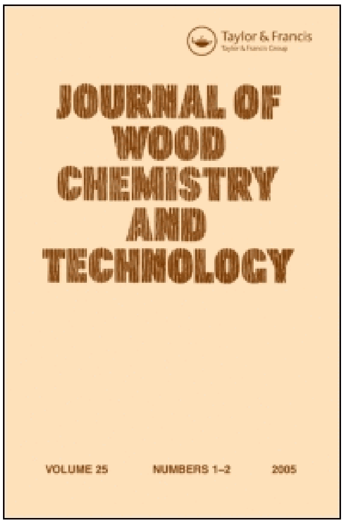

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Qiu, Z. , Ni, Y. and Yang, S.(2003) 'Using DTPA to Decrease Manganese-Induced Peroxide Decomposition', Journal of Wood Chemistry and Technology, 23: 1, 1 — 11
To link to this Article: DOI: 10.1081/WCT-120018612
URL: http://dx.doi.org/10.1081/WCT-120018612

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
Vol. 23, No. 1, pp. 1–11, 2003

Using DTPA to Decrease Manganese-Induced Peroxide Decomposition

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ABSTRACT

The catalytic activity of Mn(+II) and Mn(+III) in decomposing hydrogen peroxide was studied by using DTPA as the only stabilizer. It was found that the addition of DTPA to a Mn(+II) containing system is more effective than if it is added to a Mn(+III) containing system. To decrease the catalytic effect of Mn(+III), sodium borohydride and DTPA under an acidic condition were considered to reduce Mn(+III) to Mn(+II). The effect of pH on using DTPA to decrease Mn-induced peroxide decomposition is discussed.

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DOI: 10.1081/WCT-120018612
0277-3813 (Print); 1532-2319 (Online)

www.dekker.com

Key Words: Hydrogen peroxide; Decomposition; Bleaching; Transition metal ions; Manganese; DTPA; pH.

INTRODUCTION

The control of hydrogen peroxide decomposition is critical to peroxide bleaching. The decomposition of peroxide is greatly enhanced in the presence of transition metal ions, resulting in less active chemical available for bleaching. Among various transition metal ions, it was reported[1–3] that manganese is the most harmful species during alkaline peroxide bleaching. Therefore, it is a common practice for pulp mills to use chelating agents such as DTPA (diethylenetriaminepentaacetic acid) and EDTA (ethylenediaminetetraacetic acid) in a pretreatment to remove transition metal ions from pulp fibres.

It has been realized that Mn(+II) is much less effective than Mn(+III) and/or Mn(+IV), in decomposing hydrogen peroxide under bleaching conditions.[4–6] Based on recent studies,[5–7] it is most likely that Mn(+III) is involved in the catalytic hydrogen peroxide decomposition, in a mechanism in which the oxidation state of the manganese changes in a cyclic manner.[8] The utilization of magnesium sulfate and sodium silicate to stabilize manganese-containing peroxide solutions has been well documented.[5,6,9,10] The use of a chelating agent, Na_5DTPA (pentasodium salt of diethylenetriaminepentaacetic acid), in conjunction with silicate and magnesium, was also investigated as a way to decrease peroxide decomposition.[6,10,11] In this article we report on a study of DTPA as the only stabilizer to decrease the Mn-induced peroxide decomposition. The objectives were

- to examine the effect of the oxidation state of manganese, e.g., Mn(+II), Mn(+III), on the stability of alkaline peroxide solutions, when using DTPA as the only stabilizer
- to develop potential techniques to decrease the Mn-induced peroxide decomposition.

EXPERIMENTAL

All hydrogen peroxide decompositions were carried out in 100-mL polyethylene bottles. Diethylenetriaminepentaacetic acid was prepared from dissolving H_5DTPA (diethylenetriaminepentaacetic acid), which was obtained from Aldrich Chemical Co., in an alkaline solution, which was then neutralized. Manganese sulfate monohydrate, Mn(+III) acetate bihydrate, sodium hydroxide, sulfuric acid, sodium borohydride, and hydrogen peroxide from Fisher Scientific were used without any further purification. Deionized and distilled water was used throughout all the experiments. In all experiments involving pulp fibers, a bleached sulfite pulp which was chelated with 0.2% DTPA at 70°C for 30 min, followed by a thorough washing, was used. In the decomposition runs with pulp fibers, the pulp was added prior to the addition of sodium hydroxide and hydrogen peroxide.

In the runs where Mn(+III) acetate was reduced either by $NaBH_4$ or by the combination of $NaBH_4$ and DTPA, the Mn(+III) containing solution was mixed with the reducing agent(s). The pH of the mixture was adjusted to 3.5 and then placed into a temperature bath at 70°C for 10 min to achieve a complete reduction. After the solution was cooled down, 0.3 g o.d. pulp was added to the solution to make a 0.3% pulp suspension. Finally sodium hydroxide and hydrogen peroxide were added in that order. In some cases, a small amount of NaOH was added to reach the target pH.

The residual H_2O_2 was measured following CPPA Standard Testing Method J16P.

RESULTS AND DISCUSSION

Peroxide Decomposition in the Absence of Pulp

As shown in Run 1, Table 1, without the addition of any stabilizers, the alkaline peroxide solution containing Mn(+II) is not stable at all, and the residual peroxide was zero after 60 min at 70°C. These results are in agreement with those by Kutney and Evans,[4] Ni et al.[6] and Galbács and Csányi,[12] with or without pulp fibers.

In Run 2, DTPA was added to a polyethylene bottle containing 3 ppm Mn(+II) (the DTPA/Mn molar ratio was 1), followed by the addition of sodium hydroxide, and then hydrogen peroxide to reach the target pH. The residual hydrogen peroxide concentration after 60 min at 70°C was 1.0 g/L, indicating that under the conditions studied, the addition of DTPA completely stabilizes the alkaline peroxide solution against decomposition. When the DTPA to Mn molar ratio was further increased to 2, as in Run 3, the alkaline peroxide solution containing 3 ppm Mn(+II) was stable again.

Table 1. Effect of DTPA addition to Mn(+II) or Mn(+III) containing systems on the Mn-induced peroxide decomposition in the absence of pulp.

Run	Initial pH	Mn oxidation state	DTPA/Mn molar ratio	Residual H_2O_2 (g/L)
1	10.5	Mn(+II)	0	0
2	10.5	Mn(+II)	1	1.0
3	10.5	Mn(+II)	2	1.0
4	10.5	Mn(+III)	0	0
5	10.5	Mn(+III)	1	0.52
6	10.5	Mn(+III)	2	0.61
7	10.5	Mn(+III)	5	0.69
8	11.0	Mn(+II)	2	0.98
9	11.0	Mn(+III)	2	0.38

(3 ppm Mn(+II) or Mn(+III), 1.0 g/L initial H_2O_2, 70°C, 60 min).

We then applied the same experimental approach to systems containing Mn(+III) (added as Mn(III) acetate bihydrate). The Mn(+III)-induced peroxide decomposition is evident in Run 4. The addition of DTPA to a Mn(+III) containing system will decrease the catalytic peroxide decomposition to some extent, as shown in Runs 5, 6, and 7. However, the additional stabilizing effect of DTPA by increasing its concentration is not as drastic as in the case of Mn(+II), where complete stabilization of alkaline peroxide solution was obtained at pH 10.5 with a molar ratio of DTPA/Mn = 1. Similarly, at an initial pH of 11.0, a DTPA/Mn ratio of 2 can stabilize the Mn(+II) containing solution, but not the Mn(+III) containing system, as shown in Runs 8 and 9 (Table 1), respectively.

As shown above, Mn(+II) is much more readily stabilized than Mn(+III) by adding DTPA. We then studied the effect of reducing Mn(+III) to Mn(+II) on the stability of alkaline peroxide systems containing Mn(+III). In Run 10, Table 2, sodium borohydride was chosen as the reducing agent, its pH was 10.5 and the DTPA/Mn molar ratio was 2, the residual H_2O_2 concentration was 0.99 g/L. This is compared to a residual H_2O_2 concentration of 0.61 g/L of Run 6, Table 1, which was obtained without the reduction of Mn(+III) by sodium borohydride, under otherwise the same conditions. Run 11 (Table 2) shows the result obtained by reducing Mn(+III) with sodium borohydride, then carrying out the decomposition at pH 11.0 with a DTPA/Mn molar ratio of 2. Again, a much improved peroxide stability is evident. (Run 11 vs Run 9).

Table 2. Effect of reduction of Mn(+III) by $NaBH_4$ or DTPA on the stability of an alkaline peroxide solution containing Mn(+III) in the absence of pulp.

Run	Initial pH	Reducing agent	DTPA/Mn molar ratio	Residual H_2O_2 (g/L)
10	10.5	$NaBH_4$	2	0.99
11	11.0	$NaBH_4$	2	0.93
12	11.0	DTPA	2	0.79
13	11.0	DTPA	3	0.95
14	11.0	DTPA	4	0.95

(3 ppm Mn(+III), 1.0 g/L initial H_2O_2, 70°C, 60 min).

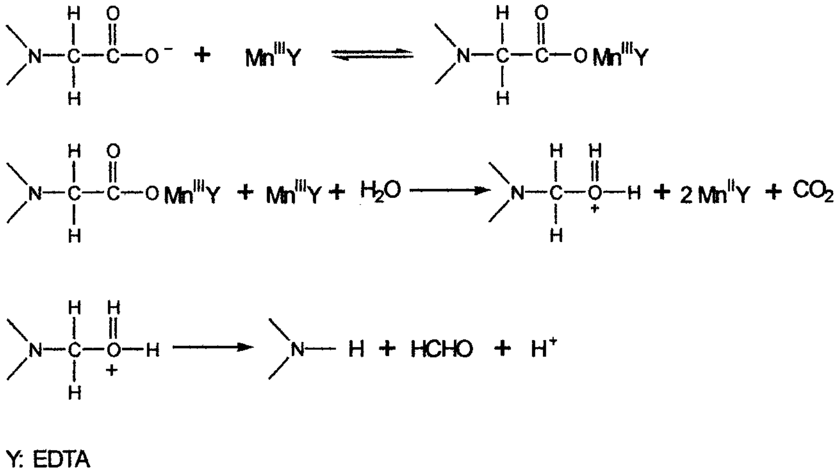

Figure 1. Mechanism of Mn(III)–EDTA reaction proposed by Schroeder and Hamm.[13]

Schroeder and Hamm[13] reported that EDTA can reduce Mn(+III) to Mn(+II) and that carbon dioxide and formaldehyde are the products from EDTA. Figure 1 illustrates the proposed reactions.[13] They found that the reaction can proceed in the pH range of 2–5. Lidén and Öhman[5] also concluded that EDTA can reduce manganese(+III) compound in slightly acidic solution because they observed the transition of the pink-colored $Mn(+III)(EDTA)^-$ complex to the colorless $Mn(+II)(EDTA)^{2-}$ complex at pH 5. Since DTPA and EDTA have similar structures, it may be reasonable to assume that DTPA can reduce Mn(+III) to Mn(+II) under slightly acidic conditions. We then designed the following experiments to confirm the hypothesis.

In Run 12, DTPA (DTPA/Mn molar ratio of 2) was added to Mn(+III) solution and its pH was decreased from 9 to 3.5. The original brown solution, characteristic of Mn(+III) solution, disappeared. This indicates that Mn(+III) is reduced to Mn(+II) by DTPA. Subsequently, sodium hydroxide and peroxide solutions were added in that order. A small amount of sodium hydroxide was finally added into the solution to bring the pH to 11. The residual peroxide concentration was 0.79 g/L, which is substantially higher than 0.38 g/L as in Run 9 where no acidification was carried out after DTPA was added to Mn(+III) solution. These results suggest that the reduction of Mn(+III) by DTPA to Mn(+II) needs an acidic condition. An increase in the DTPA charge with otherwise the same conditions and procedures as those in Run 12 resulted in further improvement in the stability of the peroxide solutions, as shown in Runs 13 and 14. The improved H_2O_2 stability at a higher DTPA charge is due to the fact that more DTPA is available to complex with Mn(+II), leading to less manganese hydroxide to be formed, as will be discussed in subsequent sections.

Effect of Pulp Fibers

We continued the study by determining the effect of pulp fibers on the Mn-induced peroxide decomposition. The results obtained at pH 10.5 are presented in Table 3. In Run 15, DTPA was added to a Mn(+II) solution followed by the addition of pulp fibers. Sodium hydroxide and hydrogen peroxide were then added to mixture in that order. Finally a small amount of sodium hydroxide was added to reach the target pH. The residual hydrogen peroxide concentration after 60 min at 70°C was 0.99 g/L, indicating that the peroxide decomposition was very small, if any. Also, in comparison with Run 3, Table 1, one may conclude that the presence of pulp fibers had a negligible effect on the peroxide decomposition.

In Run 16, DTPA was added into a Mn(+III) solution at pH 10, which is the natural pH of a 3 ppm Mn(+III) acetate solution. Note that no acid was added. The subsequent procedure was the same as that in Run 15. The residual hydrogen peroxide was 0.67 g/L after 60 min at 70°C. This should be compared to a residual hydrogen peroxide of 0.93 g/L in Run 17, Table 3, where sulfuric acid was added to reach a pH of 3.5, after the addition of DTPA to the Mn(+III) containing mixture. The difference in the peroxide decomposition between Runs 16 and 17 is due to the fact that reduction of Mn(+III) to Mn(+II) by DTPA occurs only at an acidic condition, not an alkaline condition.

Table 3. Effect of Mn(+III) reduction by $NaBH_4$ or DTPA on the stability of an alkaline peroxide solution containing Mn(+III) in the presence of pulp fibers at pH 10.5.

Run	Experimental sequence	DTPA/Mn molar ratio	Residual H_2O_2 (g/L)
15	Mn(+II) DTPA at pH 6 Pulp	2	0.99
16	Mn(+III) acetate DTPA at pH 10 Pulp	2	0.67
17	Mn(+III) acetate DTPA, pH 3.5, 70°C, 10 min Pulp	2	0.93
18	Mn(+III) acetate $NaBH_4$ and DTPA, pH from 8.0 to 3.5, 70°C, 10 min Pulp	2	0.98–0.94

(3 ppm Mn(+II) or Mn(+III), 10.5 initial pH, 0.3% pulp consistency, 1.0 g/L initial H_2O_2, 70°C, 60 min).

In Run 18, both $NaBH_4$ and DTPA were used to reduce Mn(+III) to Mn(+II). The combined effect of reduction and stabilization resulted in almost no decomposition of the peroxide in the alkaline solution. As long as Mn(+III) was reduced to Mn(+II) by $NaBH_4$ at various $NaBH_4$/Mn ratios, the addition of DTPA always stabilized the alkaline peroxide solution.

Lidén and Öhman[5] noticed the difference in redox stability of manganese in the presence and absence of pulp when using magnesium as the stabilizer. It was concluded that pulp fibers impart a colloidal nature to the magnesium precipitates formed, thus giving more efficient protection against catalytic peroxide decomposition during pulp bleaching. They proposed that the carboxylate groups on the pulp may be involved in the redox stabilization and help to stabilize manganese in the +II oxidation state by changing the physical characteristics of the coprecipitate when magnesium ions are present. However, the results in our system using only DTPA as the stabilizer show that the presence of pulp has no effect on the stability of alkaline peroxide solutions containing manganese. This can be seen by comparing Runs 15 and 16 (Table 3) with Runs 3 and 6 (Table 1), respectively.

Our explanation is as follows: when DTPA is used as the only stabilizer, since it is a stronger chelant for transition metal ions than the carboxylate groups in pulp fibres, manganese present in the system is preferably complexed with DTPA, rather than carboxylates. Therefore, when DTPA is added, the carboxylate effect, and thus the pulp effect is negligible.

We also studied the reduction of Mn(+III) by DTPA on the stability of alkaline peroxide solutions containing Mn(+III) in the presence of pulp fibres at pH 11.0. The results are shown in Table 4. In comparison with those results in Table 3, one can conclude that at pH 11.0, 2 equivalent molar DTPA is not adequate to stabilize the reduced Mn(+II) and that a good stabilization is achieved only at a DTPA/Mn molar ratio of 3 or above. This is in agreement with the results in Table 2 in the absence of pulp fibres, and can be explained by the hypothesis that an increase in pH will lead to a decrease in the chelating ability of DTPA. In a system consisting of manganous ions, DTPA, and hydroxide ions, there is a competition between chelating agent and hydroxide ions for Mn^{2+} as illustrated in the following reactions[14]:

$$Mn^{2+} + 2OH^{-} \Rightarrow Mn(OH)_2 \tag{1}$$

$$Mn^{2+} + DTPA \Rightarrow (MnDTPA)^{3-} \tag{2}$$

At a higher pH, more OH^{-} ions are present in the system, therefore, more Mn^{2+} are in the form of manganous hydroxide, $Mn(OH)_2$ while, relatively speaking, less are chelated with DTPA via Reaction 2. However, this can be compensated for by adding more DTPA to the system. This, then, is responsible for the experimental evidence that at a higher pH, more DTPA is needed to stabilize alkaline peroxide solution against the Mn-induced peroxide decomposition.

Table 4. Reduction of Mn(+III) by $NaBH_4$ or DTPA on the stability of an alkaline peroxide solution containing Mn(+III) in the presence of pulp fibres at pH 11.0.

Run	Experimental sequence	DTPA/Mn molar ratio	Residual H_2O_2 (g/L)
19	Mn(+III) acetate DTPA, pH 3.5, 70°C, 10 min Pulp	2	0.57
20		2.5	0.83
21		3	0.95
22		4	0.96

(3 ppm Mn(+III), 11.0 initial pH, 0.3% pulp consistency, 1.0 g/L initial H_2O_2, 70°C, 60 min).

A more quantitative explanation for the results in Table 4 is from the conditional stability constant, $K_{M'L'(ML)'}$, defined as

$$K_{M'L'(ML)'} = \frac{([ML]')}{(M')(L')}$$

where

(M') is the total concentration of metal in a solution that is not chelated
(L') is the total free chelating agent
$([ML]')$ is the total metal chelate concentration

It is known that the conditional stability constant is a more practical expression of chelate strength than a simple stability constant, K_{ML}. The conditional stability constant has been corrected for metal which is complexed with hydroxide ion, OH^-, and the chelating agent for interaction with H^+.[15] The conditional stability constant of $(DTPA–Mn)^{3-}$ reaches a maximum at pH 10.5, which is very close to pK_5 of DTPA, 10.42.[15] A further increase in pH beyond 10.5 leads to a decrease in the conditional stability constant, resulting in more peroxide decomposition under otherwise the same condition. This may also be used to explain the observation, most recently made by Lidén and Öhman,[9] that the effect on adding DTPA or EDTA to improve peroxide bleaching of chemical pulps is rather poor since the pH under these conditions is much higher than 10.5.

Based on the results presented in the previous sections, one can draw the conclusion that when DTPA is used as the stabilizer for Mn(+II), either from $MnSO_4$ itself or from the reduction of Mn(+III), the Mn-induced peroxide decomposition is negligible at pH 10.5 and 11.0, provided that the DTPA charge is sufficient. Its underlying mechanism could be that the Mn^{2+}–DTPA complexes are so chemically stable that the redox cycle of manganese, which is responsible for decomposing hydrogen peroxide, is stopped.

CONCLUSIONS

Diethylenetriaminepentaacetic acid, as the only stabilizer, decreased the manganese-induced peroxide decomposition. Addition of DTPA to Mn(+II) containing system is more effective than if it is added to Mn(+III) containing system. Furthermore, the higher reactivity of Mn(+III) in catalyzing peroxide decomposition can be retarded by reducing Mn(+III) to Mn(+II) and by stabilizing the reduced manganese with DTPA. Sodium borohydride and DTPA, under acidic conditions, can reduce Mn(+III) to Mn(+II). The results obtained from systems with or without pulp fibers are very similar. At a higher pH, more DTPA is needed to minimize the peroxide decomposition, a result of the hydroxide ions are competing with DTPA for the transition metal ions.

ACKNOWLEDGMENTS

The authors wish to thank Dr. J. Lidén of AssiDomän, Sweden, for his valuable suggestions to improve the manuscript. Financial support of the project was from NCE Wood Pulps Network.

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