxide with PG or BHT co-added. These samples were installed at CSI's Hilo, HI research site, and some duplicate replicate sets were installed at Saucier. [The Hilo location has ideal temperature and rainfall for wood decay. Above-ground decay rates at Hilo are 2–3-fold faster than for similarly treated samples at Saucier (Nicholas and Crawford 2003).] Additional Hilo sets were treated with a bioci:antioxidant:metal chelator:water repellent combination (Schultz and Nicholas 2002). The two-year exposure results with the quaternary:BHT treated samples in the Hilo site appear promising (Table 1), with a greater than

3-fold increase in efficacy observed at the relatively low BHT level of 2.56 kgm^{-3} compared to quaternary-treated samples without co-added BHT. The combination of four components [biocide:antioxidant:metal chelator:water repellent] has performed very well so far, with no decay observed even at the lowest biocide level. These results are based on a relatively short exposure period, however. We anticipate that the ratings from next year's inspection will help us to better evaluate this concept.

Poorer results were obtained with the samples in the two sets that were treated with the antioxidant PG and the organic biocides DDAC or propiconazole. This was surprising since, as mentioned earlier, laboratory decay tests gave better results with PG than BHT. One likely explanation for PG's poor performance in aboveground and ground-contact exterior exposure could be that PG is relatively water-soluble and may be slowly leached in long-term outdoor exposure. Conversely, leaching is not a factor in short-term laboratory decay tests. Supporting this premise was the observation that better results were obtained in above-ground exposure tests with PG when a water repellent was added to the treating solution.

TABLE 1. *Average decay ratings for mini lap-joint samples exposed at Hilo, HI, for 24 months. The samples were prepared from defect free spruce pine sapwood and treated by a full cell process. The samples with wax were treated using acetone solvent, and all other samples were treated with water/acetone.*

Treatment[1]	Retention, kgm^{-3}	Average Decay Rating[2]
0.19% Barlox 12/0.07% DDAC	1.44/0.48	8.9
0.37% Barlox 12/0.14% DDAC	2.40/0.96	9.3
0.56% Barlox 12/0.21% DDAC	3.8/1.44	9.6
0.19% Barlox 12/0.07% DDAC/0.4% BHT	1.28/0.48/2.56	9.9
0.37% Barlox 12/0.14% DDAC/0.4% BHT	2.40/0.96/2.56	10.0
0.56% Barlox 12/0.21% DDAC/0.4% BHT	3.68/1.44/2.56	10.0
0.19% Barlox 12/0.07% DDAC/0.4% BHT/0.2% Phen/1% Wax	0.96/0.32/1.92/0.92/4.80	10.0
0.37% Barlox 12/0.14% DDAC/0.4% BHT/0.2% Phen/1% Wax	1.76/0.64/1.92/0.92/4.80	10.0
0.56% Barlox 12/0.21% DDAC/0.4% BHT/0.2% Phen/1% Wax	2.56/0.96/1.76/0.96/4.48	10.0
0.4% BHT	2.08	9.0
0.2% Phen	1.12	10.0
0.25% CCA (Positive Controls)	1.12	10.0
— (Controls)	—	8.8

[1]Barlox 12 is the tradename for an amine oxide, *N,N*-dimethyldodecylamine *N*-oxide; DDAC is didecyldimethylammonium chloride; BHT is the antioxidant butylated hydroxytoluene; Phen is the metal chelator 1,10-phenanthroline; and wax is paraffin wax added as a water repellent.
[2]The results are an average of 8 replicate samples, with a "10" rating no decay, "9" a trace of decay, etc., down to a "0" or failed.

To summarize, outdoor exposure results with BHT are more promising than was originally anticipated from laboratory decay tests. Specifically, the data indicate that a lower, and therefore more economical, BHT level can be employed to protect wood than was generally employed in the laboratory tests. We are still uncertain what minimum BHT retention is necessary with a particular biocide and biocide retention. It is likely that wood in ground contact will need higher BHT levels than wood exposed above-ground, and various biocide:BHT ratios could be employed. Additional samples need to be installed, and longer exposure times are required, to determine the optimal biocide and BHT levels.

PRELIMINARY ECONOMIC ANALYSIS

Sufficient outdoor exposure results have now been obtained for a preliminary analysis of the cost of an organic biocide alone versus a reduced biocide level plus co-added BHT. This analysis is tentative due to the short outdoor exposure time and limited number of organic biocides and biocide:BHT levels examined. Two possibilities were studied; 1) ground-contact exposure with CTN, which would be used at relatively high retentions; and 2) a highly effective (low dose) biocide, propiconazole, in an above-ground application.

We obtained the current prices (Spring 2004) for the biocides chlorothalonil (US$ 11.69/kg, 100% a.i. basis, technical grade), propiconazole (US$ 55/kg), and low purity BHT (US$ 2.64/kg). (Many chemists are accustomed to obtaining prices from the Chemical Market Reporter (CMR). The price of BHT reported in this source, however, is higher than we used since CMR gives the price for highly purified BHT for food or plastic applications.)

For ground-contact applications, a CTN retention of 5.12 kgm^{-3} would be reasonable based on field test data. [The level recommended will depend on if a heavy oil carrier is used.] This gives a biocide cost of US$ 59.85/m³ of treated wood. Based on our ground-contact CTN:BHT data (Schultz et al. 2004), at least a 2-fold efficacy increase can be obtained with the addition of 9.7 kgm^{-3} BHT. If the level of CTN was reduced by half (2.56 kgm^{-3}) by adding this BHT level, the biocide and antioxidant cost would be US$ 55.54/m³.

Use of 0.30 kgm^{-3} of the highly effective bioicide propiconazole is being examined for above-ground applications in North America, for a biocide cost of US$ 16.50/m³. Based on the quaternary lap-joint samples (Table 1), 2.56 kgm^{-3} of BHT increased the biocide's efficacy by more than 3-fold. Also, laboratory decay tests indicate at least a doubling in efficacy when propiconazole was combined with BHT (Schultz and Nicholas 2000a, 2002). If we assume that the level of propiconazole can be reduced by half by adding 2.56 kgm^{-3} of BHT, then the cost of a propiconazole:BHT system would be $15.01.

Thus, based on these two tentative analyses, the use of BHT may be economically viable for totally organic systems. The above analyses are only preliminary, and other biocide:BHT levels could be considered. Longer exposures may show that BHT might eventually be depleted, and the cost of formulating BHT into a wood preservative was not considered. Positive benefits of adding BHT are that reduced biocide levels may make future disposal easier, BHT may protect the biocide against biodegradation which would reduce the initial biocide level necessary (Schultz et al. 2004), and this concept could be a "green" marketing advantage. We are continuing to inspect these samples, and hope to shortly install additional samples to study other biocides and/or BHT retentions.

PROPOSED MECHANISM TO EXPLAIN THE SYNERGISTIC EFFECT FROM BIOCIDE:ANTIOXIDANT COMBINATIONS

Based on the proposed pathways by which brown-rot fungi degrade wood (Goodell et al. 2003b, and references therein), a mechanism by which BHT [or other antioxidants] might hinder fungal degradation is proposed. Because of some uncertainty in the mechanism(s) by which brown-rot fungi degrade wood, this proposed

mechanism (Fig. 1) is only generalized. Figure 1 is specific for brown-rot fungi, as enzymatic systems play a larger role with white-rot fungi. Details of this proposed mechanism are as follows:

1. The decay fungus forms a reductant in redox cycle A; possibly an electron-rich catechol or *P*-hydroquinone compound. It is well established that fungal hyphae cell walls are highly reductive (e.g., Reading et al. 2003). Also, the environment adjacent to the decay fungus, especially in the fungal sheath material that surrounds the fungal hypha, is reported to be relatively acidic. For the above two reasons, the catechol or hydroquinone is

relatively stable and does not oxidize and, consequently, diffuses away from the hypha.

2. Once the fungal-formed reductant has diffused far enough away from the fungal hypha to be in a more oxidative and less acidic environment, the catechol or hydroquinone can complex with, and be oxidized by, Fe(III) or Cu(II), with the metal ions concurrently reduced. Specifically, the catechol/hydroquinone is oxidized to a quinone via two consecutive one-electron steps, and two metal ions concomitantly reduced to Fe(II) or Cu(I) (redox cycle B). The oxidized quinone product from redox cycle A then diffuses back to the fungal hypha where the fungus
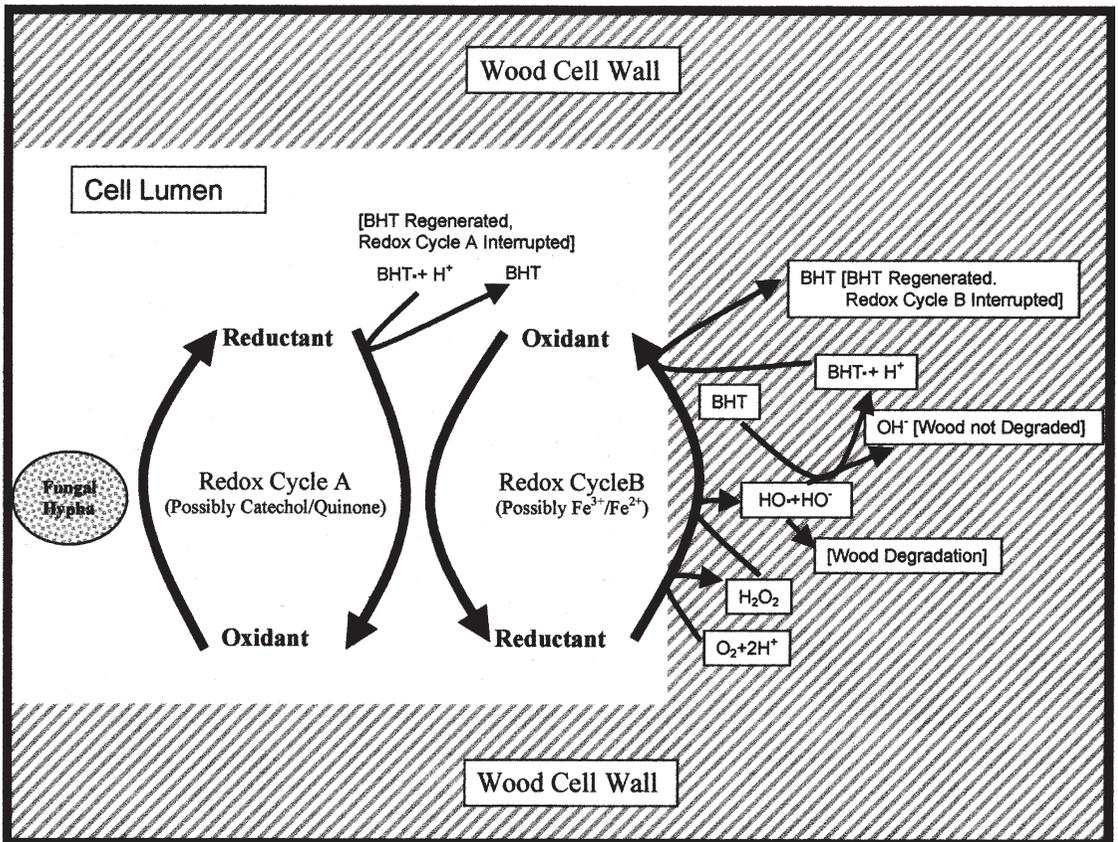

Fig. 1. Generalized hypothetical scheme of how brown-rot fungi could degrade wood with multiple interconnected redox cycles, and a proposed scheme for how BHT, or other free radical scavengers (antioxidants), might interfere with the fungal generated radical reagents which attack wood. In addition, we propose a possible mechanism by which the BHT radical, formed by scavenging a free radical, might be regenerated by the reductive portion of one or more of the fungal redox cycles.

expends energy to reduce and reform the oxidized quiniZone back to a reduced catechol or hydroquinone. Conversely, it is possible that redox cycle A consists of a catechol/semiquinone one-electron redox cycle. The semiquinone radical would be less stable than a quinone, however.

3. The reduced metal can, in turn, reduce oxygen to hydrogen peroxide, which is fairly stable and can diffuse into the wood substance.

4. Additional reduced Fe(II) or Cu(I) can react with the hydrogen peroxide via the Fenton reaction to form a highly reactive hydroxy radical which will oxidize/perturb the adjacent lignocellulosic material in the cell wall. [Fenton Reaction: Ligated Fe(II) + $H_2O_2 \rightarrow$ Ligated Fe(III) + HO^- + $HO^{\bullet}$]. Other radical or oxidizing reactants, besides or in addition to the hydroxyl radical, might be formed; e.g., superoxide anion radical, carboxylate anion radical, peroxyl radicals, etc.

5. The reductive portion of redox cycle A, where catechol/hydroquinone is formed, likely occurs only adjacent to the fungal hypha. The oxidative portion of redox cycle A, and the entire redox cycle B, can occur away from the fungal hypha, including within the cell wall as the fungal degradation progresses. Hydrogen peroxide formation via autoxoidation of iron and/or enzymatically will occur close to or in the cell wall and away from the fungal hypha. While hydrogen peroxide is stable and can diffuse to the wood cell wall or fungal hypha, the reductive and highly acidic environment which surrounds the fungus prevents the Fenton reaction from occurring (Goodell et al. 1997; Xu and Goodell 2001). Thus, no destructive radicals are formed near the fungal hypha.

6. If the radical/oxidizer comes into contact with a free radical scavenger (antioxidant), such as BHT, the radical is reduced to an inert compound by a one-electron process and the antioxidant becomes a stable radical. Specifically, with BHT the phenoxy group donates a $H^{\bullet}$ and forms a phenoxy radical.

The BHT phenoxy radical is stable for a relatively long time due to the two large bulky *t*-butyl groups on each side of the phenoxy radical; specifically, BHT is a radical "trap." Over a long time, however, the BHT phenoxy radical can lose a hydrogen atom from the methyl group and, ultimately, dimerize and undergo further radical-scavenging reactions until rendered inert (Dexter 1992).

7. The stable BHT radical could be reduced to reform BHT by any fungal redox cycle that has an electrode potential greater than about 0.8 V (Ni et al. 2000). Many of the proposed fungal redox cycles have electrode potentials about or greater than 0.8 V (e.g., Reading et al. 2003; Goodell 2003; Henry 2003). If this reduction occurs two events occur that protect the wood and inhibit fungal degradation: A) the BHT antioxidant is regenerated, thus explaining the relatively low depletion mentioned earlier; and B) the reductive portion of one or more of the fungal redox cycles is disrupted. BHT is known to be regenerated in reductive chemical and biological environments (e.g., Kagan et al. 1990). However, radical intermediates are inherently unstable and side reactions occur (Dexter 1992) which eventually oxidize and/or degrade the BHT. Thus, BHT is unlikely to be endlessly regenerated and, under continuous exposure to fungal-generated free radical would, over time, be degraded.

8. The fungal redox cycle which actually degrades the lignocellulosic material is the reductive portion of redox cycle B. This phase likely starts at the cell-wall/lumen interface during the initial fungal colonization and progresses into and degrades the cell-wall material as the fungal colonization and attack/degradation progress.

9. The antioxidant BHT only scavenges the fungal-generated free radicals which degrade the wood. While BHT may disrupt the fungal redox cycles, it is not capable of directly attacking the fungus; i.e., BHT is not a biocide. Thus, BHT alone only protects wood for a short period in laboratory

decay tests (Schultz and Nicholas 2000a, 2000b).

10. The combination of BHT and a biocide is more effective than either component alone. The antioxidant prevents free-radical degradation and, consequently, protects the cell wall from being perturbed during the initial stage of fungal colonization. The biocide directly attacks the fungus. There is also the possibility that the antioxidant may also protect an organic biocide from being degraded by microbial-generated radicals.

Notes:

- Only two interconnected brown-rot fungal redox cycles are shown in Fig. 1, but multiple redox cycles are almost certainly present, and the different classes of fungi (brown-, white- and soft-rot) have different fungal redox cycles.

- Antioxidants typically work by donating a hydrogen atom ($H^\bullet$) to stabilize/render inert any radical in materials such as plastics. However, in decaying wood where free water is present, it is possible that a hindered phenolic antioxidant might quench radicals by a consecutive, two-step mechanism: 1) loss of a proton ($H^\bullet$), followed by 2) electron (e^-) transfer. If this occurs, then the electrode potential would likely be lower than typical electrode potential values experienced for antioxidants in hydrophobic plastics. An antioxidant's water solubility and acidity might be a factor if the latter mechanism occurs.

- If sufficient biocide is co-added with an antioxidant to inhibit appreciable fungal growth, then the stoichiometric demand on BHT consumption may be quite small, and regeneration of BHT within the fungal redox cycle(s) may never be needed (and, indeed, may not even occur at all).

If this pathway is understood fully, then it may be possible to optimize this concept. Consequently, we are continuing to study this concept and will report on further data as results are obtained.

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