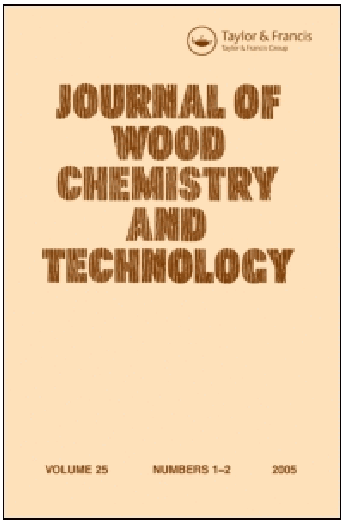

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TWO-STAGE PEROXIDE BLEACHING OF EUCALYPT-SGW WITH CHROMIUM CATALYSTS

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ABSTRACT

The addition of chromium nitrate to a two-stage hydrogen peroxide bleach of *Eucalypt* SGW can enhance the brightness of the pulp. It is proposed that radicals produced in the catalytic decomposition of hydrogen peroxide by chromium under acidic conditions participate in reactions which render the chromophores more susceptible to bleaching in the alkaline stage. This two-stage process, under optimised conditions, consumes no more peroxide than a traditional single stage alkaline bleach and allows the pulp to be bleached to a given brightness in a shorter time. Enhanced bleaching response was also observed for a two-stage acid/alkali peroxide bleaching sequence without the addition of chromium, and we have attributed this effect to catalytic effects of transition metal ions which occur naturally in the pulp.

INTRODUCTION

Catalytic processes have been developed and utilised to a much less significant extent in the pulp and paper industry than in many other important chemical process industries. The reason for this may lie partly in the greater difficulty encountered in catalyst recovery and recycling in heterogeneous systems with liquid and solid components compared to vapour/solid systems. The soda-anthraquinone pulping process[1-4] represents an important exception, where a catalytic process received widespread interest and has been subsequently developed through to a commercial scale. There are many reports in the literature concerning catalytic effects during bleaching of pulp, particularly with regard to the effect of transition metal ions[5-10]. In most cases, however, the reported catalytic influences during bleaching are considered to have a detrimental effect on overall efficiency.

For example, colloidal sulfur is thought to promote the catalytic decomposition of sodium dithoinite during bleaching of mechanical pulp under acidic conditions[11] producing thiosulfate ions which are a major source of corrosion in paper machines[11-14]. Certain transition metal ions including copper and iron are found to have negative influences during both oxygen delignification[5,6] and bleaching with hydrogen peroxide[7-10] under alkaline conditions. During oxygen delignification the presence of catalytic amounts of transition metals can cause both reduction in delignification rate and loss of pulp viscosity[5,6]. Catalytic decomposition of hydrogen peroxide by transition metal ions is well established[15,16], and can lead to loss of bleaching efficiency unless reagents such as DTPA, magnesium or sodium silicate are introduced[17,18].

There are fewer reports of beneficial effects resulting from the presence of catalytic species during bleaching[19-24]. Introduction of manganese has been shown to accelerate delignification and reduce carbohydrate degradation in studies of oxygen delignification[5,20]. Transition metal species have also been shown to be effective in catalyzing oxygen delignification of residual lignin in chemical pulps[21,22]. Recent studies have also shown that transition metal catalysts can promote peroxide bleaching efficiency during two-stage processes, initially using acidic conditions followed by a conventional alkaline peroxide step[21-24]. In this study we have investigated the use of chromium catalysts in this type of bleaching sequence for a stone ground eucalypt pulp.

EXPERIMENTAL

Materials

Hydrogen peroxide (30%) and sulfuric acid (98%) were obtained from Ajax chemicals. Chromium nitrate (99%), magnesium nitrate (99.999%), sodium silicate

(30%) and potassium hydroxide (99.99%) of semiconductor purity were supplied by Aldrich chemicals. Semiconductor grade potassium hydroxide was used as the source of alkali as this introduces very low levels of transition metal ion impurities[16,18].

Procedures

Blocks of *Eucalyptus Regnans* wood were soaked for three days in Milli-Q water and then ground at 80°C in the presence of dilute sodium hydroxide on a small scale grindstone at ANM, Boyer. The pulp was washed with distilled water and filtered to increase the consistency from 1.5% to 20%. The pulp was then stored at 4°C until used.

Bleaching studies were carried out in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. Bleaching experiments were performed by adding the required amounts of pulp, hydrogen peroxide, chromium nitrate and acid or alkali to give a total volume of 500mL with addition of Milli-Q water[16,18]. In some bleaching experiments the required amounts of sodium silicate and magnesium nitrate were added to the bleaching solution. All experiments were performed at 1% pulp consistency and the solutions were stirred[25] throughout the bleaching runs. The initial charge of hydrogen peroxide was 6% on o.d. pulp. For bleaching under acidic conditions the pH was adjusted to the appropriate level (generally 5.8) with either potassium hydroxide or sulfuric acid. After the prescribed time sufficient potassium hydroxide was added to adjust the pH to the level required for the second stage (generally 11.0).

Chelated pulps were prepared by treating the pulp with 0.5% EDTA (on o.d. pulp) at 2% consistency for 15 minutes then filtering and washing the pulp thoroughly before use[26]. Metal ions present in the original pulp and after chelation were determined by atomic absorption spectroscopy. 5.00g o.d. pulp was digested in 50 mL concentrated nitric acid and 5 mL sulfuric acid until no pulp was visible, 5 mL concentrated perchloric acid was then added and the solution heated until a clear solution was obtained. The results are given in Table 1.

Iodometric determinations of hydrogen peroxide were performed before the pulp was added, and to the initial filtrate at the completion of the bleaching run. After addition of acidified potassium iodide and a few drops of ammonium molybdate solution the liberated iodine was titrated against sodium thiosulfate solution[27].

TABLE 1. Metal ion content of Pulps used in this work.

	Metal ion (ppm)*		
Wood type	**Iron**	**Manganese**	**Copper**
Eucalypt SGW	32	8	72
Chelated *Eucalypt* SGW	32	1	32

* Concentration determined by atomic absorption after digestion of pulp.

Hydrogen peroxide levels were also determined at the completion of the acidic treatment and sufficient peroxide was added to restore the level to 6% on o.d. pulp at the start of the alkaline stage.

The brightness (%ISO) of the bleached pulps were measured on a Zeiss Elrepho using a 457nm filter. Handsheets were also regularly prepared to monitor any changes in the original pulp with storage time and to allow brightness gains to be calculated. The brightness of the unbleached pulp was in the range 53-55 %ISO.

RESULTS AND DISCUSSION

Transition Metal Ion Catalysts

Transition metal ions are known to catalytically decompose hydrogen peroxide[28,29]. This catalytic decomposition is generally considered detrimental during bleaching processes due to increased consumption of peroxide and much work has been carried out to reduce the effect of the catalytically active species[28-30]. Traditionally the perhydroxyl anion, HO_2^-, is thought of as the active bleaching species[31-33]. Transition metal catalysed decomposition of hydrogen peroxide is thought to proceed

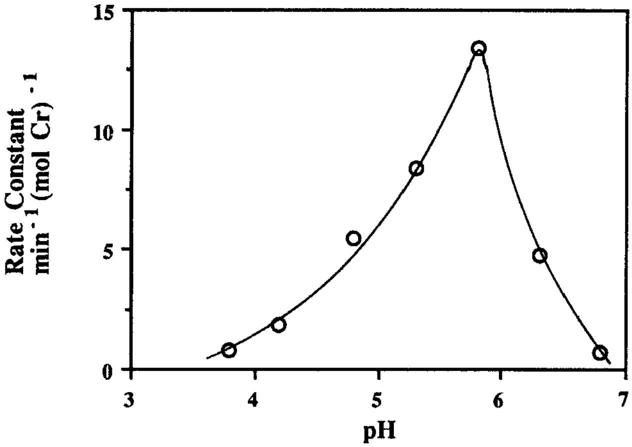

FIGURE 1. Variation in the first order rate constant with pH for decomposition of hydrogen peroxide in the presence of chromium at 20°C. Initial concentration of hydrogen peroxide 0.10M; concentration of chromium 2.5 x 10^{-4}M.

via free radical chain reactions, producing intermediate species such as $OH^{\bullet}$ and $^{\bullet}O_2^-$, and there has been recent interest in the possible role of these active species in chromophore elimination[34,35]. Chromium is unusual in that the maximum decomposition rate for hydrogen peroxide in the presence of this transition metal occurs under slightly acidic conditions (at pH 5.8) as shown in Fig. 1, while the rate of decomposition is negligible at pH > 8.0. In contrast, transition metal ions including manganese, copper and iron, which are often present in pulp samples, have maximum activity under alkaline conditions[36,37]. This observation for the behaviour of chromium may allow the pulp to be exposed to radicals produced by the catalytic decomposition of hydrogen peroxide in a pH range where traditional bleaching is ineffective, which enables us to study effects which occur under both acidic and alkaline conditions separately.

Fig. 2 shows the effect of a two-stage peroxide treatment with chromium nitrate (0.13% Cr on o.d. pulp) initially introduced. In the first stage, the pH was maintained at 5.8, with an initial charge of 6% peroxide (on o.d. pulp). After 30 minutes the concentration of hydrogen peroxide was restored to its initial level before adding alkali to raise the pH to 11.0 in the second stage of the bleaching sequence. Curve (a) shows

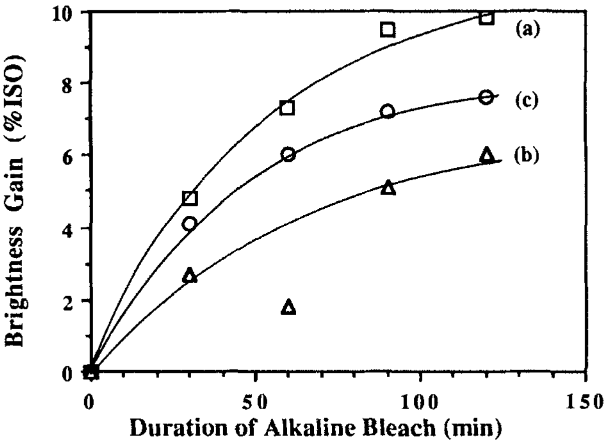

FIGURE 2. Brightness gain plotted against time of alkaline bleach (pH 11.0). (a) acidic treatment (pH 5.8) for 30 minutes with 0.13% chromium (on o.d. pulp) (2.5 x 10^{-4}M); (b) no acidic treatment; (c) acidic treatment (pH 5.8) for 30 minutes with no added chromium.

the increase in brightness with time during the second stage of the bleaching process, at a constant pH under alkaline conditions. This can be compared with curve (b), which corresponds to bleaching under the same conditions, but without pre-treating the pulp with acidic peroxide or introducing chromium. It is apparent that chromophore elimination occurs more rapidly for the pulp which has been subjected to the two-stage bleaching sequence. It is important to point out that no brightness gain could be detected for these pulps after only the first (acidic) stage. It would appear that even though chromophores are not eliminated by acidic peroxide treatment in the presence of chromium, the chromophores present are rendered more susceptible to subsequent removal by alkaline peroxide bleaching. Previous work[24,38,39] has shown that a two-stage hydrogen peroxide bleaching sequence involving an acidic stage followed by alkaline treatment can give an enhanced brightness over a conventional one stage alkaline bleach. Curve (c) in Fig. 2 shows the effect of an acidic treatment followed by an alkaline treatment without initial introduction of chromium. It is apparent that the bleaching response for this pulp under alkaline conditions is intermediate between the case where no acidic pre-treatment is applied, and that in which chromium is introduced

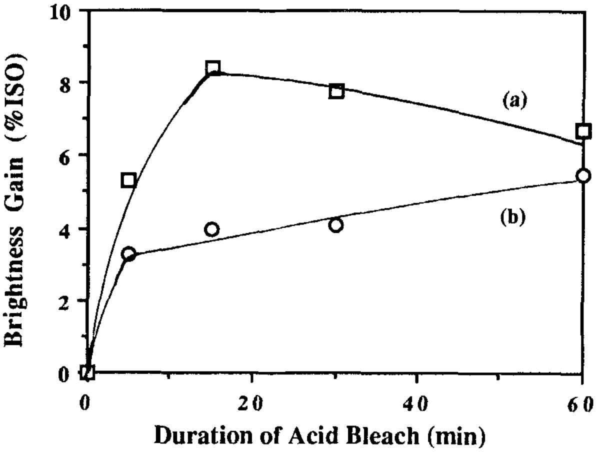

FIGURE 3. Effect of removing metal ions from the pulp prior to bleaching: (a) unchelated pulp; (b) chelated pulp. Acid stage: pH 5.8; alkaline stage: pH 11.0, 120 minutes.

with acidic peroxide. These effects can be explained on the basis of other metal ions which occur naturally in the wood, or have been introduced during pulp production. Manganese, iron and copper are found to be typically present in mechanical pulps[7,26], as shown in Table 1 for our SGW eucalypt pulp. We believe that the presence of these transition metal ions can induce effects on the chromophores in the presence of acidic peroxide similar to those produced in the presence of chromium. The total effect seen (curve (a)) in Fig. 2 can therefore be attributed to the combined effects of chromium and the other metal ions in the pulp.

Evidence for the effect of the residual metal ions can be obtained by bleaching experiments with chelated pulps. Table 1 shows that chelation with DTPA removes most of the manganese initially present in the pulp, and also produces a significant reduction in copper content. The amount of iron present, however, is little influenced by the chelation procedure, and these results are consistent with previous reports[26]. Fig. 3 shows that the brightness gain for two-stage acid/alkali bleaching in the presence of chromium is significantly reduced using the chelated pulp compared to an unchelated pulp. It can be concluded that the presence of manganese and copper, and possibly other metal ions initially present in the pulp, contribute to the observed effects on brightness enhancement for the two-stage bleaching sequence.

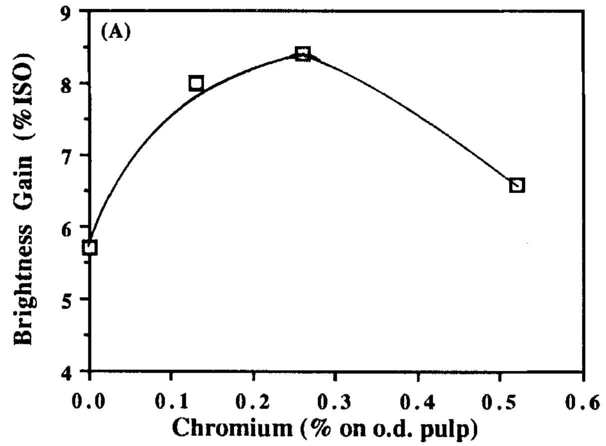

FIGURE 4A. The effect of varying the dose of chromium catalyst on the brightness gain. Acid stage: 15 minutes, pH 5.8; Alkaline stage: pH 11.0.

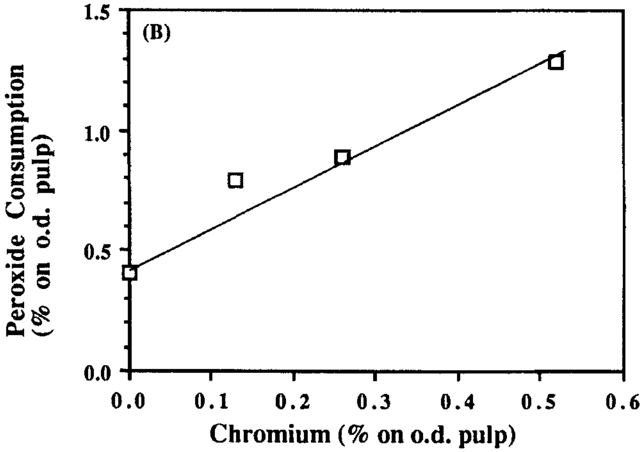

FIGURE 4B. Effect of varying the amount of chromium on the peroxide consumption after the first (acidic) stage. Acid stage: pH 5.8, 15 minutes.

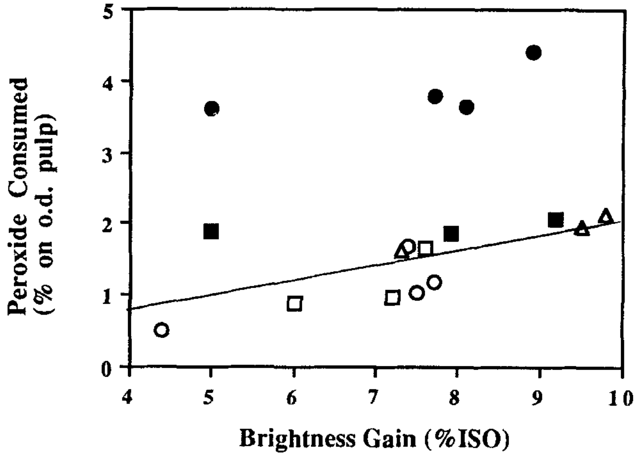

FIGURE 5. Plot showing the correlation between peroxide consumed and the brightness gain. Acid stage: 30 minutes, pH 5.8; alkaline stage: 30 - 120 minutes, pH 11.0.□; 0% Cr added,△; 0.13% Cr added, ■; 0.26% Cr added,● ; 0.52% Cr added,○ ; single stage alkaline bleach only, no added Cr.

Optimization of Conditions and Peroxide Consumption

Fig. 4A shows the effect of varying the amount of chromium introduced prior to the two-stage acid/alkali peroxide bleaching sequence. It is clear that there is an optimum range for addition of chromium to achieve maximum brightness gain of the eucalypt pulp. This effect may be attributed to the additional reduction in peroxide concentration under acidic conditions as the chromium concentration is increased (Fig. 4B). At the highest level of chromium addition shown, about 25% of the initial peroxide charge was consumed at the end of the first stage. The presence of high levels of chromium also leads to excess total consumption of peroxide to reach a given level of brightness after the alkaline bleaching stage. Fig. 5 shows that addition of chromium beyond the optimum range results in increased total consumption of peroxide without a proportional increase in pulp brightness. At lower chromium levels, peroxide consumption is approximately proportional to brightness gain for both the two-stage acid/alkali bleaching sequence and single-stage alkali treatment.

With the conditions used in this study (1% consistency, 6% hydrogen peroxide on o.d. pulp, 50°C, no stabilisers) our experiments showed that a maximum brightness

TABLE 2. Time to Reach a Brightness Gain of 8 Points.

wt% Cr (on o.d. pulp)	Time (min) acid	alkali	total	Peroxide^{+} Consumed (% on pulp)	Brightness Gain/ Weight Peroxide (ISO/%)	Bleaching Efficiency* (ISO/%/hour)
0	-	170	170	2.08	3.83	1.35
0	30	120	150	1.74	4.59	1.84
0.13	15	120	135	1.58	5.03	2.24
0.26	30	60	90	1.86	4.30	2.87
0.52	30	60	90	3.64	2.19	1.46

Bleaching experiment at 50°C, 1% consistency. Acid stage: pH 5.8, initial peroxide charge 6.0% on o.d. pulp. Alkaline stage: pH 11.0, initial peroxide charge 6.0% on o.d. pulp. Initial brightness of eucalypt pulp 54.0.

* Efficiency = Brightness Gain / % peroxide consumed (on o.d. pulp) / time (hours)

$^{+}$ It should be noted that, due to the restoration of the peroxide charge to its initial level after the first stage of the two stage bleaching process, the peroxide charge is higher than 6.0% in some cases.

gain of approximately 10 %ISO can be achieved for this eucalypt pulp. The more rapidly this level is reached, and the smaller the amount of peroxide consumed, the more efficient will be the process. Table 2 shows that the two-stage acid/alkali treatment enables a target brightness increase of 8 units to be reached in less time compared to a single stage alkali process while consuming a similar amount of peroxide.

Fig. 6A shows the effect on brightness gain resulting from varying the pH of the first stage of the two-stage bleaching sequence. Both in the presence and absence of chromium a minimum response is observed in the pH range 4-5, whereas at pH 7 the response is similar both with and without chromium. The lower curve (b) can be attributed to the effects of metal ions in the original pulp (e.g. manganese and copper). Fig. 6B shows the effect of chromium alone, obtained by taking the difference between

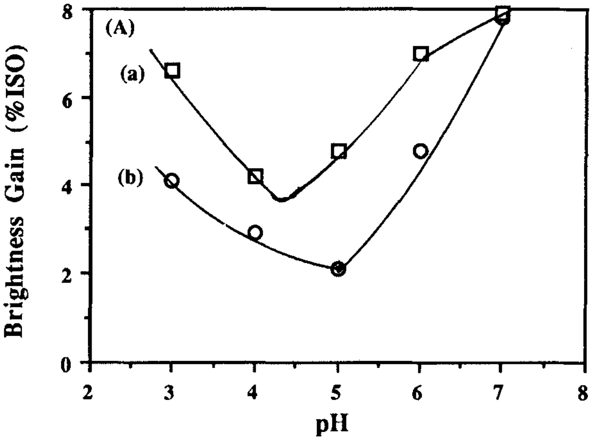

FIGURE 6A. The effect of varying the pH of the acidic stage for (a) 0.26% chromium (on o.d. pulp) added; (b) no added chromium. Acid treatment: 30 minutes; alkaline stage: pH 11.0, 120 minutes.

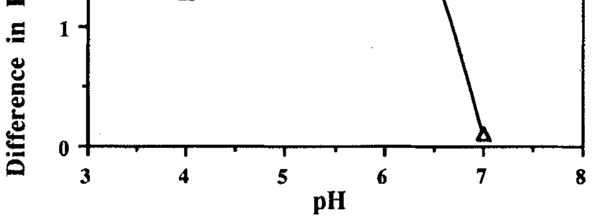

FIGURE 6B. Difference in the brightness gain after the alkaline stage (pH 11.0, 120 minutes) for the pulps bleached in Fig. 6A.

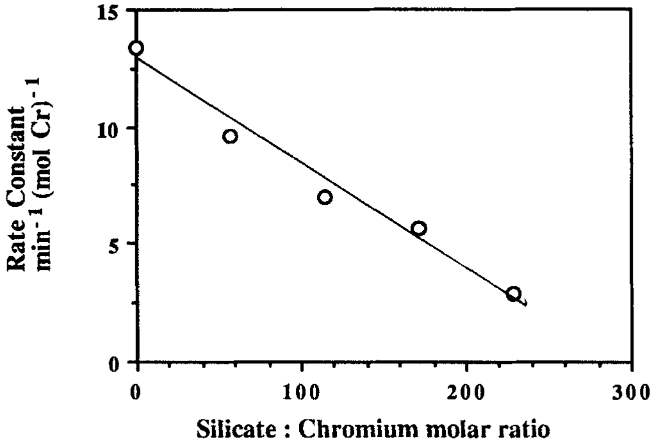

FIGURE 7. The effect of varying the chromium : silicate molar ratio on the rate of decomposition of hydrogen peroxide. Initial hydrogen peroxide concentration 0.10M, 20°C, chromium concentration of chromium 2.5 x 10^{-4}M.

the two curves in Fig. 6A. Fig. 6B shows a maximum in the pH range 5-6, and this may be compared with Fig. 1, which also shows a maximum in this range for peroxide decomposition catalyzed by chromium. This apparent correlation between catalyzing peroxide decomposition under acidic conditions and inducing brightness gain in the subsequent alkaline step may be significant. The result may show that it is the products from catalytic decomposition of hydrogen peroxide (i.e free radicals) which are active under acidic conditions in causing changes in the susceptibility of chromophores to subsequent alkaline peroxide treatment, where there are much higher concentrations of the perhydroxyl anion[40].

There has been recent interest in the idea that free radical species, particularly the hydroxyl radical ($HO^{\bullet}$), may indeed play an important role in peroxide bleaching, under conventional alkaline bleaching conditions as well as under acidic conditions[41,42]. Model compound studies with alpha-methyl syringyl alcohol, a model lignin compound, shows a maximum rate of oxidation by hydrogen peroxide at pH 11, and the mechanism for this process has been discussed in terms of free radical intermediates derived from hydrogen peroxide[43]. The idea that free radicals as well as the

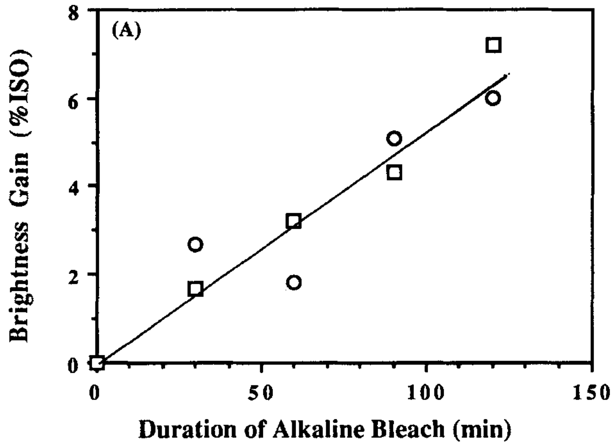

FIGURE 8A. Plot of the brightness gain against time for an alkaline bleach (pH 11.0) with (○) no added silicate; (□) 18% silicate (on o.d. pulp) added.

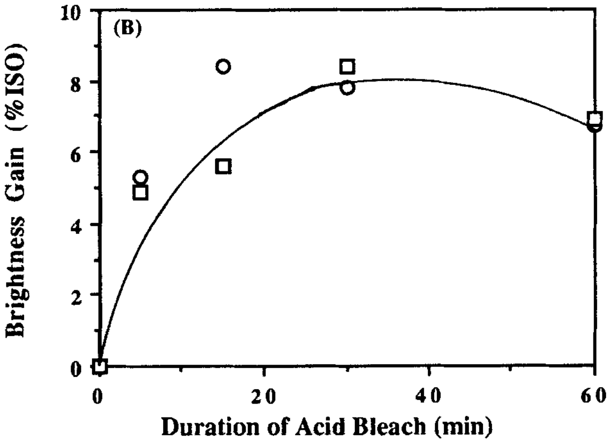

FIGURE 8B. Plot of the brightness gain against time for a two-stage bleach (Acid stage: pH 5.8; alkaline stage: pH 11.0, 120 minutes) with (○) 0.26% chromium (on o.d. pulp); (□) 0.26% chromium (on o.d. pulp) and 18% (on o.d. pulp) silicate. (Si:Cr molar ratio 114:1)

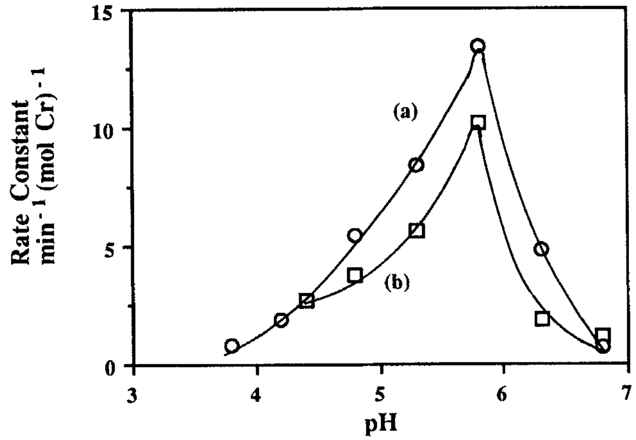

FIGURE 9. Variation in the rate of decomposition of hydrogen peroxide against pH at 20°C (a) in the presence of 2.5 x 10^{-4}M chromium; (b) in the presence of 2.5 x 10^{-4}M chromium and 5.0 x 10^{-3}M magnesium. Initial concentration of hydrogen peroxide 0.10M.

perhydroxyl anion may be active in brightness development during peroxide bleaching suggests that there may be more than one mechanism for chromophore elimination. A recent analysis of kinetic phenomena during peroxide at various pH levels was based on the assumption of two distinct mechanisms of chromophore removal, one dependent on the perhydroxyl anion concentration and the other depending on participation of free radicals[24]. The results of the present study also provide support for the concept of a dual mechanism for chromophore elimination.

Effect of Magnesium and Silicate

Both magnesium salts and sodium silicate are commonly used as stabilisers for peroxide bleaching liquors[28,29,44-46]. The effect of these stabilisers has been investigated in the two-stage process currently being studied. Silicate reduces the rate of hydrogen peroxide decomposition in the presence of chromium at pH 5.8 as shown in Fig. 7. Silicate is thought to retard transition metal ion catalysed decomposition of hydrogen peroxide by acting as a free radical trap[47]. Other studies have also concluded

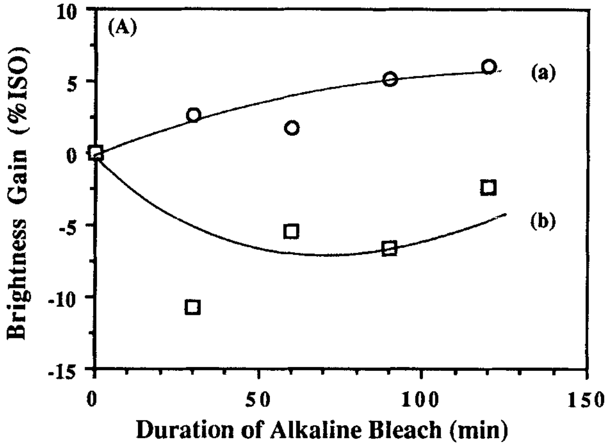

FIGURE 10A. Plot of brightness gain against time for an alkaline bleach (pH 11.0) with (a) no added magnesium; (b) 2.44 % magnesium (on o.d. pulp) added.

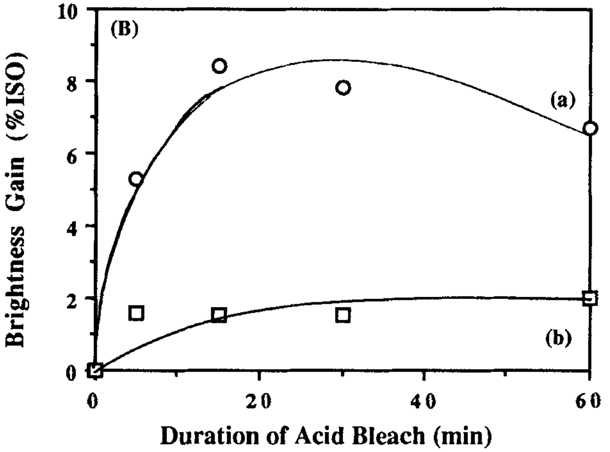

FIGURE 10B. Plot of the brightness gain against time for a two-stage bleach (Acid stage: pH 5.8,; alkaline stage: pH 11.0, 120 minutes) with (a) 0.26% chromium (on o.d. pulp); (b) 0.26% chromium and 2.44% magnesium (on o.d. pulp). (Mg:Cr molar ratio 20:1) that sodium silicate is effective in stabilising peroxide under alkaline bleaching conditions through buffering action[32] and through deactivation of metal ions[28]. Fig. 8A shows that similar brightness gains were observed in a single stage alkaline bleach in the presence or absence of silicate, although the amount of peroxide consumed was reduced in the presence of silicate. Similar brightness gains were also observed in a two-stage process in the presence of silicate and chromium, as shown in Fig. 8B, again with slightly lower peroxide consumption.

Magnesium also inhibits the rate of chromium catalysed decomposition of hydrogen peroxide as shown in Fig. 9. In a single stage alkali bleach, magnesium, as shown in Fig. 10A, has the effect of reducing the brightness of the pulp. This is an interesting result in view of the common practice of including magnesium salts as a stabilising agent during commercial bleaching of mechanical pulps with hydrogen peroxide. The effectiveness of magnesium as a stabiliser under alkaline conditions appears to be related to the nature of the other metal ions present in the pulp. It has been shown[15] that addition of magnesium to solutions containing manganese ions causes a significant increase in catalytic activity towards peroxide decomposition. In contrast, addition of magnesium to solutions containing iron produces a stabilising effect[16], and this has been attributed to formation of an iron-magnesium complex[16]. The observed loss in pulp brightness observed here on addition of magnesium cannot be explained simply on the basis of peroxide stability. However, it is likely that the nature of catalytic species present is modified by the addition of magnesium which may in turn modify the types and concentrations of decomposition products formed. Fig. 10B shows that in a two-stage process a much lower brightness is also obtained in the presence of magnesium, the lower brightness probably being caused by the presence of the magnesium in the alkali stage.

CONCLUSION

The presence of transition metal ions during a two-stage hydrogen peroxide bleach of *Eucalypt* SGW has been found to enhance the brightness of the pulp. The total effect produced appears to be derived from the influence of chelatable ions naturally present in the pulp and also introduced chromium species. The influence of these metal species during acidic peroxide treatment renders the chromophores present in the pulp more easily removed during subsequent bleaching under alkaline conditions.

This effect may be related to generation of active radical species through catalytic decomposition of hydrogen peroxide at low pH. Using such a process, optimised for dose of catalyst and time of acidic treatment, brightness gains can be achieved in less time while consuming no additional peroxide.

This study has shown that there is potential scope for development of beneficial catalytic processes for the enhancement of peroxide bleaching. Such processes may utilise the presence of metal ions naturally present in the wood pulp, or species which may be introduced prior to peroxide treatment. The development of such processes would appear to depend on recent concepts of peroxide bleaching in which species other than the perhydroxyl anion are implicated in chromophore removal. This may in turn revise the traditional view that the presence of transition metal ions in wood pulp should be associated with adverse effects in bleaching sequences.

ACKNOWLEDGEMENT

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