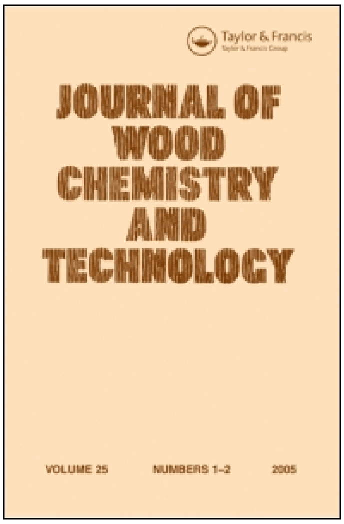

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Methoxy-P-Benzoquinone and Methoxyhydroquinone as Models for Chromophore Changes in the Bleaching of Softwood Mechanical Pulps. I the Detection of Methoxyhydroquinone in the Spent Liquor from the Peroxide Bleaching of Thermo-Mechanical Pulp

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METHOXY-p-BENZOQUINONE AND METHOXYHYDROQUINONE AS MODELS FOR CHROMOPHORE CHANGES IN THE BLEACHING OF SOFTWOOD MECHANICAL PULPS. I THE DETECTION OF METHOXYHYDROQUINONE IN THE SPENT LIQUOR FROM THE PEROXIDE BLEACHING OF THERMO-MECHANICAL PULP

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ABSTRACT

Methoxyhydroquinone was detected in the spent liquors of peroxide-bleached loblolly pine thermomechanical pulp. The potential effect of this leucochromophore and the corresponding quinone on the brightness and brightness stability of mechanical pulps bleached with peroxide is discussed.

INTRODUCTION

Ortho and para quinones are frequently included in lists of chromophores proposed as contributing to the color of wood and wood pulp[1-4]. The origin of the aforementioned chromophores may be traced to the autoxidation of catechol and hydroquinone units present in the lignin macromolecule[5]. p-Hydroxybenzyl alcohol and p-hydroxyphenyl ketone units in lignin have also

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been postulated[6-7] as giving rise to p-benzoquinonoid and hydroquinonoid moieties during peroxide bleaching through elimination of side chains via the "Dakin-like" and Dakin reactions, respectively. Depending on the redox potentials of the various organic and inorganic constituents in the bleach liquor, some quinone-hydroquinone interconversion may also be anticipated. The validity of the foregoing concepts has been reinforced by the detection of small amounts of methoxy-p-benzoquinone and methoxyhydroquinone following the oxidation of monomeric[8-11] and dimeric[13-17] softwood lignin model compounds with alkaline hydrogen peroxide under simulated technical bleaching conditions. The low yields recorded for these two compounds were ascribed to subsequent oxidative breakdown and/or alkali-induced condensation reactions.

As a preface to additional experiments aimed at characterizing the effect of methoxy-p-benzoquinone and methoxyhydroquinone and their reaction products on the optical properties of peroxide bleached pulps, a study was initiated to demonstrate the formation of either or both of these compounds during the peroxide bleaching of mechanical pulps by attempting to identify them in the corresponding spent liquors. In these tests, samples of thermomechanical pulp were bleached with peroxide under technical conditions except that in one instance the pH was maintained at 10.5 by the periodic addition of alkali. The bleach liquors were subsequently analyzed by gas chromatographic and gas chromatographic/mass spectrometric procedures.

RESULTS AND DISCUSSION

Methoxyhydroquinone was detected in 0.1-0.3% yield (lignin basis) in the extract of the spent liquor in the case where the pH was allowed to drop to 7.9. However, only trace amounts of the hydroquinone were detected in the extract of the spent liquor where the pH was maintained at 10.5 during bleaching. This trend is consistent with that found by Omori and Dence[14] who reacted ω-guaiacoxyacetoguaiacone with alkaline peroxide under comparable conditions. Failure to analyze detectable amounts of the hydroquinone in the liquor from the bleach maintained at 10.5 can be attributed to further oxidation to the corresponding quinone or alkali induced condensation[18]. In contrast, at a final pH of 7.9 the conditions for oxidation or condensation were less favorable and the hydroquinone survived the bleach.

Bailey[8] and Kempf[16], using α-methylvanillyl and α-methylsyringyl alcohols, respectively, were able to detect mono- and dimethoxy-p-benzoquinones after reaction with alkaline hydrogen peroxide. Omori[15] detected methoxy-p-benzoquinone, albeit in trace amounts, after reacting guaiacylglycerol-β-guaiacyl ether with alkaline peroxide under conditions similar to those employed by Bailey and Kempf. Similarly, Nonni[17] detected only trace amounts of methoxy-p-benzoquinone in the product mixtures from the reaction of β-1 dilignol model compounds with alkaline hydrogen peroxide. Thus, it seems probable that methoxy-p-benzoquinone units are formed either from p-hydroxybenzyl alcohols ("Dakin-like" reaction) or by autoxidation of hydroquinonoid units that are formed by the action of hydrogen peroxide on p-hydroxyphenacyl-containing units present in lignin (Dakin reaction). However, methoxy-p-benzoquinone was not detected in either of the two bleach liquor extracts. The presumption is that such units were formed, but were too reactive to survive the conditions of the bleach and were consumed in alkali-promoted condensation reactions or in reactions with other nucleophiles in the liquor.

As indicated by the results of a study to be reported as Part 2 of the present series, methoxyhydroquinone and methoxy-p-benzoquinone structures are potentially capable of affecting the brightness and brightness stability of peroxide-bleached pulps. Methoxyhydroquinone and methoxy-p-benzoquinone themselves should have no effect on pulp brightness assuming they or their reaction products remain solubilized in the bleaching liquor and can be washed from the pulp. On the other hand, there is the likely probability of methoxyhydroquinonoid and methoxy-p-benzoquinonoid moieties being generated from p-hydroxy carbonyl- or p-hydroxybenzyl alcohol-containing lignin units that are joined to the remainder of the lignin macromolecule through 5, 5', β-5, 4-O-5 and similar peroxide-stable linkages known to exist in lignin[19]. In this situation, the hydroquinone and p-benzoquinone moieties would be largely retained with the lignin on the pulp fiber and exert the same deleterious effect on fiber optical properties as the corresponding uncondensed units exert on the solution properties of the bleach liquor.

CONCLUSIONS

Previous studies of the reactions of phenolic lignin model compounds with alkaline hydrogen peroxide have shown that hydroquinones are generated either by the action of peroxide itself or its decomposition products[8-15]. In addition, it has been demonstrated at the model compound level that the hydroquinones so generated may undergo conversion to chromophoric substances which consume peroxide and which partially resist further oxidative breakdown[6,16-18].

The identification of methoxyhydroquinone in a peroxide bleaching liquor has corroborated the findings of the model compound studies with respect to the formation of hydroquinonoid intermediates. This lends credence to the supposition that when generated during peroxide bleaching these intermediates are subsequently oxidized to quinonoid structures which adversely affect brightness when retained by the pulp. Thus the previous use of methoxyhydroquinone and methoxy-p-benzoquinone as models for leucochromophores and chromophores formed during the peroxide bleaching of mechanical pulps appears to be justified.

EXPERIMENTAL

Bleaches were performed using 10 g (o.d. basis) samples of a loblolly pine TMP supplied by the C. E. Process Equipment Company, Springfield, Ohio. The chemicals applied to the pulp were in the order stated as follows: 0.5% diethylenetriamine-pentaacetic acid, pentasodium salt (Na_5DTPA); 0.05% $MgSO_4.7\ H_2O$, 1.5% H_2O_2, and sufficient distilled water and alkali to provide a consistency and initial pH of 12% and 10.5, respectively. The pulp was bleached in plastic bags at 50 + 0.1°C for three hours. In bleach No. 1 the pH was allowed to drop, while in bleach No. 2 the pH was readjusted to 10.5 by the periodic addition of small portions of alkali.

At the conclusion of the bleach, the pulp was filtered under vacuum and the residual peroxide in the filtrate was determined to be 19% and 2% for bleaches 1 and 2, respectively. After adjustment of the pH to 5.0, the spent liquors were thoroughly extracted with reagent grade ethyl acetate. A 10-ml sample of the ethyl acetate extract was evaporated to dryness at 30°C in vacuo and the residue was redissolved in 1.0 ml of dry tetrahydrofuran (THF) and 0.5 ml of N, O-bis-(trimethylsilyl) acetamide (BSA, Aldrich Chemical Co.).

Gas chromatographic analysis of the silylated samples was performed on a Varian Model 3740 gas chromatograph equipped with a 1 m X 0.32 cm stainless steel column packed with 3% OV-101 on 80/100 mesh Chromosorb G, which was heated in a linear programming mode from 80°C to 150°C at 10°C/minute. The injection port and detector temperatures were 150°C and 250°C, respectively. The retention time of a peak in the chromatogram of the spent liquor extract coincided exactly with that of authentic silylated methoxyhydroquinone (7.42 min).

The THF solutions of the silylated liquor extracts were also analyzed on a Finnigan Model 4000 gas chromatograph/quadrapole mass spectrometer/data system (GC/MS/DS). Electron impact fragmentations were performed at 70 eV. The gas chromatographic separation was performed on a 1.8 m X 0.32 cm glass column packed with 3% SE-30 on 100/120 mesh Chromosorb Q. The mass spectral fragmentation pattern of authentic disilyl methoxyhydroquinone was (m/e, % relative abundance): 285 (M+1, 16.5), 284 (M^+, 70.2), 269 (12.2), 254 (100.0), 239 (10.3), 211 (1.5), 179 (2.7), 147 (0.6), 73 (29.0). The mass spectral fragmentation pattern of the corresponding compound in the spent liquor extract was (m/e, % relative abundance): 285 (M+1, 13.0), 284 (M^+, 57.0), 269 (11.3), 254 (100.0), 239 (11.9), 211 (1.6), 179 (3.2), 147 (4.1), 73 (38.0).

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