# Oxygen Formation During Peroxide Bleaching Of A Thermomechanical Pulp And Its Relationship To Bleaching Performance

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## ABSTRACT

*The hydrogen peroxide decomposition during peroxide treatment of a TMP has been determined by following oxygen formation. Such information allows the calculation of the total hydrogen peroxide consumption between peroxide consumed in pulp oxidation and that consumed in decomposition. A comparison of mill chelated and well chelated pulps was made with respect to oxygen formation and its effect on the bleaching performance. The results support the conclusion that in addition to less peroxide available for pulp oxidation, the transition metal ion induced peroxide decomposition leads to the generation of new chromophores induced by reactive species formed during the decomposition reactions.*

*Key words: oxygen formation, hydrogen peroxide, decomposition, bleaching performance, pulp oxidation, TMP.*

## INTRODUCTION

Hydrogen peroxide is a traditional chemical for bleaching high yield pulps. Recently, its use in bleaching of chemical pulps has been increasing. Under typical bleaching conditions, in addition to the desirable bleaching reactions with lignin, hydrogen peroxide is consumed by decomposition reactions, namely, alkali induced and transition metal ion induced. Therefore, it is important to understand and monitor hydrogen peroxide decomposition to minimize these wasteful reactions during peroxide bleaching.

The alkali induced peroxide decomposition has been investigated extensively (1-5), and the following reactions have been proposed:

$$H_2O_2 + HO^- \rightarrow HOO^- + H_2O \quad (1)$$

$$H_2O_2 + HOO^- \rightarrow O_2 + H_2O + OH^- \quad (2)$$
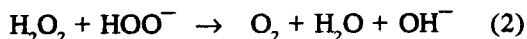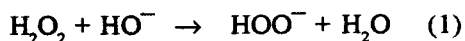
The maximum decomposition rate occurs at a pH of 11 to 11.5 (3-5), which is almost equal to the pKa of hydrogen peroxide. This is not unexpected since reaction 2 is a bimolecular reaction involving both hydrogen peroxide and perhydroxyl ion. As shown, oxygen is formed from the alkali induced decomposition.

Numerous studies have covered the transition metal ion induced peroxide decomposition (4-10). Manganese, iron and copper, representative of typical harmful transition metal ions, exhibit a significant catalytic effect under typical peroxide bleaching conditions. The reaction mechanism has been a subject of a number studies, usually involving radical species.

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Oxygen is also formed in such decompositions (4).

Evidently, the formation of oxygen is an important parameter during peroxide bleaching. Experimental results have shown that oxygen is formed during peroxide treatment of cotton (11), spruce groundwood (2) and spruce - balsam fir groundwood (10). For example, Martin (2) has reported that 20-40% of the peroxide charged was decomposed to oxygen at a pH of 10.5 to 12.0 in the absence of either magnesium salts or silicate. However, the development of oxygen formation during peroxide bleaching and its relationship to the brightness gain have not been examined.

The objective of the present study is to folow oxygen formation and brightness gain during peroxide bleaching of a TMP. This information will then be used to differentiate the peroxide consumption attributable to either bleaching or decomposition reactions.

## EXPERIMAENTAL

The sample used in this investigation was a spruce/fir TMP (initial brightness of 57.0% ISO) received from a mill in Eastern Canada. Laboratory chelation with DTPA was carried out in a polyethylene bag. The conditions were 50°C, 30 min, 0.2% DTPA, pH 5-6, 2% pulp consistency. After the required retention time, the pulp was washed thoroughly with deionized water.

Peroxide bleaching experiments in Table-1 were carried out in a Parr reactor. The reactor was preheated in a water bath. Either $O_2$ or $N_2$ was used to purge the reactor at least three times. After the required retention time, the pulp was removed from the reactor and cooled immediately. The residual peroxide was measured and handsheets were made following CPPA standard method J. 16 P and TAPPI standard method T 452 om-92, respectively.

Other peroxide bleaching experiments were carried out in 8.0 L polyethylene gas sampling bag equipped with a single polypropylene fitting which accepts 1/4" I.D. flexible tubing. The required chemicals and pulp, except $H_2O_2$, were charged to the bag. Kneading was provided to ensure good mixing, The bag was sealed properly and the trapped air was removed from the bag by filling it with helium via the fitting and then evacuating it with a water pump. This procedure was repeated several times so that the residual oxygen in the bag was negligible. Subsequently, the bag was filled with helium, and its amount controlled so that an oxygen concentration of

0.5 -5% was obtained at the end of the bleaching experiment. Finally, the required hydrogen peroxide was injected into the bag with a syringe through a septum of the fitting. The contents of the bag were kneaded uniformly and put into a water bath to start the bleaching run.

Peroxide decomposition was measured by determining the amount of oxygen evolved during the reaction. The total volume of gas in the bag was measured by the volume displacement technique described elsewhere (12). The oxygen concentration was measured by GC following the technique used in the measurement of gas formation during peracetic acid treatment of kraft pulp (12). The amount of peroxide decomposed was calculated from the oxygen formed and the $H_2O_2/O_2$ stoichiometry of two.

The residual peroxide was determined following the iodometric titration in accordance with CPPA standard method J.16P. The total peroxide consumption during bleaching was calculated from the difference between the peroxide charged and the residual peroxide. The peroxide consumption in pulp oxidation was calculated as the difference between the total peroxide consumption and the peroxide consumed in decomposition.

After bleaching, the pulp slurry was neutralized by the addition of $H_2SO_4$ to pH 4-6, washed thoroughly with deionized water and made into handsheets.

Pulp brightness was measured according to TAPPI test method T452 om-92.

The manganese content in the TMP was measured according to TAPPI test method T266 om-94.

## RESULTS AND DISCUSSION

We first determined the stoichiometry between oxygen formed and hydrogen peroxide consumed for both the alkali induced and the transition metal ion induced peroxide decomposition. The experimental results confirmed that the consumption of two moles of hydrogen peroxide results in the generation of one mole of oxygen, for both the alkali- and transition metal ion-induced decomposition.

The common practice of evaluating the peroxide bleaching performance is to compare the bleaching efficiency, defined as the ratio of brightness gain to peroxide consumption. However, the total peroxide consumption during peroxide bleaching consists of two parts: peroxide consumed in reactions with

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## TABLE 1. EFFECT OF OXYGEN IN PEROXIDE BLEACHING

| Experimental Runs | $H_2O_2$ charge (% on pulp) | Residual $H_2O_2$ (% on pulp) | End pH | Brightness (% ISO) |
|---|---|---|---|---|
| 75 psi $O_2$ Pressure | 3 | 1.65 | 9.5 | 73.5 |
| $N_2$ atmosphere | 3 | 1.78 | 9.5 | 73.2 |

Conditions: well chelated pulp, 60°C, 120 min, 3% $Na_2 SiO_3$, 0.05% $MgSO_4$, 12% Consistency, 2.4% NaOH

chromophores (effective peroxide consumption ) and peroxide consumed in decomposition (wasteful peroxide consumption). Most researchers report that oxygen generated from peroxide decomposition represents the loss of bleaching chemical. In contrast, other {9}, based on a model compound study, proposed that oxygen may contribute to the breakdown of chromophores during peroxide bleaching. Therefore, we further studied the effect of oxygen on the brightness development during peroxide bleaching. We used two different conditions: one in the presence of $O_2$, the other in the presence of $N_2$. The results in Table 1 show that the presence of oxygen has a negligible effect the overall performance in the bleaching of TMP. These results further support the conclusion that the bleaching effect by oxygen formed during peroxide treatment of mechanical pulps is very small, if any.

We then determined brightness, oxygen formation and total peroxide consumption during peroxide bleaching at varying peroxide charges. The results obtained from the mill chelated pulp are listed in Table 2. The total peroxide consumption (column 5) is obtained by the difference between hydrogen peroxide initially charged and residual peroxide. The hydrogen

peroxide consumption in decomposition (column 6) was calculated from the amount of oxygen formed and a stoichiometry of two between oxygen formed and hydrogen peroxide decomposed. The hydrogen peroxide consumption in pulp oxidation (column 7) was obtained by subtracting column 6 from column 5. The percent peroxide decomposition (column 8) is the ratio of peroxide consumption in decomposition to the total peroxide consumption. As shown for this pulp, the percent peroxide decomposition is very high, ranging from 31-47%. This is related to the fact that this pulp contains significant amount of residual managenese (40ppm). Column 9 is the pulp oxidation efficiency. which is defined as the ratio between brightness gain and hydrogen peroxide consumption in the pulp oxidation (column7).

It is interesting to note in Table 2 that an increased peroxide charge leads to a significant decrease in pulp oxidation efficiency. The following two reasons may be likely:

1) There are different chromophores originally present which have different reactivities towards hydrogen peroxide. Consequently, at the beginning

## TABLE 2. BLEACHING RESPONSES OF MILL CHELATED PULP AT VARIOUS PEROXIDE CHARGES

| $H_2O_2$ charge (% on pulp) | Alkali charge (% on pulp) | Brightness (%ISO) | End pH | $O_2$ Formation (mmol/%$H_2O_2$ consumption) | $H_2O_2$ Consumption (% on pulp) | | | % $H_2O_2$ decomp. | Pulp oxidation efficiency |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Total | In Decom position | In Pulp Oxidation | | |
| 1.89 | 1.6 | 67.1 | 8.9 | 1.83 | 1.27 | 0.4 | 0.87 | 31.5 | 11.55 |
| 3.11 | 2.4 | 68.6 | 9.5 | 2.55 | 2.79 | 1.21 | 1.58 | 43.4 | 7.32 |
| 4.49 | 3.2 | 69.8 | 9.9 | 2.81 | 4.32 | 2.06 | 2.26 | 47.7 | 5.68 |

Conditions: 60°C, 120 min, 3% $Na_2 SiO_3$, 0.05% $MgSO_4$, 12% Consistency

### TABLE 3. BLEACHING RESPONSES OF WELL CHELATED PULP AT VARIOUS PEROXIDE CHARGES

| H₂O₂ charge (% on pulp) | Alkali charge (% on pulp) | Brightness (%ISO) | End pH | O₂ Formation (mmol/%H₂O₂ consumption) | H₂O₂ Consumption (% on pulp) | | | % H₂O₂ decomp. | Pulp oxidation efficiency |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Total | In Decom position | In Pulp Oxidation | | |
| 2.98 | 2.4 | 71.9 | 0.7 | 0.4 | 1.35 | 0.09 | 1.26 | 6.67 | 11.78 |
| 4.03 | 3.2 | 73.4 | 10 | 0.57 | 1.83 | 0.18 | 1.65 | 9.84 | 9.95 |
| 5.24 | 4 | 74.5 | 10 | 0.75 | 2.59 | 0.33 | 2.26 | 12.7 | 7.73 |

Conditions: well chelated pulp, 60°C, 120 min, 3% Na₂ SiO₃, 0.05% MgSO₄, 12% Consistency

of the bleaching process, the more reactive chromophores are preferentially attacked. Stoichiometrically, these reactions need less hydrogen peroxide. As bleaching continues, the more reactive chromophores become depleted and brightness gain is achieved only by the destruction of the less reactive chromophores which require more hydrogen peroxide.

2) The radical products formed the transition metal ion induced composition, such as hydroxyl radicals, superoxide radicals can generate new chromophores. The consequence of generation of these quinoid or related chromophore systems during pulp bleaching would be to increase the amount of peroxide required to reach a given brightness level (13,17). For this mill chelated TMP which contains about 40 ppm residual manganese, it is expected that the amount of reactive species generated increases with increasing peroxide charge. Therefore, there is a greater brightness loss due to the formation of new chromophores by the reactive species at a higher peroxide charge.

We then applied the same experimental technique to a well chelated TMP sample. Results are shown in Table 3. A comparison of the percent peroxide decomposition in Tables 2 and 3 confirms that better chelation leads to much less peroxide decomposition, obviously due to the much lower mangenese content of the well chelated pulp (2.5ppm).

Traditionally, the bleaching efficiency of a peroxide stage is evaluated by plotting brightness gain against the total hydrogen peroxide consumption., However, as discussed earlier, total hydrogen peroxide consumption consists of both the peroxide consumed

in lignin oxidation (effective peroxide consumption) and that in decomposition (wasteful peroxide consumption). Here, by correcting for the hydrogen peroxide consumption due to decomposition, we were able to plot the brightness gain against the peroxide consumption in pulp oxidation. The comparison of such plots for the well chelated and mill-chelated pulps is shown in Figure 1. Clearly, at a given peroxide consumption in pulp oxidation, the brightness gain for the well chelated pulp is much more than for the mill chelated pulp. This is not related to the difference in peroxide decomposition since this factor has been corrected for. Instead, the difference may be ascribed to the generation of new chromophores in mill-chelated pulp caused by reactive species generated from the transition metal ion induced peroxide decomposition reactions.

The formation of new chromophores from the reactions of lignin compounds and radical species, such as hydroxyl and superoxide anion radicals (13), has been reported. In both cases, orthoquinonoid structures were generated. Such structures might represent new chromophores and/ or leucochromophores, responsible for the decreased pulp oxidation efficiency exhibited by the mill chelated pulp in Figure 1.

The above results support the concept that the presence of transition metal ions leads to the following two negative consequences during peroxide bleaching:

1) More hydrogen peroxide is decomposed, leading to less peroxide being available for bleaching.

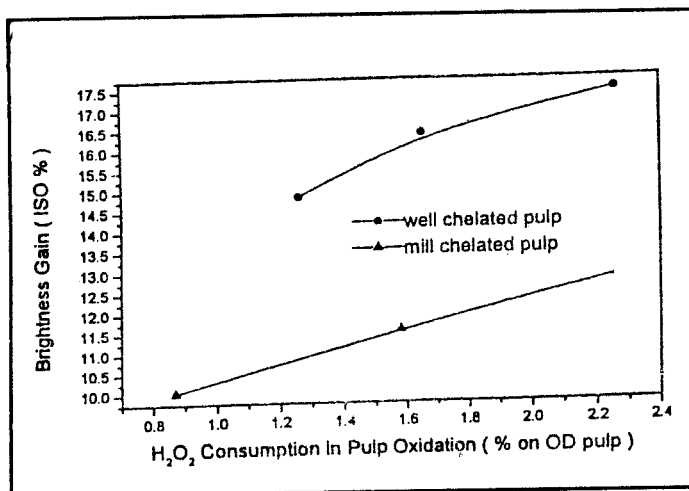(2) New chromophoric structures are generated by the reactive species from the d ecomposition

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**Figure 1. Comparison of Pulp Oxidation Efficiency ow Well-Chelated and Mill-Chelated Pulps**

and decomposition competes during the course of the bleaching process. The brightness development is initially fast and it can be partly explained by the destruction of very reactive chromophores. In addition, for this well chelated pulp, which has a very low Mn content, the transition metal ion-induced peroxide decomposition is very small. Consequently, one may expect that the generation of new chromophores by the reactive species from the decomposition reactions is also negligible. From Table 4, one can observe that although the peroxide decomposition is very small (only 3-5%), the pulp oxidation efficiency decreases (column8) as the bleaching continues. This may be attributed to the presence of different chromophores, leading to a lower peroxide demand by the more reactive chromophores at the beginning, and a higher peroxide demand by the less reactive chromophores at the end of the bleaching.

reactions, a counter-productive reaction route for pulp bleaching.

We then followed the development of brightness, oxygen formation, total peroxide consumption, peroxide consumtpion in decomposition and peroxide consumption in pulp oxidation as a function of bleaching time. The results obtained for the well chelated pulp are shown in Table 4. The hydrogen peroxide and alkali charges were kept constant at 3% and 2.4% respectively.

As expected, the pulp brightness increases as the bleaching continues, while oxygen is gradually formed, indicating that peroxide consumption in pulp oxidation

We further studied the effect of temperature of the peroxide consumption due to decomposition for both the well chelated and Mill chelated pulps. The results are listed in Table 5. As expected, the $H_2O_2$ consumption in de composition is much less for the well - chelated pulp than for the mill - chelated pulp. Table 5 also shows that for the well - chelated pulp, the hydrogen peroxide consumption due the decomposition remains almost unchanged when the temperature increases from 40 to 80°C. This is because for a pulp containing so low residual manganese, the peroxide decomposition is in significant. On the other hand, Table 5 shows that for the mill - chelated pulp, the peroxide consumption due to decomposition increases

## TABLE 4. DEVELOPMENT OF PULP OXIDATION EFFICIENCY DURING PEROXIDE BLEACHING OF THE WELL CHELATED PULP

| Time (min) | Brightness (% ISO) | O₂ Formation (mmol/%H₂O₂ consumption) | H₂O₂ Consumption (% on pulp) | | | % Peroxide decomp. | Pulp oxidation efficiency |
|---|---|---|---|---|---|---|---|
| | | | Total | In Pulp Oxidation | In decomposition | | |
| 0 | 57 | --- | --- | --- | --- | --- | --- |
| 6 | 64.7 | 0.15 | 0.6 | 0.62 | 0.02 | 3.12 | 12.4 |
| 16 | 68.7 | 0.19 | 1.1 | 1.03 | 0.04 | 3.74 | 11.28 |
| 62 | 71.4 | 0.28 | 1.5 | 1.38 | 0.07 | 4.83 | 10.38 |
| 94 | 71.9 | 0.31 | 1.6 | 1.48 | 0.08 | 5.13 | 10.03 |
| 120 | 72.5 | 0.32 | 1.7 | 1.61 | 0.09 | 5.29 | 9.59 |

Conditions: 60°C, 120 min, 3% Na₂ SiO₃, 0.05% MgSO₄, 2.4% NaOH, 12% Consistency, 3% H₂O₂

| TABLE 5. BLEACHING RESPONSES AT DIFFERENT TEMPERATURES | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | Temperature ($^\circ$C) | H$_2$O$_2$ charge (% on pulp) | H$_2$O$_2$ Consumption (% on pulp) | | | Brightness (%ISO) | End pH | Pulp oxidation efficiency |
| | | | Total | In Pulp Oxidation | In decomposition | | | |
| well- chelated | 40 | 2.8 | 0.96 | 0.9 | 0.06 | 69.5 | 10 | 13.8 |
| | 60 | 2.95 | 1.31 | 1.24 | 0.07 | 72.2 | 9.8 | 12.21 |
| | 80 | 3 | 1.52 | 1.46 | 0.07 | 72.6 | 9.7 | 10.69 |
| mill- chelated | 40 | 3.14 | 2.16 | 1.23 | 0.93 | 68.2 | 9.7 | 9.11 |
| | 60 | 3.11 | 2.79 | 1.58 | 1.21 | 68.6 | 9.6 | 7.32 |

Conditions: 120 min, 3% Na$_2$ SiO$_3$, 0.05% MgSO$_4$, 2.4% NaOH, 12% Consistency

significantly as the bleaching temperature increases. Consequently, more harmful reactive species are generated, resulting in the formation of more new chromophores (14-16). This, in combination with less peroxide available for pulp oxidation, is responsible for the lower pulp oxidation efficiency at a higher temperature than a lower temperature in Table 5.

It is noted that for the well chelated pulp, the pulp oxidation efficiency also decreases as the temperature increases. Since peroxide decomposition is similar at different temperatures, the lower bleaching efficiency could be related to the fact that the higher brightness gain at a higher temperature requires the destruction of less reactive chromophores, which have a higher hydrogen peroxide stoichiometry.

## SUMMARY

The oxygen formation during peroxide bleaching of a TMP was measured. It was established that the loss of hydrogen peroxide from both the alkali-and the transition metal - induced peroxide decomposition can be accounted for by the formation of oxygen. Based on the amount of oxygen formed, we calculated the hydrogen peroxide consumption in both the decomposition (wasteful reactions) and the pulp oxidation (desirable reactions). It was found that hydrogen peroxide is consumed continuously in two competitive reactions : pulp oxidation and decomposition. For a mill chelated pulp, 30-48% of total hydrogen peroxide consumption during peroxide bleaching is wasted, but for a well chelated pulp only 6-13% is consumed in decomposition reactions.

Experimental evidence was provided to support

the conclusion that the reactive species from transition metal ion-induced peroxide decomposition leads to the creation of new chromophores. This, in combination with the fact that less peroxide is available for pulp oxidation due to more peroxide decomposition, is responsible for the poor bleaching results when significant amount of transition metals are present during peroxide bleaching. The above explanation can then be used to account for the negative effect of high temperature on peroxide bleaching performance, and the observation that the plots of brightness against peroxide consumed in pulp oxidation are different for the well - chelated and mill -chelated pulps under otherwise identical conditions.

## ACKNOWLEDGEMENTS

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