Photostabilizing Milled Wood Lignin with Benzotriazoles and Hindered Nitroxide[†][¶]

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ABSTRACT

The inhibitory processes operating when a 2(-2′-hydroxyphenyl) benzotriazole-based ultraviolet absorber (UVA) and a hindered nitroxide free radical are applied to high-yield pulps were studied using milled wood lignin and filter paper as a model. Using quantitative ^{31}P NMR it was determined that the UVA is almost completely photostable during irradiation, suggesting that its protective mechanism is based primarily on ultraviolet absorption. Furthermore, the nitroxide was found to protect the UVA from photodegradation. Analysis of irradiated lignin samples involved derivatization followed by reductive cleavage of β-arylether groups. The phenolic-OH groups thus released were quantified using ^{31}P NMR. The benzotriazole/nitroxide stabilizing system was found to cooperatively inhibit the cleavage of β-arylether groups. Furthermore, this system was found to have a synergistic inhibitory effect on the formation of catechol structures. These results suggest that the synergism observed between benzotriazole-based UV screens and nitroxyl radicals on the inhibition of yellowing could be a result of their ability to slow the formation of catechol structures and β-O-4 cleavage in addition to the possibility of a UVA-regeneration mechanism.

INTRODUCTION

Technological advances in mechanical pulping and bleaching have made it possible to produce high-yield pulps at brightness and strength levels suitable for the production of high quality papers. The major obstacle to the widespread utilization of such pulps is their tendency to photoyellow upon exposure to light and heat. Undoubtedly, the main chemical species that causes the yellowing is lignin (1).

Numerous research efforts have been carried out in an attempt to discern the exact mechanism by which mechanical pulps photoyellow. It is generally accepted that phenoxy radicals are a key intermediate involved in the photoyellowing process and that they can readily become oxidized to form colored compounds in lignin (2). Phenoxy radicals can be formed through a variety of pathways including direct absorption of near-UV light by free phenolic groups or by abstraction of phenolic hydroxyl hydrogen by excited α-carbonyl groups (3). Gierer and Lin (4) first demonstrated that phenoxy radicals are formed following the light-induced cleavage of phenacyl arylethers. Recently, it has been shown that the most significant photodegradative pathway leading to the formation of phenoxy radicals is the 'ketyl radical' pathway and involves the breakdown of arylglycerol-β-O-4-arylethers (5,6).

Methods of inhibiting yellowing can be grouped into two broad categories. The first approach involves chemically modifying the structure of the reactive functional groups in lignin so as to halt the initiation and subsequent radical-based reactions leading to the formation of chromophoric compounds in mechanical pulps. Proposals have included reduction of lignin α-carbonyl groups (7–9), alkylation (methylation or acetylation) of lignin phenolic groups (10,11) and catalytic hydrogenation of lignin aromatic rings (12,13); however, none of these methods has been fully effective (1).

The second category of inhibition efforts involves the use of chemical additives applied to the paper to retard or eliminate the formation of colored compounds (14–16). Among the additives proposed for the inhibition of photoyellowing, ultraviolet absorbers (UVA)[‡] and radical scavengers have consistently provided encouraging results. Unfortunately, no individual additive has met all the commercial conditions required for successful photoyellowing inhibition (2). Combined approaches have been reported; however, they show that the use of a radical scavenger and a UVA applied jointly onto mechanical pulp can provide performance unmatched by any single additive when applied alone (17,18).

Recently, a novel inhibition system has been found in which a benzotriazole-based UVA is applied to mechanical pulp in combination with a hindered nitroxide free radical (19). Nitroxides are known to combine rapidly with carbon-centered radicals and thus act as efficient radical traps in

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[‡]*Abbreviations:* DFRC, derivatization followed by reductive cleavage; HALS, hindered amine light stabilizer; 4-hydroxy-TEMPO, 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl; MWL, milled wood lignin; UVA, ultraviolet absorber.

chain oxidations (20,21). Most researchers agree that hindered amine light stabilizers (HALS), which have been used extensively to inhibit the photodegradation of synthetic polymers, are converted to the corresponding nitroxide radicals under photooxidative conditions. Furthermore, it is generally accepted that the intermediate nitroxide radicals are the active inhibiting species during such photostabilization reactions (22).

Despite their remarkable effectiveness as stabilizers for polyolefins, HALS has never before been found successful for the stabilization of mechanical pulps (14,19,23). In contrast, McGarry *et al.* (19) have demonstrated that the application of the hindered nitroxide radical 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (4-hydroxy-TEMPO) in amounts as low as 0.1% will inhibit both light-induced and thermally-induced yellowing of mechanical pulps. Moreover, these compounds have been shown to behave synergistically with UVA, imparting brightness stability to mechanical pulps, which is comparable to the stability of bleached kraft pulp (19). The authors provide a series of suggestions as to how exactly this additive combination lends UV stability to lignin-rich pulp, but at present the mechanism is still uncertain. This uncertainty has prompted us to embark on an investigation into the precise photochemical interactions that occur when high-yield pulps are treated with a 2-(2′-hydroxyphenyl) benzotriazole-based UVA in conjunction with the hindered nitroxide. In this paper we report on our studies into the photochemistry of lignin-rich pulp in the presence of this stabilizing system using milled wood lignin (MWL) as a model.

MATERIALS AND METHODS

The MWL sample used in this work (Klason + UV lignin content 93.06%) was isolated from black spruce (*Picea mariana*) wood chips according to the methods of Brownell (24) and Bjorkman (25). Test sheets were prepared using Whatman No. 1 filter paper. Base-hydrolyzed Tinuvin 1130 (Scheme 1) was received as a gift from Dr. A. P. Rodenheiser. The hindered nitroxide 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl free radical (Scheme 1) is commercially available from Ciba Specialty Chemicals. All solvents were purchased from Aldrich (St. Louis, MO) and used as received.

Impregnation and irradiation protocols. Tinuvin 1130 and/or 4-hydroxy-TEMPO were mixed with MWL and dissolved in a minimum of acetone/water (80:20 vol/vol). These solutions were then applied homogeneously to both sides of precut Whatman No. 1 filter paper sheets using a syringe. The treated test-sheets were dried overnight under partial vacuum over P_2O_5. The total amount of lignin impregnated onto the filter paper comprised approximately 30% of the weight of the sheet in order to mimic the lignin content in mechanical pulp papers. The applied charge of UV stabilizer was 1.0% (wt/wt) for Tinuvin 1130 and 0.5% (wt/wt) for the 4-hydroxy-TEMPO. These charges were chosen based on the values used in the work of McGarry *et al.* (19); in addition, a 1% charge of base-hydrolyzed Tinuvin 1130 was determined to be sufficient for accurate integration in the ^{31}P NMR spectrum.

Samples of MWL absorbed onto cellulose in the absence of any UV stabilizers were used as controls and all experiments were carried out in triplicate.

For accelerated exposure, lignin-impregnated test-sheets were placed in a custom-made photoreactor that was maintained at 30℃ and contained four 350 nm black lights. The intensity of the irradiation was measured using a digital power monitor; the incident light energy supplied by this experimental setup was determined to be 166.5 mJ/cm² min⁻¹. Each side of the paper was photolyzed for half of the desired irradiation period.

After irradiation, the products were recovered by exhaustively extracting the filter paper with an 80:20 (vol/vol) acetone/water mixture (5 × 5 mL). The combined extracts were filtered and concentrated under reduced pressure at 22℃. The photolyzed lignin/additive samples were freeze-dried and then further dried with a high-vacuum pump at room temperature for 24 h. This procedure typically yielded 80–95% lignin recovery.

Quantitative ^{31}P NMR spectroscopy. Functional group analyses of the recovered lignin/additive samples was accomplished using quantitative ^{31}P NMR following published procedures (26,27). Samples were prepared by dissolving 30–40 mg of recovered lignin in a pyridine/CDCl₃ solution (1.6:1 vol/vol) and all labile protons were phosphitylated using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Cholesterol was used as the internal standard and chromium acetylacetonate (Cr(acac)₃) was added as the relaxation reagent.

All spectra were recorded at 81.0 MHz using inverse-gated decoupling on a Varian XL 200 NMR spectrometer equipped with a 5 mm broad-band probe. In each case at least 256 transients were acquired with a pulse width corresponding to a 90° flip angle and a pulse delay of 5 s. All chemical shifts are reported relative to the reaction product of the derivatization reagent with water, which has been observed to give a sharp signal at 132.2 ppm.

Derivatization followed by reductive cleavage. The derivatization followed by reductive cleavage (DFRC) procedure used was similar to that developed by Lu and Ralph (28,29); however, the precise amounts of lignin and reagents used were modified as suggested by Tohmura and Argyropoulos (30). Acetyl bromide (AcBr), dioxane, acetic acid and zinc dust were purchased from Aldrich and used as supplied.

Acetyl bromide derivatization. To a 50 mL round bottom flask containing approximately 50 mg (accurately weighed) of lignin was added 15 mL of an acidic AcBr stock solution (AcBr:acetic acid, 10:90 vol/vol). The flask was sealed and gently stirred at 50℃ for 3 h. The solvent was then evaporated to dryness under reduced pressure at 35℃.

Reductive cleavage. The above residue was dissolved in 15 mL of an acidic reduction medium (dioxane:acetic acid:water, 5:4:1 vol/vol/vol). Zinc dust (approximately 235 mg) was added and the mixture was stirred at room temperature for 30 min. The reaction mixture was then quantitatively transferred to a separatory funnel using methylene chloride (10 mL). To this 100 µL of an internal standard solution (cholesterol, 195.0 mg in 5 mL of methylene chloride) was added for subsequent ^{31}P NMR analysis. Saturated ammonium chloride (NH₄Cl) solution (8 mL) was added and the organic layer was separated. The water phase was extracted two more times with methylene chloride (2 × 8 mL). The combined extracts were dried with anhydrous sodium sulfate and the filtrate was evaporated to dryness under reduced pressure. Finally, the residue was redissolved in approximately 5 mL of a dioxane/water solution (80:20 vol/vol) and then the sample was freeze-dried overnight. Functional group analysis of the recovered lignin samples was accomplished using quantitative ^{31}P NMR as described by Tohmura and Argyropoulos (30). Error bars provided in all figures represent standard deviation values.

RESULTS AND DISCUSSION

At present, the effectiveness of UV stabilizing systems for mechanical pulp is evaluated primarily by measuring brightness values and absorption/scattering coefficients. Although this information is important, it provides little insight into the precise chemical mechanism of the exerted photostabilization. In the present effort, quantitative ^{31}P NMR has been used to systematically examine for photoinduced molecular changes within MWL under conditions of benzotriazole/nitroxide inhibition. Furthermore, by combining ^{31}P NMR techniques (26,27) with a procedure known as DFRC (28,29), it became possible to quantitatively evaluate the photoinitiated cleavage of noncondensed β-arylether groups as a function of time under controlled conditions of irradiation/inhibition.

Table 1. The percentage (%) of remaining phenolic hydroxyl belonging to Tinuvin 1130 in the presence of MWL as a function of irradiation time

Irradiation time (h)	Tinuvin 1130	Tinuvin 1130 in the presence of TEMPO	Tinuvin 1130 on a cellulose support
0	100	100	100
24	95.2	99.9	100
72	93.5	99.2	100
120	90.5	97.9	100

Figure 1. Plots of the increase in catechol structures as a function of irradiation time for a control MWL sample and samples impregnated with Tinuvin 1130 (1.0% wt/wt), 4-hydroxy-TEMPO (0.5% wt/wt) and a combination of both Tinuvin 1130 and 4-hydroxy-TEMPO (1.0 + 0.5%, respectively).

The photochemical fate of the UV stabilizers

The photochemical sustainability of a UVA is of extreme importance in relation to its photostabilization efficiency when applied on high-yield pulps. Traditionally, UVA based on 2-hydroxybenzophenone and hydroxyphenyl benzotriazole derivatives were thought to function by absorbing UV light and redistributing it as nonharmful thermal energy through reversible intramolecular transformations (31); however, this has recently become a matter of significant discussion. Some researchers suggest that UV absorbers may also operate as excited state quenchers of active chromophores (32–34) while others propose that these types of stabilizers act through radical scavenging or antioxidant reactions (18,35,36). According to some studies, 2-(2′-hydroxyphenyl) benzotriazoles may act exclusively as UV absorbers, whereas 2-hydroxybenzophenones confer additional stability through energy transfer reactions (37,38).

Recently, Peng and Argyropoulos (39) demonstrated that the phenolic hydroxyl groups of various UV screens could be analyzed using ^{31}P NMR. Using this technique, it was demonstrated that 2-hydroxybenzophenone-based UV screens are actively involved in photochemical reactions with lignin, resulting in partial elimination of their phenolic-OH groups. In contrast, we used the same ^{31}P NMR technique to follow the fate of the phenolic-OH of base-hydrolyzed Tinuvin 1130 and found it to be almost completely photostable under identical irradiation techniques. As shown in Table 1, even after 120 h of irradiation in the presence of MWL over 90% of the original Tinuvin 1130 was found to be intact. It can also be seen that the presence of 4-hydroxy-TEMPO has been found to protect the Tinuvin 1130 from photodegradation (Table 1). After 120 h of irradiation in the presence of MWL and 4-hydroxy-TEMPO, 97.9% of the original Tinuvin 1130 was recovered unaltered. These results suggest that the beneficial photostabilization effects observed when a UV absorber and an antioxidant are jointly applied onto mechanical pulp can be partly attributed to UVA-regeneration mechanism (40). Obviously, it would have been quite informative to follow the fate of the hydroxyl group of the 4-hydroxy-TEMPO as a function of irradiation time using ^{31}P NMR. Unfortunately, due to the free radical nature of the compound it was impossible to obtain a signal in the NMR spectrum.

Irradiation of the benzotriazole on a cellulose support in the absence of lignin showed that this stabilizer is completely photostable. This indicates that the small amount of degradation that does occur is most likely caused by a photo-induced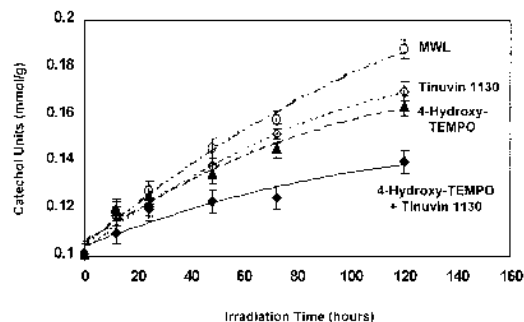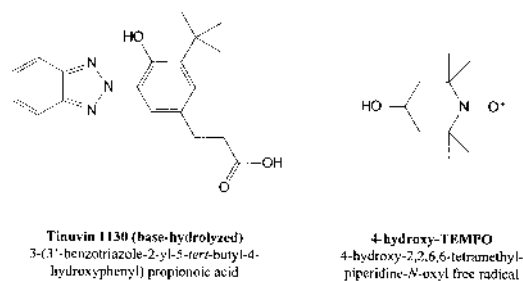 chemical reaction with the lignin. This result is in accordance with conclusions drawn by other researchers (18,41) and lends support to the theory that 2-(2′-hydroxyphenyl)-benzotriazoles act exclusively as UV absorbers, whereas 2-hydroxybenzophenones confer stability through other mechanisms.

Formation of catechol structures during irradiation

The formation of catechol structures during the photodegradation of lignin is intimately related to the formation of chromophores and to *ortho*-quinoid formation in particular (42,43). In this effort, it was possible to use ^{31}P NMR to quantify the formation of catechol structures in irradiated MWL samples as a function of time. As outlined in Fig. 1, the results of this work show a steady increase in the amount of catechol units with irradiation. Furthermore, it can be seen that Tinuvin 1130 displays a moderate inhibitory effect on the formation of catechol structures. It is reasonable to assume that this UVA retards catechol formation by reducing the total flux of light that is able to reach and interact with the lignin to form phenoxy radicals.

The hindered nitroxide, 4-hydroxy-TEMPO, appears to slow the formation of catechol structures somewhat more efficiently than Tinuvin 1130. Assuming that the amount of catechol structures formed is qualitatively related to the amount of yellowing observed on high-yield pulp, this result mirrors that obtained by McGarry *et al.* (19) in which the hindered nitroxide was found to give better yellowing inhibition than a benzotriazole-based UVA (Tinuvin 328). Presumably, the protective effect of 4-hydroxy-TEMPO rests on its ability to scavenge carbon-centered radicals and thereby slow the formation of phenoxy radicals *via* the ketyl radical pathway.
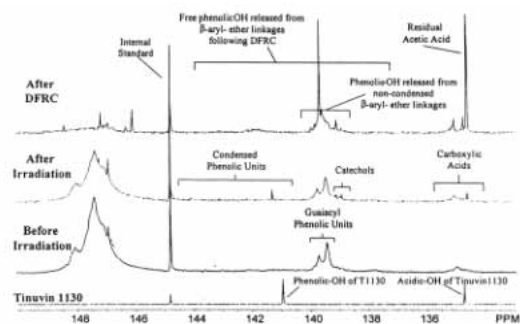

Tinuvin 1130 (base-hydrolyzed)
3-(3′-benzotriazole-2-yl-5-*tert*-butyl-4-hydroxyphenyl) propionoic acid

4-hydroxy-TEMPO
4-hydroxy-2,2,6,6-tetramethyl-piperidine-*N*-oxyl free radical

Figure 2. Quantitative ^{31}P NMR spectra of recovered MWL samples before and after irradiation and DFRC.

Figure 3. Plots of the observed cleavage of noncondensed β-*O*-4-arylether units in irradiated lignin samples for a control MWL sample and samples impregnated with Tinuvin 1130 (1.0% wt/wt), 4-hydroxy-TEMPO (0.5% wt/wt) and a combination of both Tinuvin 1130 and 4-hydroxy-TEMPO (1.0% + 0.5%, respectively).

It can also be seen in Fig. 1 that when Tinuvin 1130 and 4-hydroxy-TEMPO were applied jointly onto the lignin-containing samples, the combination was found to display a remarkable synergistic effect on the inhibition of catechol formation. Specifically, the presence of both Tinuvin 1130 and 4-hydroxy-TEMPO reduces the formation of catechol structures by 0.048 mmol/g over the unprotected sample. In comparison, the formation of catechol structures is reduced by 0.018 mmol/g in the presence of Tinuvin 1130 alone and by 0.024 mmol/g in the presence of 4-hydroxy-TEMPO alone. If the effect of Tinuvin 1130 and 4-hydroxy-TEMPO together were additive, then the combined reduction of catechol structures would amount to only 0.042 mmol/g. These data indicate that the protective effect of the UVA/nitroxide combination is greater than the effect of the UVA plus the effect of the nitroxide.

Once again, the effect of these stabilizers on the inhibition of catechol structures mirrors the effective photoyellowing inhibition that was observed by McGarry *et al.* (19). Specifically, these researchers found that the combination of a benzotriazole-based UVA and 4-hydroxy-TEMPO provided mechanical pulp with remarkable additive photoyellowing inhibition. Of course, these values cannot be quantitatively compared due to the fact that different light sources and irradiation times were used. In fact, the light source used in this work was considerably more intense than that used by McGarry *et al.* (19) in order to ensure that the light-induced changes within the lignin were significant enough to quantify in the NMR spectrum. Moreover, catechol formation is related to the formation of yellow color in paper; however, it is not the only source of reversion.

Due to its observed photostability, it is likely that the Tinuvin 1130 protects the lignin by acting primarily as a UV absorber and that the 4-hydroxy-TEMPO cooperates by reacting with carbon-centered radicals; however, one would expect this type of cooperation to be additive rather than synergistic. It has been shown in this work that although the Tinuvin 1130 is relatively photostable during irradiation, the nitroxide does provide protection from the small amount of degradation that is seen to occur. Alternatively, it is feasible that the presence of the benzotriazole is protecting the nitroxide from photodegradation, thereby improving its performance. Unfortunately, the likelihood of this suggestion could not be evaluated using ^{31}P NMR.
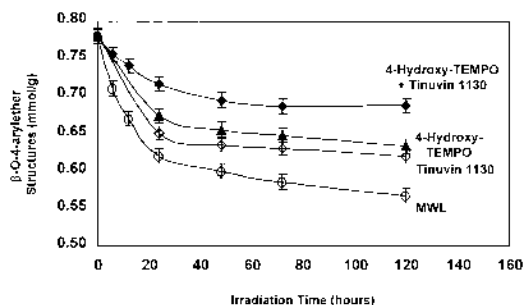
The cleavage of β-*O*-4-arylether linkages during irradiation

Quantitative ^{31}P NMR spectroscopy allows for the structural elucidation of all hydroxyl-bearing moieties in lignin (26,27); however, it is limited in that it cannot provide information about the etherified bonding patterns of lignins. Given that the cleavage of β-*O*-4-arylether linkages is believed to be the most significant mechanistic pathway at work during the photoyellowing of mechanical pulps, this is a considerable limitation with respect to using ^{31}P NMR to study the brightness reversion mechanism of MWL. This shortcoming can be circumvented, however, by first cleaving the arylether groups using a mildly depolymerizing technique known as DFRC (28,29). Once cleaved, the corresponding phenolic hydroxyl moieties that are released can be readily phosphitylated and quantified using ^{31}P NMR. The various experimental and other issues pertaining to the quantitative reliability of the technique have been reported elsewhere (30).

In this work, the combined use of DFRC and quantitative ^{31}P NMR provided a unique opportunity to quantify the amount of noncondensed β-arylether linkages present in the recovered MWL and to monitor the decrease in the concentration of these units as a function of irradiation time. Typical quantitative ^{31}P NMR spectra and signal assignment of MWL before and after irradiation and DFRC are shown in Fig. 2.

The plots in Fig. 3 demonstrate the decrease in the concentration of β-*O*-4-arylether groups as a function of irradiation time in the presence and absence of UV stabilizing systems. The total amount of noncondensed β-arylether linkages that were found to have cleaved in the control sample following 120 h of irradiation is equal to 0.213 mmol/g or 27% of the original units present before irradiation.

It can be seen that the application of Tinuvin 1130 acted to inhibit the photoinduced cleavage of β-arylether linkages in the lignin. If Tinuvin 1130 acts solely as a UV absorber, as suggested earlier, it is likely that this additive inhibits this cleavage by reducing the flux of UV light that is able to react with the lignin and generate free radicals. It therefore reduces the cleavage of β-*O*-4-arylether units by reducing the amount of free radicals that are available to abstract a benzylic hydrogen to initiate the reaction.

It is also apparent in Fig. 3 that 4-hydroxy-TEMPO is

effective in inhibiting the cleavage of β-arylethers, most likely by scavenging carbon-centered radicals in competition with the lignin. It can be seen that the nitroxide is slightly more effective in inhibiting this reaction than the Tinuvin 1130, which is reminiscent of the earlier observation regarding the inhibition of catechol formation. This also supports the observation made by McGarry *et al.* (19) that the 4-hydroxy-TEMPO is somewhat more effective in inhibiting the photoyellowing of mechanical pulps than is the benzotriazole UVA. However, in this case it appears that at later time scales the inhibitory effect of the 4-hydroxy-TEMPO may begin to slow down, after which Tinuvin 1130 may begin to out-perform the nitroxide free radical.

A very significant result evident from the plots of Fig. 3 is that the Tinuvin 1130 and 4-hydroxy-TEMPO appear to be working cooperatively to inhibit the cleavage of β-*O*-4-arylether units. In fact, after approximately 72 h, all cleavage appears to have halted, and 88% of the original noncondensed β-arylether units remain intact. Because the effectiveness of the 4-hydroxy-TEMPO declines slightly at later time scales, an effect that is not seen when nitroxide is combined with Tinuvin 1130, one possible suggestion for this cooperative effect is that the benzotriazole is acting to protect the 4-hydroxy-TEMPO from photodegradation. This data provides evidence that the remarkable photostabilization of mechanical pulps provided upon application of 4-hydroxy-TEMPO in combination with a benzotriazole-based UVA is due, at least in part, to the ability of these molecules to inhibit the cleavage of β-*O*-4-arylether linkages in lignin.

CONCLUSIONS

Using quantitative ^{31}P NMR, it has been determined that the benzotriazole-based UVA Tinuvin 1130 (base-hydrolyzed) is almost completely photostable when irradiated in the presence of MWL, suggesting that the inhibitory mechanism of this molecule is based purely on UV absorption. It has also been shown that the hindered nitroxide 4-hydroxy-TEMPO acts to protect this UVA from photodegradation, which suggests the possibility of a UVA-regeneration mechanism and provides some insight into the cooperative action that is observed when these molecules are applied jointly onto mechanical pulp.

It has been shown that the combination of ^{31}P NMR with the DFRC procedure allows for the quantification of noncondensed β-arylether groups present in a sample of lignin and that this technique can be used to follow the cleavage of β-arylether groups as a function of irradiation time. Furthermore, it can be concluded that both Tinuvin 1130 and 4-hydroxy-TEMPO free radical are able to inhibit the cleavage of β-arylether groups.

Finally, quantitative ^{31}P NMR has been used to demonstrate that both the Tinuvin 1130 and 4-hydroxy-TEMPO inhibit the formation of catechol structures in MWL and that when these materials are used in combination, their inhibitory action on catechol formation is synergistic.

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