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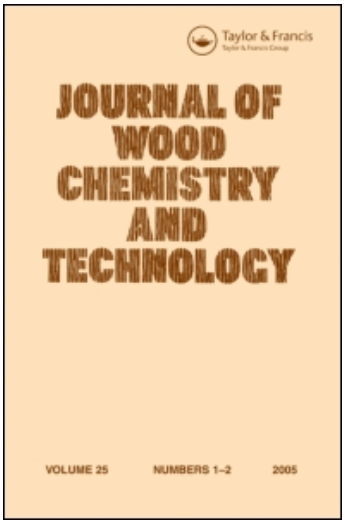

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IMPROVING PEROXIDE BLEACHING OF CHEMICAL PULPS BY STABILIZING MANGANESE

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ABSTRACT

Based on the earlier results[1] that unlike Mn(III), Mn(II) is not catalytically active towards manganese induced peroxide decomposition under alkaline conditions, we studied to improve peroxide bleaching of an oxygen delignified pulp by reducing the manganese in the pulp fibers from its high oxidation state and then stabilizing the reduced manganese with additives such as DTPA. It was shown that pulp fibers under an acidic condition are effective reducing agents and so is sodium hydrosulfite. With such a strategy it was found that the peroxide decomposition catalyzed by the residual manganese present in pulp fibers can be minimized and, consequently, the peroxide bleaching performance can be improved.

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INTRODUCTION

Hydrogen peroxide may be decomposed to form oxygen under conditions typically encountered in the alkaline hydrogen peroxide bleaching. This is particularly so when transition metal ions, such as manganese, are present. The hydrogen peroxide decomposition represents a loss of the potential bleaching power of the hydrogen peroxide charged. Therefore, prior to an alkaline hydrogen peroxide stage, it is common practice to remove the harmful transition metal ions.[2,3,4]

Conventionally, transition metal ions are removed by chelating with sequesters, such as DTPA and EDTA. However, in an industrial practice even with a good chelation, residual transition metal ions are unavoidable in pulps coming to the bleaching stage. Therefore, minimization of the catalytic effect of these residual transition metal ions, particularly manganese, in decomposing an alkaline peroxide solution may improve the bleaching efficiency of a peroxide stage.

An earlier work[1] showed that different oxidation states of manganese behave differently in decomposing an alkaline peroxide solution. Mn(II) is non-reactive while higher oxidation states, such as Mn(III) and Mn(IV), are extremely reactive during the course of the reaction. Its practical implication is that reduction of the high valency manganese to its low valency form and subsequently stabilization of the residual manganese at its low valency may result in an improvement in peroxide bleaching due to a decreased peroxide decomposition.

Under an alkaline condition, such as kraft pulping, it seems unlikely that manganese would be present as Mn(II), as it is well known[5,6] that under such a condition Mn(II) can be easily oxidized by air to Mn(III) and (IV). Consequently, one may expect that manganese present in wood fibers resulting from alkaline pulping processes is in the form of Mn(III) and Mn(IV).

In this paper we will first examine various methods to reduce the high valency manganese present in pulp fibers to its low valency form. Subsequently, we will report the results obtained from peroxide bleaching of an oxygen delignified softwood kraft pulp by reducing the transition metal ions and stabilizing the reduced transition metal ions with the addition of DTPA or sodium silicate.

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EXPERIMENTAL

Chemicals

Reagent grade 30% H_2O_2 solution, manganese (Mn(II)) chloride, DTPA, magnesium sulfate, sodium silicate and sodium hydroxide (1 mol/L) from Fisher Scientific were used in the experiments without further purification.

Pulp Samples

A fully bleached pulp with a brightness of 84.0% ISO was prepared from a hemlock kraft pulp following the DEDED sequence. The details on each of the five stages were given elsewhere.[7]

An oxygen delignified softwood kraft pulp, was received from a mill in Ontario, Canada, and its properties are listed in Table 1 (as Sample 1, unchelated pulp). The unchelated pulp was subjected to a chelation stage with 0.5% DTPA at pH 5.9, 70 °C, and 3% pulp consistency for 30 min. The pulp slurry was then filtered in a Büchner funnel and washed thoroughly with distilled water. The properties of the resulting pulp are listed in Table 1 (as Sample 2, Q_1). Also, another chelated pulp was obtained at pH 2.5 under otherwise the same conditions as above. The sample was named as Sample 3, Q_A (Table 1). Finally, Sample 4 (Q_m) is a mixture of Samples 1 and 3.

Reduction of Mn(III) with pulp fibers and sodium hydrosulfite, by following the pulp brightness

Mn(II) (3 ppm) and 1.6 g of the fully bleached pulp were added to a 250 mL flask containing 100 mL distilled water. Sodium hydroxide was subsequently charged to the flask to adjust its pH to 11. The pulp slurry turned to brown from colourless, which indicates that Mn(II) is oxidized to Mn(III).[5] Furthermore, the presence of Mn(III) was confirmed by following an iodometric titration method developed for the determination of oxidation state for manganese.[1] For those runs

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TABLE 1
Properties of the Pulp Samples Used

No.	Sample description	Kappa no.	Viscosity (cP)	Brightness (% ISO)	Transition metal contents (ppm)		
					Mn	Fe	Cu
1	Unchelated pulp	12.1	22.9	37.5	54.2	30	0.8
2	Q_1 sample, pH 5.9, 0.5% DTPA, 70°C, 30 min	11.2	22.2	37.5	4.5	21	---
3	Q_A sample, pH 2.5, 0.5% DTPA, 70°C, 30 min	10.8	22.5	37.8	4.1	7	0.5
4	Q_m sample, Mixtures of Samples 1 and 3	11.7	22.6	37.6	22.9	26	0.8

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of reduction by pulp fibers, the pH of the content in the flask was subsequently adjusted with sulfuric acid to various pH values, which is regarded as the reduction pH in Figure 1. The reduction at a given pH was conducted at 70°C for 30 min. After the completion of the reduction time, the pH of the pulp slurry was adjusted to neutral, and immediately a handsheet for brightness measurement was made following Tappi test methods, T218.

Experiments with sodium hydrosulfite as the reducing agent were performed under the conditions of pH 5 - 6, 70°C, 30 min. After the completion of the reduction time, the pH of the pulp slurry was adjusted to neutral, and then handsheets were made.

The reason for neutralization prior to the handsheet preparation for brightness measurement is to minimize the manganese loss during the handsheet making process. This was confirmed experimentally.

E+O+P Treatment

The E+O+P stage was performed in a specially designed bomb fitted with a

TABLE 2
Conditions of Reductions with Pulp Fibers or Sodium Hydrosulfite

Reducing agent	Pulp	$Na_2S_2O_4$
Conditions	Various pH 10% pulp consistency 70°C 30 min	0.2% $Na_2S_2O_4$ pH 5 - 6 10% pulp consistency 70°C 30 min

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Teflon liner. The control run without the addition of DTPA was performed as follows; the required chemicals, i.e. NaOH, $MgSO_4$ and H_2O_2, were first mixed in a beaker, and then the mixture was transferred from the beaker to a polyethylene bag containing 10 g of pulp which was well disintegrated in a desired pulp consistency. The content in the polyethylene bag was mixed with kneading and subsequently transferred to the bomb reactor to start the E+O+P stage. At the completion of the reaction time, the pulp was washed thoroughly with distilled water and saved for further analysis. The control run with the addition of DTPA was performed in exactly the same manner as above except that the required amount of DTPA was added to the beaker as one of the mixture.

For those runs with reduction (by pulp under an acidic condition or by sodium hydrosulfite), the O_2 delignified pulp was treated under the specified reductive conditions (see Table 2) in a polyethylene bag. Immediately then, 0.5% DTPA and 0.2% $MgSO_4$ were added to the pulp slurry and a good mixing was provided by peroxide were added as a mixture to the polyethylene bag, and then the content in the kneading for a couple of minutes. Subsequently, sodium hydroxide and hydrogen bag was transferred to the bomb reactor. The runs with sodium silicate as the stabilizer were performed under exactly the same conditions as those with DTPA as the stabilizer except that sodium silicate replaces DTPA to be added to the reaction system.

RESULTS AND DISCUSSION

Reduction of Mn(III) to Mn(II)

We added sodium hydroxide to a flask containing 1.6 g of bleached pulp fibers and 3 ppm Mn(II) so that the pH of the solution was 11. The initially colourless pulp slurry turned brown due to oxidation of Mn(II) to Mn(III) by air under the alkaline condition. The higher oxidation state manganese in its hydroxide form then adsorbs on the pulp fibers and decreases the pulp brightness from 83.8% ISO to 66.2% ISO (Figure 1). The decrease in pulp brightness caused by adsorption of oxidized Fe(II) and Mn(II) at pH 11 for bleached birch kraft pulp has been observed by others.[8]

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Next, we studied the reduction of high oxidation state manganese to its low oxidation state with the DEDED pulp at various pHs. This was measured experimentally by determining the brightness of the pulp which was acidified to various pH levels. See detailed procedures in the Experimental section. The increase in pulp brightness upon acidification is rather obvious to naked eyes. The low brightness can be used as an indirect measure of the presence of Mn(III) and the effectiveness of reduction of Mn(III) to Mn(II) can be correlated to the brightness increase.[8] Therefore, we followed the brightness development as a function of pH during the reduction, shown in Figure 1. One can observe that pH is an important parameter to reduce the high oxidation state of manganese by pulp fibers. At a pH of about 3, the reduction appears to be complete. These results support our hypothesis that pulp fibers can be effective in reducing high oxidation state manganese under an acidic condition. The slightly lower brightness achieved after the reduction of manganese than the original brightness of the bleached pulp (Figure 1) is likely due to the fact that in the former, some complexes are formed between transition metal ions and pulp fibers.[9,10,11] These complexes may be slightly coloured.

We then studied the reduction of Mn(III) to Mn(II) with sodium hydrosulfite, a commonly used reducing agent in bleaching of mechanical pulps, by adding sodium hydrosulfite to brown pulp slurry containing manganic (Mn(III)) hydroxide, which

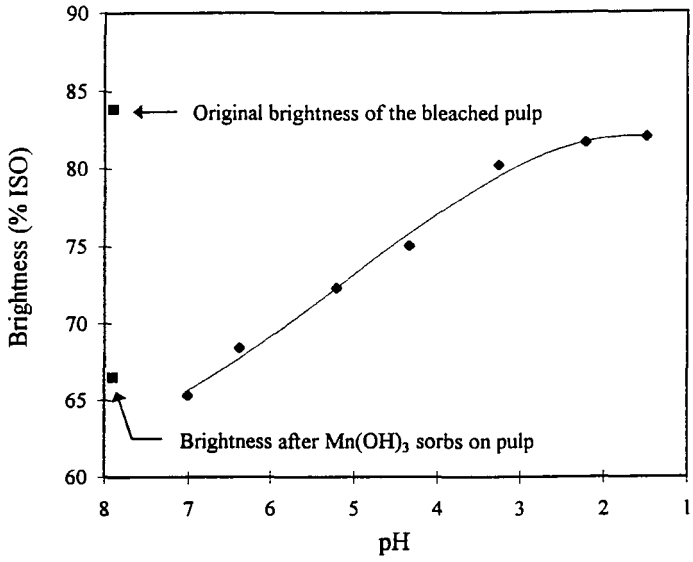

FIGURE 1 Reduction of Manganese by Acidification/Pulp (3 ppm manganese, pulp consistency 1.6%, 70°C, 30 min)

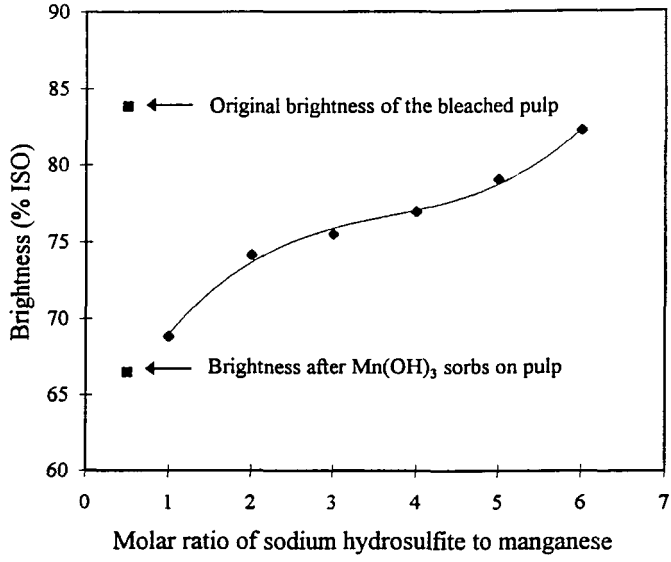

FIGURE 2 Reduction of Manganese with Sodium Hydrosulfite (3 ppm manganese, pulp consistency 1.6%, 70°C, 30 min)

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was prepared in a same manner as above. Figure 2 shows the brightness versus the molar ratio of sodium hydrosulfite to manganese. As expected, the brightness increases as the molar ratio increases, indicating that the reduction of Mn(III) takes place.

So far we have shown that pulp fibers under an acidic condition and sodium hydrosulfite, are very effective in reducing Mn(III) to Mn(II). Subsequently, if stabilizers, such as chelants and sodium silicate, are added to retard the oxidation of Mn(II) to Mn(III), the peroxide decomposition will be decreased. As a result, one may expect that improved bleaching results can be obtained. In the next section, we will show the results by applying the above concept to an E+O+P treatment of an oxygen delignified kraft pulp.

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E+O+P Bleaching

Table 3 shows the results obtained from the unchelated pulp with a manganese content of 54.2 ppm (Sample 1). Trial 1 represents a control run without the addition of DTPA. At the completion of the reaction time, no residual hydrogen peroxide was detected. In Trial 2 , DTPA was directly added as part of the chemicals required for the E+O+P stage. The resulting pulp from Trial 2 has a higher pulp brightness than the corresponding pulp from Trial 1. This may indicate that the addition of DTPA under such conditions decreases the peroxide decomposition to some extent. Since no reduction was performed, manganese in Trial 2 is still in its high oxidation states. These results confirm that an addition of DTPA to a system containing high oxidation states of manganese exhibited a limited stabilization effect on an alkaline peroxide solution, which is consistent with our earlier study[1] on manganese-induced peroxide decomposition.

In Trial 3, the reduction of high oxidation states of manganese to its low oxidation state was achieved with pulp fibers under an acidic condition (pH 3). Table 3 demonstrates that 9.2% of the charged hydrogen peroxide remained at the completion of the E+O+P stage, which is in contract to Trials 1 and 2. In addition,

TABLE 3
E+O+P Bleaching of the Unchelated Pulp (Sample 1, 12.1 initial kappa no.)

Trial	Description	Residual H_2O_2 (% on charge)	Brightness (% ISO)	Viscosity (cP)	Kappa No.
1	Control, without DTPA	0	55.6	19.0	6.9
2	Control, with 0.5% DTPA	0	57.1	19.5	7.0
3	Acidification → 0.5% DTPA	9.2	60.1	19.4	6.8

Conditions: 2% H_2O_2, 1% NaOH, 0.2% $MgSO_4$, 90°C, 50 psi O_2 pressure for 120 min

TABLE 4
E+O+P Bleaching of the Q_A pulp (Sample 3, 10.8 initial kappa no.)

Trial	Description	Residual H_2O_2 (% on charge)	Brightness (% ISO)	Viscosity (cP)	Kappa No.
4	Control, without DTPA	4.3	68.7	18.1	5.9
5	Control, with 0.5% DTPA	22.5	69.6	18.0	5.4
6	Acidification → 0.5% DTPA	52.4	72.6	19.2	5.1

Cond.: 2.4% H_2O_2, 1% NaOH, 0.2% $MgSO_4$, 110°C, 70 psi O_2 pressure for 120 min

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the resulting pulp from Trial 3 has the highest brightness, supporting that the manganese-induced peroxide decomposition is further reduced in comparison with Trials 1 and 2. It should be pointed out that the amount of manganese present in Trial 3 is the same as that in Trial 1 or 2, since washing/filtration was not performed during the acidification/chelation process.

The E+O+P bleaching results obtained from Sample 3 are shown in Table 4. Much stronger conditions of 2.4% H_2O_2 charge, 110°C and 70 psig O_2 pressure, the so-called P(O) and/or P_{HT} processes, were used for Sample 3 than Sample 1. Table 4 further supports that reduction of high valency manganese and stabilization of the reduced manganese with DTPA leads to an improved peroxide bleaching in comparison with the control runs. Based on these results, one can conclude that the

TABLE 5
E+O+P Bleaching of the Q_m Pulp (Sample 4, 11.7 initial kappa no.)

Trial	Description	Residual H_2O_2 (% on charge)	Brightness (% ISO)	Viscosity (cP)	Kappa No.
7	Control, without DTPA	1.8	57.4	19.5	6.6
8	Control, with 0.5% DTPA	3.4	57.9	19.8	6.4
9	Acidification → 0.5% DTPA	24.5	66.5	19.8	6.1

Conditions: 2% H_2O_2, 1% NaOH, 0.2% $MgSO_4$, 90 °C, 50 psi O_2 pressure for 120 min

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beneficial effect of this reduction/stabilization concept can be extended to high temperature peroxide bleaching systems, such as the P(O) process[12] and the P_{HT} process.[13]

It is noticed that the difference in transition metal content between Sample 1 (Table 3) and Sample 3 (Table 4) is quite drastic. We performed another set of experiments with Sample 4, which has the transition metal ion profile between Samples 1 and 3. The results are shown in Table 5. Evidently, Trial 9, which was conducted in accordance with the reduction/stabilization concept has the best results, in comparison with Trials 7 and 8. The decreased catalytic activity of reduced and stabilized transition metal ions towards peroxide decomposition is again demonstrated.

It was shown[1] that addition of other stabilizers, such as sodium silicate, to a Mn(II) containing peroxide solution can retard the oxidation of Mn(II) to Mn(III) and consequently decrease the manganese induced peroxide decomposition. Therefore, here we also studied the improvement in peroxide bleaching by adding sodium silicate to a pulp slurry containing the reduced manganese. Sample 2 was used in this set of experiments and the results are listed in Table 6. The reduction of transition metal ions was achieved by both acidification/pulp (Trial 12) and sodium hydrosulfite (Trial 13) (see Experimental for detailed procedure). It is evident that

TABLE 6
E+O+P Bleaching of the Q_1 pulp (Sample 2, 11.2 initial kappa no.)

Trial	Description	Residual H_2O_2 (% on charge)	Brightness (% ISO)	Viscosity (cP)	Kappa No.
10	Control, without Na_2SiO_3	15.9	61.3	18.4	6.6
11	Control, with 4% Na_2SiO_3	33.1	61.6	18.5	6.4
12	Acidification → 4% Na_2SiO_3	44.5	61.4	18.9	6.3
13	$Na_2S_2O_4$ treatment → 4% Na_2SiO_3	45.6	61.8	19.3	6.6

Conditions: 2% H_2O_2, 1% NaOH, 0.2% $MgSO_4$, 90 °C, 50 psi O_2 pressure for 120 min

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similar results can be obtained in both cases, and that the reduction/stabilization technique produced better results in comparison with the control runs (Trials 10 and 11).

CONCLUSIONS

The potential of pulp fibers as reducing agents to convert high valency manganese (Mn(III)) to its low oxidation state (Mn(II)) was studied. It was found that under an acidic condition, pulp fibers can effectively reduce the high oxidation state manganese. Consequently, if a stabilizer, such as DTPA or sodium silicate, was added to the pulp slurry containing reduced manganese, followed by the addition of other chemicals required for an E+O+P stage, the bleaching performance is improved in comparison with the conventional E+O+P stage under otherwise the same process conditions. This is attributed to the reduced manganese induced peroxide decomposition because Mn(II) is not catalytically active.[1] Mn(II), when in complexation with DTPA, may not be further oxidized to Mn(III) under the E+O+P condition. Sodium hydrosulfite can also effectively reduce manganese from its high oxidation state and the improved peroxide bleaching can also be achieved with sodium hydrosulfite as the reducing agent following the reduction/stabilization technique.

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