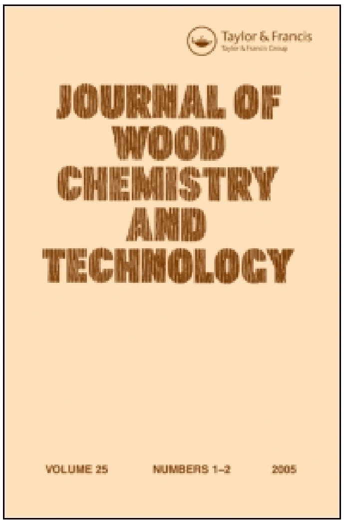

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Methoxy-P-Benzoquinone and Methoxyhydroquinone As Models for Chromophore Changes in the Bleaching of Softwood mechanical pulps. II. The Effect of Peroxide Charge, Reaction Ph, and Transition Metal Ions

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METHOXY-p-BENZOQUINONE AND METHOXYHYDROQUINONE AS MODELS FOR CHROMOPHORE CHANGES IN THE BLEACHING OF SOFTWOOD MECHANICAL PULPS.

II. THE EFFECT OF PEROXIDE CHARGE, REACTION pH, AND TRANSITION METAL IONS

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ABSTRACT

Methoxy-p-benzoquinone and methoxyhydroquinone were reacted with hydrogen peroxide in the presence of either Na_5DTPA/Mg^{2+} or silicate/Mg^{2+} stabilization systems. The conditions used approximated those in the technical bleaching process, and the resulting effect on color was ascertained by monitoring the absorbance at 457 nm. The results revealed that the initial color of solutions of the quinone and hydroquinone increased dramatically with the application of relatively small amounts of alkaline peroxide and was "bleached" to its original level only after application of excessively large amounts of this oxidant. Subsequent experimentation, in which the pH of the of the reaction mixture, order of reagent addition and mixing regimen were varied, provided evidence suggesting that the observed increase in "color" on alkaline peroxide treatment of the quinone was attributable to alkali-promoted condensation reactions, the products of which were only partly decolorized through action of the peroxide. The effect on "color" produced by the addition of transition metal ions was found to depend on the particular

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metal and the peroxide stabilization system employed. The responses of the quinone/hydroquinone and mechanical pulps toward alkaline peroxide in terms of optical properties are compared.

INTRODUCTION

A variety of chromophoric structures have been implicated as sources of color in whole and defiberized wood[1-6]. Although the responses of these chromophoric systems to alkaline hydrogen peroxide have not been examined on an individual basis in all instances, the composite effect of such a treatment is color reduction, thereby giving evidence for at least a partial conversion of the chromophores to colorless structures. On the other hand, results reported by Spittler and Dence[7] and by Oki et al[8] indicate that new chromophoric systems are concurrently generated during peroxide bleaching which, if resistant to further breakdown by peroxide, may partially offset the bleaching effect resulting from chromophore destruction. These opposing phenomena of chromophore creation and destruction may in fact account for the so-called "brightness ceiling" associated with the bleaching of mechanical pulps.

Of the structures identified as possibly contributing to color in any chromophore-generating process accompanying peroxide bleaching, the methoxy-p-benzoquinone moiety is perhaps the most extensively documented[9-13]. Hosoya et al[14] have observed the resistance of this compound to decoloration on treatment with alkaline peroxide under simulated technical bleaching conditions. Methoxy-p-benzoquinone is visualized as arising by the attack of molecular oxygen or peroxy radicals on p-hydroxybenzyl alcohol groupings in lignin[15,16]. Methoxyhydroquinone units, generated by the reaction of alkaline hydrogen peroxide on p-hydroxyphenyl ketone units in lignin, as reported in Part I of this series[17], may also give rise to methoxy-p-benzoquinone derivatives in a subsequent oxidation step. In addition to the p-benzoquinoid units generated in peroxide bleaching, some have been postulated as being initially present in the lignin[2,18], while others are thought to arise from autoxidation of methoxyhydroquinone units in the lignin during defibration of wood[6].

p-Benzoquinone structures are susceptible to further oxidation by alkaline hydrogen peroxide in which process they are transformed to colorless structures[19]. Competitive base-catalyzed reactions may, however, mediate the conversion of p-quinonoid units to other chromophoric systems with diminished susceptibility to further breakdown by peroxide or its decomposition products. These alternative routes are illustrated in Fig. 1. The relative extents to which the aforementioned p-benzoquinone breakdown and condensation processes occur during technical peroxide bleaching can be visualized as influencing the brightness gain ultimately achieved.

To examine this possibility further, methoxy-p-benzoquinone and its leucochromophoric precursor, methoxyhydroquinone, were reacted with peroxide under simulated technical bleaching conditions. The effects of varying peroxide charge, reaction pH, and addition of transition metals on the

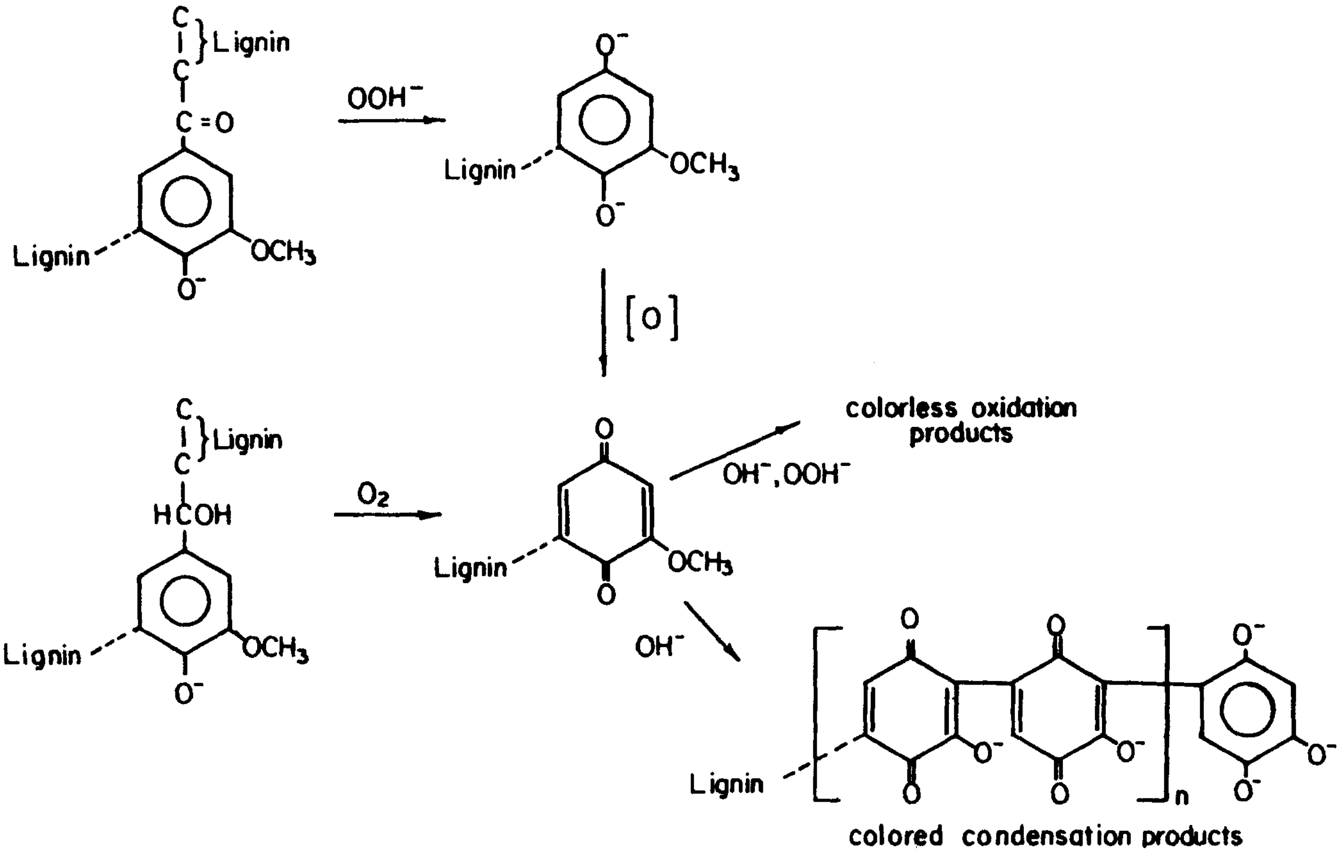

FIGURE 1. Sequence for Formation and Subsequent Competing Reactions of p-Benzenoid Units with Peroxide and Alkali

final color were determined by monitoring the absorbance of the product mixture at 457 nm following acidification.

RESULTS AND DISCUSSION

The general procedure followed in the oxidation was to add aqueous solutions of the quinone and hydroquinone to stabilized ($MgSO_4$ and sodium silicate or Na_5DTPA) peroxide solutions initially adjusted to the desired pH and either maintained at that level by intermittent addition of alkali or allowed to fall as dictated by the formation of acidic oxidation products. The reaction was allowed to proceed for four hours at 40°C. Absorbance readings were taken at 457 nm at predetermined intervals throughout the course of the reaction and at its conclusion, following acidification of sample aliquots. Peroxide residuals were determined by colorimetric analysis at the conclusion of the treatment.

The Effect of Peroxide Charge

The effect of increasing peroxide application at a fixed pH of 10.5 on the color (measured as absorbance at 457 nm) of the peroxide/methoxy-p-benzoquinone product mixtures is illustrated by the appropriate plots in Figure 2. These plots indicate that, irrespective of the stabilization system employed, addition of the quinone to relatively small amounts of peroxide caused a marked enhancement of the absorbance above that contributed by an unreacted neutral solution of the quinone. Rate measurements revealed that most of the increase in

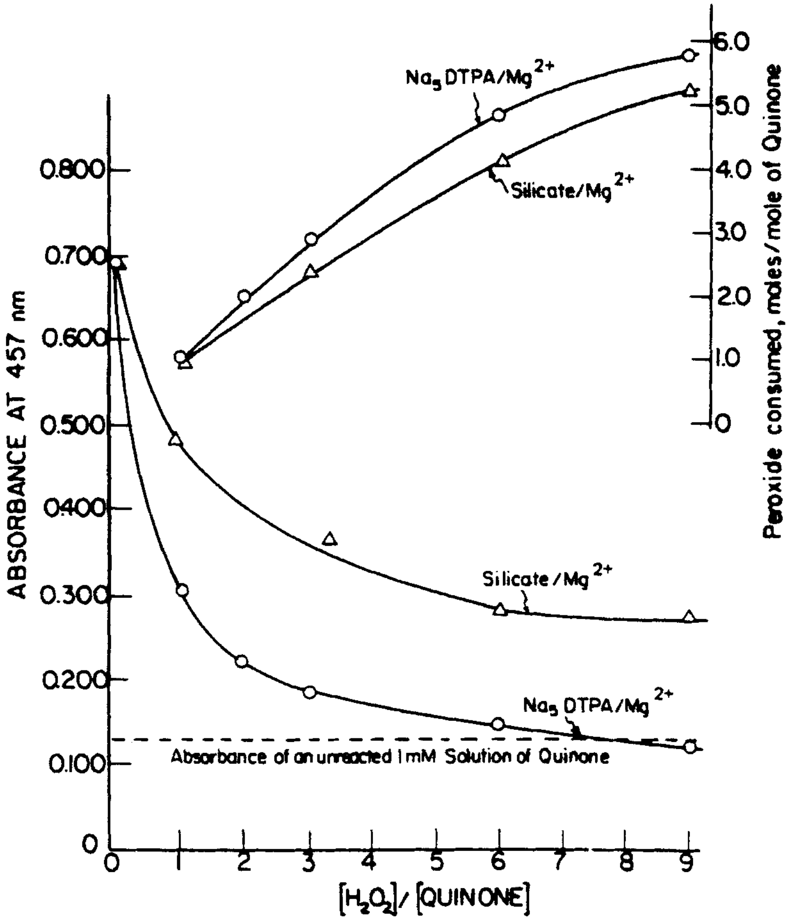

FIGURE 2. The Effect of Peroxide Application on "Color" Reduction in the Reaction of Methoxy-p-Benzoquinone with Alkaline Hydrogen Peroxide (Quinone, 1.0 mM, 4 Hrs, 40°C, pH 10.5 Maintained) Order of addition: stabilizer, H_2O_2, OH^-, quinone.

absorbance occurred within 15 minutes of the time when the quinone was added to the alkaline peroxide solution.

Regardless of the stabilization systems employed (Na_5DTPA/Mg^{2+} or silicate/Mg^{2+}), there was a pronounced levelling off with respect to "color" reduction when peroxide in excess of approximately 3-4 moles/mole of quinone was added, even in the presence of unreacted peroxide. However, only at the highest application of peroxide in the presence of the Na_5DTPA/Mg^{2+} stabilization system was the absorbance of the acidified product mixture reduced to that of the unreacted quinone.

Generally, less "color" and peroxide remained at any given peroxide application when the reaction of the quinone was performed in the presence of Na_5DTPA/Mg^{2+} as opposed to silicate/Mg^{2+} (Fig. 2). This disparity does not appear to be related to peroxide stability, since the peroxide residuals were nearly identical for the two stabilization systems when the reactions were performed under otherwise identical conditions in the absence of quinone.

The rapid and substantial increase of "color" resulting from treatment of methoxy-p-benzoquinone with low peroxide charge possibly can be attributed to the effect of alkali in promoting condensation and other reactions yielding new chromophoric structures[21] in competition with oxidative breakdown of the quinone. Based on the results reported above (Figs. 2 and 3), these newly-created chromophores are comparatively resistant toward further oxidative breakdown, with the consequence that excessively large applications of peroxide were required merely to restore the "color" to the level contributed by the unreacted quinone. The "color" reduction achieved by large applications of peroxide is probably a combination of effects, including enhanced oxidative breakdown of the methoxy-p-benzoquinone at the expense of

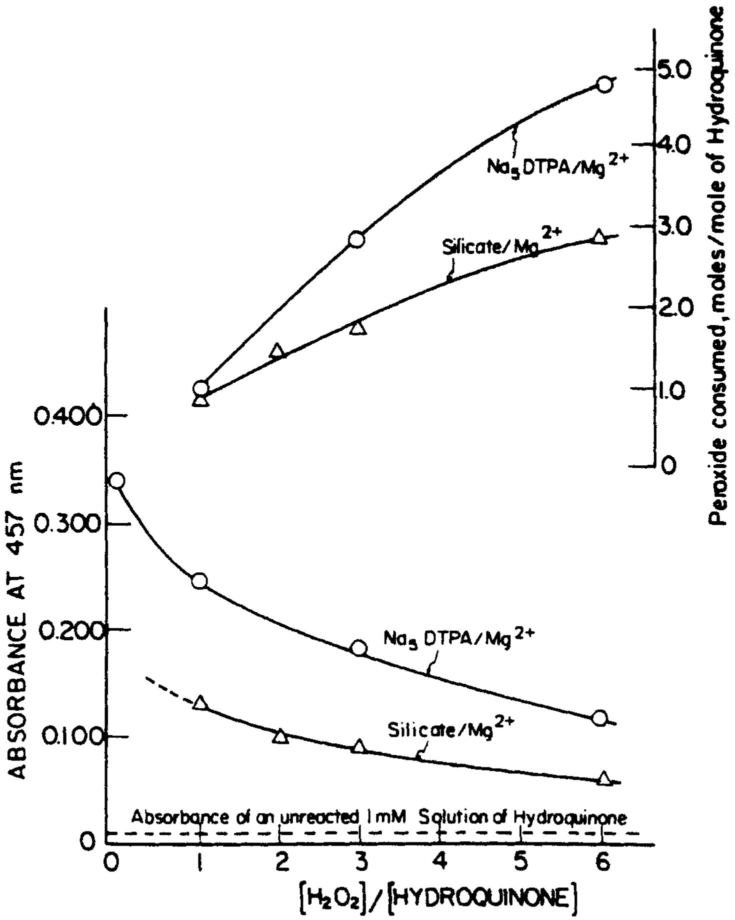

FIGURE 3. The Effect of Peroxide Application on "Color" Reduction in the Reaction of Methoxyhydroquinone with Alkaline Hydrogen Peroxide (Hydroquinone, 1.0 mM, 4 Hrs, 40°C, pH 10.5 Maintained)

alkali-promoted condensation reactions and more extensive breakdown of whatever condensed chromophores are formed.

Although the chromophores responding sluggishly to alkaline peroxide have not been identified, one possibility is that they are structurally related to hydroxyquinones[19,20], and/or phenyl-substituted p-benzoquinones[14,21-24], as illustrated in Fig. 1.

The response of methoxyhydroquinone to increasing amounts of peroxide stabilized by Na_5DTPA/Mg^{2+} and silicate/Mg^{2+} is shown by the plots in Fig. 3. Duplicating the effect observed previously in the treatment of methoxy-p-benzoquinone with peroxide, the "color" of the product mixture decreased progressively with the addition of increasing amounts of peroxide. In no instance, however, was the absorbance reduced to its pretreatment level under the test conditions.

The observed increase in absorbance or "color" logically can be attributed to the oxidation of the methoxyhydroquinone to the corresponding quinone which is the progenitor of colored material formed through alkali-induced condensation reactions as postulated above. Oxidation of the hydroquinone occurs in part from the action of dissolved atmospheric oxygen and from oxygen formed by decomposition of the peroxide. Thus, an alkaline solution of the hydroquinone showed considerably less gain in coloration when continuously purged with nitrogen.

As is apparent from the plots in Fig. 3, more "color" was generated in the system stabilized with Na_5DTPA/Mg^{2+} than in that stabilized with silicate/Mg^{2+}. In this respect, the relative effects of silicate and Na_5DTPA were opposite of those noted in the peroxide treatment of methoxy-p-benzoquinone, although peroxide consumption in each case was greater when the peroxide was stabilized with Na_5DTPA/Mg^{2+}. Thus, oxidation was seemingly more pronounced in the system stabilized with Na_5DTPA/Mg^{2+}, with the result that methoxy-p-benzoquinone and its colored coupling products were "bleached" to a greater degree than when the silicate/Mg^{2+} combination was used. Conversely, a more intensive oxidation of methoxyhydroquinone conceivably may have had the negative effect of producing a greater amount of methoxy-p-benzoquinone and accompanying condensation products unless offset by large applications of peroxide.

The Effect of Reaction pH

In these tests, the pH was maintained at 10.5 or 9.5 or allowed to drop from an initial value of 10.5. The results obtained when methoxy-p-benzoquinone and methoxyhydroquinone were reacted with peroxide stabilized with Na_5DTPA/Mg^{2+} are shown in Figs. 4 and 5, respectively. A beneficial effect of higher pH on "color" is seen in the case of the quinone (Fig. 4), especially at the low end of the peroxide application range, whereas an increase in alkalinity has an adverse effect when the hydroquinone is similarly reacted (Fig. 5).

The effect of pH on "color" formation and elimination was also demonstrated by altering the order of reagent addition and the manner in which the reactants were mixed, as is illustrated by the bar graphs in Fig. 6. In these situations, the mixing of quinone and alkali prior to peroxide addition or the postponement of mixing until reagent addition was completed led to substantially greater solution coloration and to higher peroxide residuals. The apparent common element in these two situations is that, for all or part of the time, some of the quinone was in contact with alkali in the absence or near absence of peroxide, with the result that

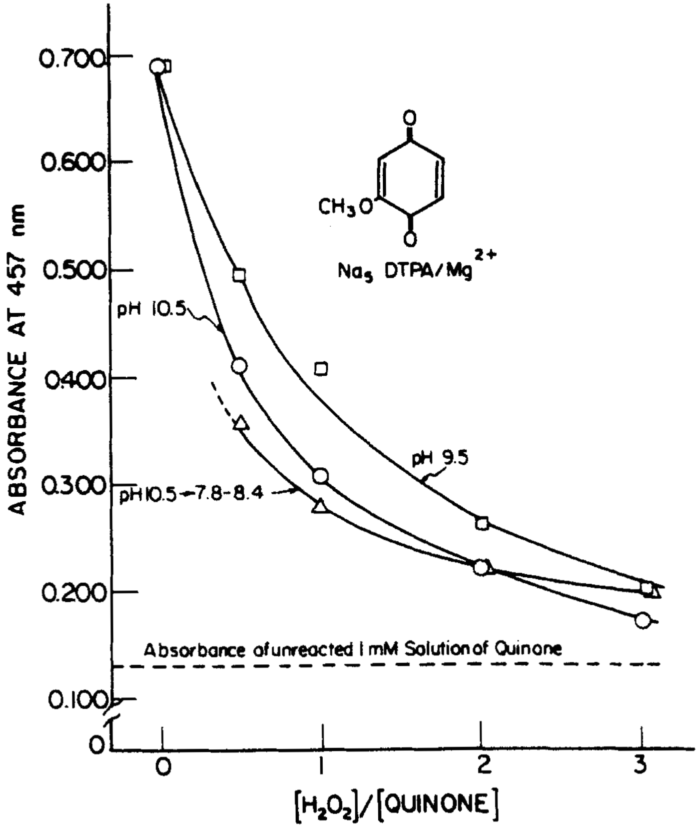

FIGURE 4. The Effect of Reaction pH on "Color" in the Reaction of Methoxy-p-Benzoquinone with Alkaline Hydrogen Peroxide (Quinone, 1.0 mM, 4 Hrs, 40°C, Na_5DTPA/Mg^{+2}) Order of addition: stabilizer, H_2O_2, OH^-, quinone.

chromophore-producing reactions took precedence over the competing oxidative breakdown (i.e.,"bleaching") of the quinone. The final absorbance readings appeared to be especially sensitive to small variations in the reagent addition and mixing procedures, as evidenced by their frequently observed poor reproducibility. A number of associations can be made between the behavior of the quinone and

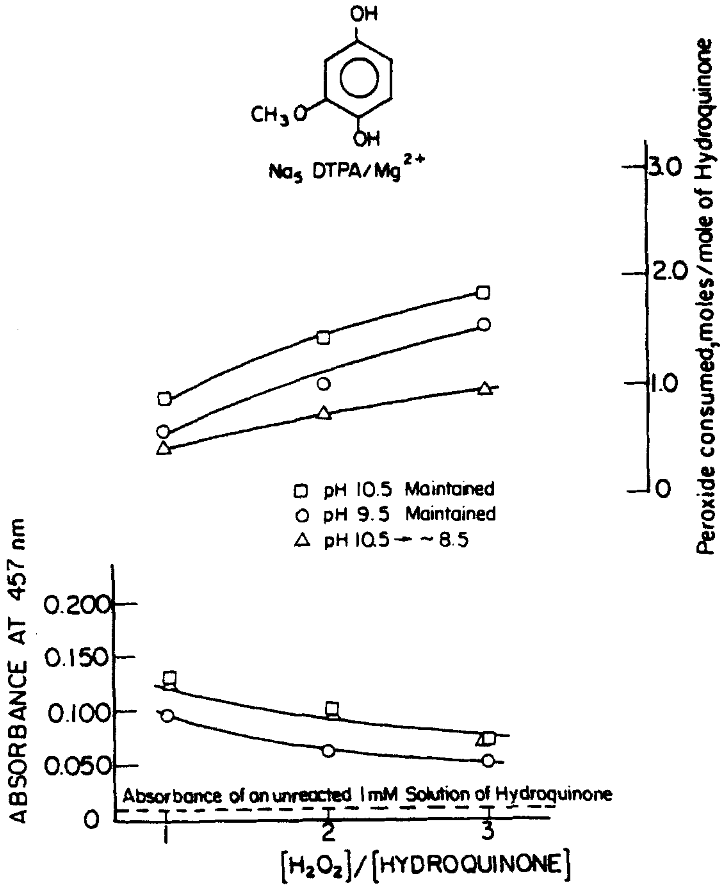

FIGURE 5. The Effect of pH on "Color" in the Reaction of Methoxyhydroquinone with Alkaline Hydrogen Peroxide (Hydroquinone 10 mM, 4 Hrs, 40°C, Na_5DTPA/Mg^{2+})

hydroquinone and pulp in a technical peroxide bleaching process, and these relationships are discussed in considerable depth below.

The Effect of Transition Metals

In these experiments, copper and manganese were applied as copper (II) and manganese (II) chlorides,

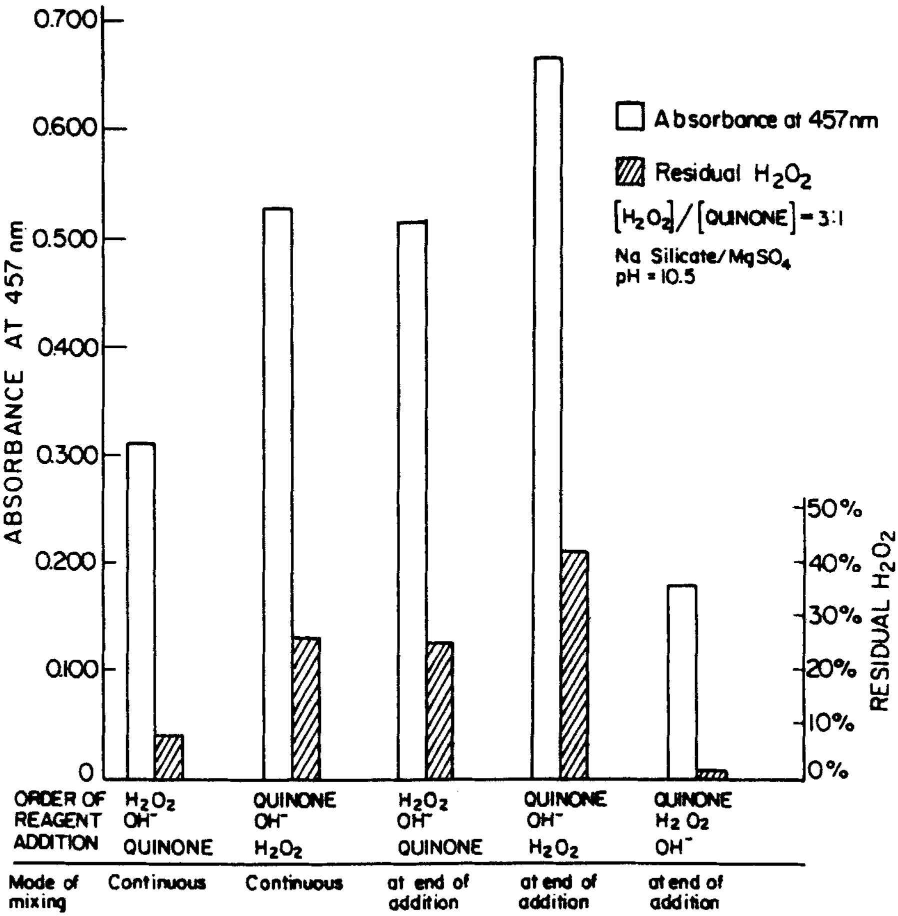

FIGURE 6. The Effect of Order of Reagent Addition and Mixing Mode on Product Mixture Absorbance and Residual Peroxide in the Reaction of Methoxy-p-Benzoquinone with Alkaline Hydrogen Peroxide.

whereas iron was applied both in the form of iron (III) chloride and as goethite, a water-insoluble crystalline compound whose structure is represented as α-FeOOH[25]. This latter form of iron was mainly used since it is considered to be more representative of

TABLE 1

Effect of Transition Metals on the Decomposition of Hydrogen Peroxide in the Presence of Silicate and Na_5DTPA

Metal	Residual Peroxide, % of Applied Na_2SiO_3/Mg^{2+}	 Na_5DTPA/Mg^{2+}
None	79	82
Copper ($CuCl_2$)	56	77
Manganese ($MnCl_2$)	69	78
Iron (goethite)	79	81
Iron ($FeCl_3$)	81	N.D.

Reaction conditions: 10 ppm of metal; 3 mM H_2O_2; 40°C, 4 hrs, pH 10.5

the state of iron in mechanical pulps[26]. The stability of peroxide in the presence of the various metals is indicated by the data in Table 1. These data show the general superiority of Na_5DTPA over silicate with respect to peroxide stabilization under the test conditions.

The effect of the transition metals on "color" in the reaction of methoxy-p-benzoquinone with alkaline peroxide (pH 10.5) is portrayed graphically in Fig. 7. The values plotted in this figure (and in Fig. 8) were corrected for any absorbance contribution of the metal itself. These plots show that, regardless of the peroxide stabilization system used, the addition of iron as goethite and manganese had the effect of increasing and decreasing, respectively, the "color" of the reaction mixture as compared to the situation where no transition metals were added. In the presence of copper, "color" enhancement resulted only

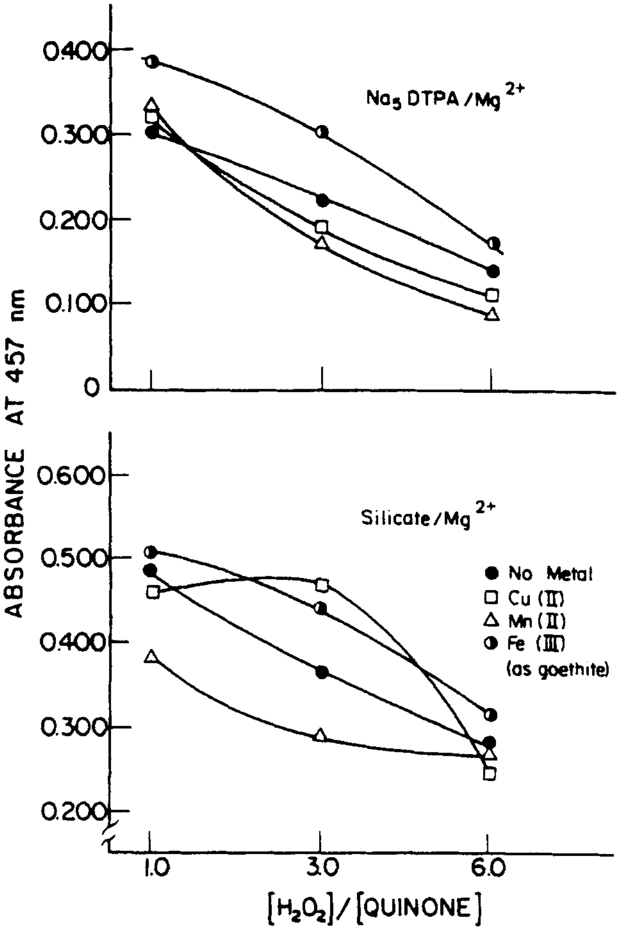

FIGURE 7. The Effect of Transition Metals on the "Color" of the Product Mixtures in the Reaction of Alkaline Hydrogen Peroxide with Methoxy-p-Benzoquinone (Quinone, 1.0 mM, 10 ppm of Metal, 4 Hrs, 40°C, pH 10.5 Maintained)

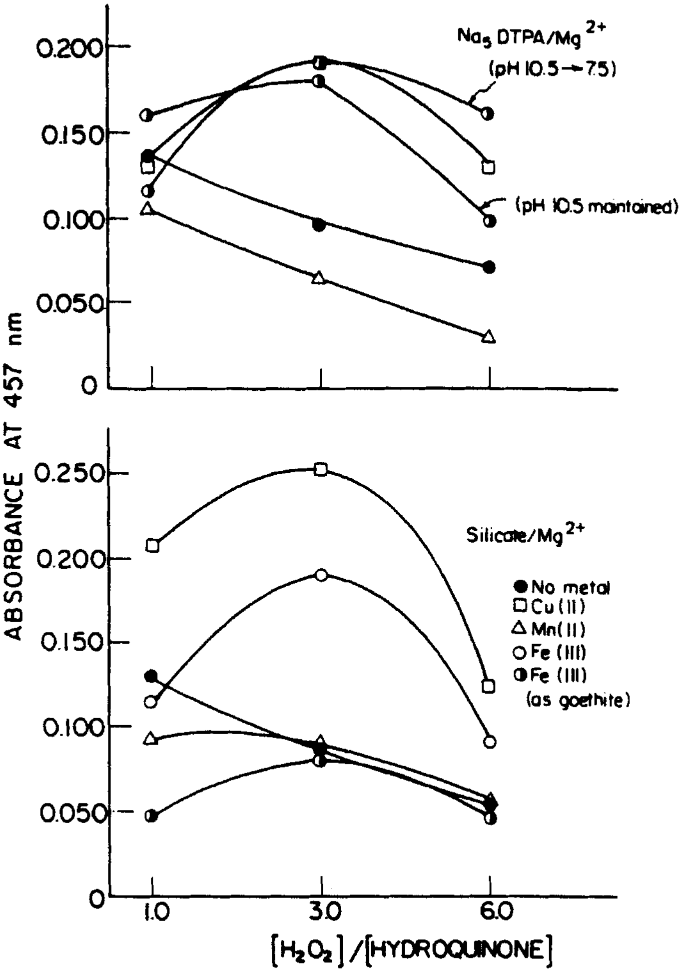

FIGURE 8. The Effect of Transition Metals on the "Color" of the Product Mixtures in the Reaction of Alkaline Hydrogen Peroxide with Methoxyhydroquinone (Hydroquinone, 1.0 mM, 10 ppm of Metal, 4 Hrs, 40°C, pH 10.5 Maintained)

in the case where the reaction was stabilized with silicate/Mg^{2+}.

Also noteworthy is the observation that irrespective of the metal added, the absorbance of the reaction mixture was consistently higher when the peroxide was stabilized with silicate/Mg^{2+} as compared to the case when it was stabilized with Na_5DTPA/Mg^{2+}. Since this same trend was seen previously in the absence of transition metals (Fig. 2), any difference in the interaction of the metals with the stabilization systems affecting "color" can be regarded as minor. Lacking an in-depth product analysis, differences in the individual effects of the transition metals on "color" are difficult to interpret but logically can be attributed to complex interactions of the metal, in a chelated or unchelated form, with the quinone and its reaction products.

The effect of transition metals on "color" in the peroxide oxidation of methoxyhydroquinone is shown by the plots in Fig. 8. In the presence of copper and iron, "color" maxima were observed at or about a peroxide/hydroquinone molar ratio of 3 irrespective of the stabilization system used. The profile of the absorbance/copper II plot in Fig. 8 was verified by performing the peroxide treatments at additional peroxide concentration levels. These maxima probably represent the formation of a colored metal-organic complex which was degraded upon the addition of increasing amounts of peroxide.

In the silicate-stabilized system and, to a lesser extent, in the Na_5DTPA-stabilized system, the enhancement of "color" of the product mixtures observed when the hydroquinone was reacted with peroxide in the presence of copper may be related to the finding that the peroxide was totally consumed in each case and that the ability of the stabilization systems (especially silicate/Mg^{2+}) to control metal-catalyzed decomposition of the peroxide was minimal for copper. Iron (as goethite) also caused a considerable enhancement of "color" in the reactions where the peroxide was stabilized with Na_5DTPA.

The effect of permitting the pH to fall during an oxidation was examined in a run in which goethite was added to a system stabilized with Na_5DTPA. As shown by the plot in Fig. 8, a "color" maximum appeared once more at a peroxide/hydroquinone molar ratio of approximately 3, and the absorbance readings were slightly different at the lower and higher peroxide application levels than for the case where the pH was maintained at 10.5 throughout the reaction.

When iron was added to the reaction mixture in the form of $FeCl_3$ rather than as goethite, more "color" was produced at each level of peroxide application (Fig. 8, bottom). This effect may be ascribed to differences in the solubility of the two compounds in the reaction mixture and/or to differences in the availability in each instance of ferric ions for participation in those reactions requiring the ionic form. Based on the supposition that iron is mainly present in wood or pulp in the form of an oxide such as goethite, this finding suggests that in terms of a catalytic effect at least, this metal may be less of a problem in peroxide bleaching than hitherto thought.

THE POTENTIAL EFFECT OF p-BENZOQUINONOID AND HYDROQUINONOID UNITS ON THE OPTICAL PROPERTIES OF MECHANICAL PULPS BLEACHED WITH HYDROGEN PEROXIDE

As pointed out in the introduction, the p-quinonoid and hydroquinonoid units initially present in the lignin are augmented by the formation of additional such units when mechanical pulps are bleached with peroxide. These p-quinonoid and hydroquinonoid moieties are basically very reactive intermediates which, in the presence of alkali and of hydrogen peroxide and its decomposition products, undergo rapid and extensive transformations to more stable structures. As a consequence of their high reactivity, quinonoid and hydroquinonoid structures are present in the bleach only in low concentrations, making their detection and especially their measurement very difficult. The contributions of p-quinonoid and hydroquinonoid moieties to brightness and brightness reversion, therefore, ultimately depend to a major extent on the structure and reactivity of their reaction products and to what degree they are chemically and/or physically attached to the pulp fiber, as opposed to becoming solubilized in the bleach liquor.

As can be discerned from the following discussion, the behavior of methoxy-p-benzoquinone and methoxyhydroquinone toward peroxide is similar in many respects to several of the phenomena recognized in the technical peroxide bleaching of mechanical pulps, providing in some instances a basis for their interpretation. First, a similarity can be recognized between the difficulty encountered in completely decolorizing alkaline solutions of the quinone and hydroquinone (or more likely their coupling products) and in bleaching mechanical pulps to ultra-high brightness even with what could be considered as excessive amounts of peroxide. Moreover, with increasingly larger applications of peroxide to the quinone and hydroquinone, the corresponding decreases in absorbance of "color" became progressively smaller, thereby mimicking the "brightness ceiling" effect routinely observed when increasing amounts of peroxide are applied to mechanical pulps.

The beneficial effect of increasing pH on "color" reduction noted above in connection with the peroxide treatment of methoxy-p-benzoquinone is consistent with the generally observed improvement on bleaching efficiency seen when the pH is similarly increased in the peroxide bleaching of mechanical pulp. The leveling off of brightness improvement generally found as pH 12 is approached may be attributed to the increasing contribution of base-catalyzed reactions resulting in the formation of chromophores relative to the breakdown of chromophores through the action of hydroperoxy anion. Furthermore, at pH 12, hydrogen peroxide is essentially all in the form of hydroperoxide anion.

Similar to the previously demonstrated (Figs. 2 and 3) adverse effects of alkali on the color of solutions of methoxy-p-benzoquinone and methoxyhydroquinone, the exhaustion or near exhaustion of peroxide under alkaline conditions during mechanical pulp bleaching produces the negative effect on brightness referred to as "browning." Apart from adding larger amounts of peroxide to the bleach, or bleaching to a sufficiently high peroxide residual, the effect of "browning" should be minimized by insuring that the pulp slurry is adequately mixed throughout the entire bleaching period so as to avoid regions of low peroxide concentration stemming from localized over-reaction. Another approach with a potential for brightness benefits consists of steeping the pulp with a peroxide solution in the presence of a suitable stabilization system and then "activating" the peroxide by the addition of alkali. In this way, the peroxide can be distributed more evenly throughout the fiber mass with the expectation that oxidation reactions will compete more favorably with the ensuing alkali-promoted adverse reactions. A preliminary experiment along these lines has indicated the production of less "color" than by any other mode of mixing (Fig. 6, last set of bars on right).

Closely allied to the foregoing is the beneficial effect on brightness resulting from increasing the consistency in peroxide bleaching[27]. This effect is readily explicable in terms of the competition between peroxide-mediated destruction and alkali-induced creation of chromophores. Regardless of the consistency employed in a peroxide bleach, the initial pH does not vary greatly (i.e., the initial OH^- concentration is relatively constant). The peroxide concentration, on the other hand, increases with increasing consistency of the bleach. As a consequence, high consistency should and does in fact favor chromophore destruction over chromophore creation.

The generally recognized effect of transition metal ions on brightness in the peroxide bleaching of mechanical pulps has been linked to metal-induced decomposition of peroxide[28]. Thus, irrespective of whether silicate/Mg^{2+} or Na_5DTPA/Mg^{2+} was present, the addition of iron (III), manganese (II), and copper (II) ions to demineralized stone groundwood had the effect of increasing peroxide decomposition and decreasing brightness in the order Fe > Mn > Cu. The adverse effect of iron on "color" was also apparent in the reaction of methoxy-p-benzoquinone with peroxide (Fig. 7) in the case at hand. Additionally, the superiority of the Na_5DTPA/Mg^{2+} stabilization system over the silicate/Mg^{2+} combination with respect to reduced peroxide consumption and decomposition and to improved brightness demonstrated for the peroxide bleaching of groundwood was also duplicated in the reaction of methoxy-p-benzoquinone with peroxide in terms of reaction "color." In the latter situation, peroxide decomposition data were not available for comparison.

Contrary to the trends noted above in connection with the reactions of groundwood and methoxy-p-benzoquinone with peroxide, maximum "color" resulted in the reaction of methoxyhydroquinone with peroxide in the presence of copper rather than iron, especially in the reaction mixture containing silicate. Moreover, peroxide was totally consumed at all levels of application in contrast to the situations where iron and manganese were present. Thus, the behavior of methoxyhydroquinone when reacted with peroxide in the presence of the three transition metals was inconsistent with the response of groundwood to peroxide under similar conditions, thereby underscoring the need for additional experimentation aimed at defining more exactly and thoroughly the roles of transition metal ions in peroxide bleaching, especially in the presence of stabilization systems.

Collectively, the foregoing observations suggest that p-benzoquinonoid units, initially present in the liquor or generated during peroxide bleaching have a greater impact on brightness than do methoxyhydroquinonoid moieties. This supposition is also consistent with the generally higher color levels associated with the reaction of methoxy-p-benzoquinone with peroxide as compared to when the hydroquinone was similarly treated. It should be emphasized, however, that in suggesting that p-benzoquinonoid units are contributory structures affecting brightness and brightness stability in peroxide bleached mechanical pulps, the intention is not to rule out the likelihood of other chromophore groups having as great or even greater bearing on these properties.

CONCLUSION

The conclusion to be drawn from the findings of the present study is that in the competitive base-catalyzed condensation and oxidative breakdown reactions representing chromophore creation and destruction pathways, respectively, the former gives evidence of predominating. As applied to the peroxide bleaching of mechanical pulps, the intervention of chromophore producing reactions in the overriding brightening reaction sequences may partially offset brightness gain, thereby contributing to the familiar "brightness ceiling" effect. Hence, the problem of "brightness ceiling" reduces to one of finding the means for promoting "bleaching" reactions while simultaneously repressing "reversion" reactions without violating the usual technique and economic constraints inherent in such an undertaking.

EXPERIMENTAL

Methoxyhydroquinone[10] was converted to methoxy-p-benzoquinone by oxidation with sodium metaperiodate according to the procedure of Adler and Magnusson[29] and subsequently purified by vacuum sublimation (mp 144°, lit. mp 142-146[29]). Goethite (α-FeOOH) was prepared using a modification[30] of the procedure of Atkinson *et al*[25].

Na_5DTPA (diethylenetriaminepentaacetic acid penta sodium salt, Versenex 80) was obtained from Dow Chemical U.S.A. All other chemicals were obtained from Fisher Scientific Company.

In a typical reaction, deionized distilled water was thoroughly sparged with nitrogen and ~50 ml portions were placed in the requisite number of 100-ml volumetric flasks. The flasks were again purged with nitrogen, stoppered, and placed in a thermostatted water bath maintained at 40 ± 0.5°C. After the flasks reached temperature, the stabilizer (Na_2SiO_3 or Na_5DTPA),$MgSO_4$, and a solution of the transition metal compound (if required) were added in the order stated. The mixture was thoroughly mixed, blanketed with nitrogen, and allowed to equilibrate at the bath temperature. The required volume of hydrogen peroxide was added, and the pH was recorded and adjusted (if necessary) to the desired level by the addition of 0.1

N NaOH. Finally, methoxy-p-benzoquinone or methoxyhydroquinone was added to the flasks as 2 mg/ml solutions through a burette while the contents were being simultaneously mixed by a stream of nitrogen. The contents of the flasks were diluted to 100 ml with deionized distilled water and allowed to react for 4 hours. The initial concentrations of the reagents were the following in all instances: quinone or hydroquinone, 1.0 mM; $MgSO_4$, 1.23 mM; Na_5DTPA, 0.79 mM; sodium silicate, 19.0 mM.

At the end of the reaction, the pH was recorded and the reaction mixtures made acidic (pH 2-3) by the addition of 0.1 N H_2SO_4. The absorbance of the acidified solution (and occasionally the alkaline reaction mixture) was measured at 457 nm in a Gilford 2000 modified Beckman DU spectrophotometer. Residual hydrogen peroxide was determined using the colorimetric method of Eisenberg[31] with the exception that a 2% solution of titanium oxysulfate was used as the color-forming reagent and the absorbance contributions from organic materials were corrected for in a blank.

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