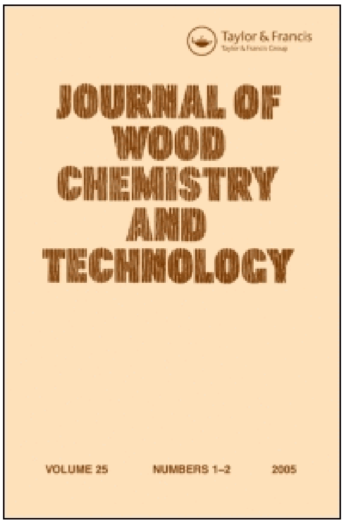

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Chemical Aspects of Hydrogen Peroxide Bleaching. Part II the Bleaching of Kraft Pulps

Göran Gellerstedt[a]; Ingegerd Pettersson[a]
[a] Swedish Forest Products Research Laboratory, Stockholm, Sweden

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CHEMICAL ASPECTS OF HYDROGEN PEROXIDE BLEACHING. PART II * THE BLEACHING OF KRAFT PULPS.

Göran Gellerstedt and Ingegerd Pettersson
Swedish Forest Products Research Laboratory
Box 5604, S-114 86 Stockholm, Sweden

ABSTRACT

Kraft pulps contain a considerable amount of transition metal ions. It is demonstrated that unless these ions are thouroughly removed, alkaline hydrogen peroxide is an inefficient bleaching agent for kraft pulps due to a rapid decomposition into oxygen. If, on the other hand, the metal ions are removed from the pulp prior to bleaching under carefully selected conditions, alkaline hydrogen peroxide can be used to increase considerably the brightness of kraft pulps without seriously affecting the pulp viscosity.

The results are interpreted with emphasis on the organic and inorganic chemical reactions of hydrogen peroxide. It is also suggested that the bleaching effect is a result of a simultaneous degradation and dissolution of lignin starting with phenolic lignin units.

INTRODUCTION

In a series of papers, the fundamental chemistry of hydrogen peroxide decomposition and hydrogen peroxide oxidation of various lignin structures under alkaline conditions has been extensively clarified.[2-6] The results obtained have provided a chemical description of the reactions taking place when mechanical pulps are bleached with alkaline hydrogen peroxide. Thus, the results reveal that in order to utilize alkaline hydrogen peroxide as an efficient lignin-retaining bleaching agent precautions must be taken to avoid

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*Part I. See Ref. 1.

a decomposition of hydrogen peroxide. In practice this is prevented by choosing mild alkaline bleaching conditions, addition of sodium silicate and magnesium sulfate for hydrogen peroxide stabilization and removal of transition metal ions from the pulp by treatment with a chelating agent prior to bleaching. Despite these measures mechanical pulp bleaching seems to consume a fairly large amount of hydrogen peroxide in reactions with little additional improved brightness, at least when hydrogen peroxide is applied in amounts exceeding ∿ 1 % (on o.d. pulp). It was suggested that this "extra" consumption was due to reactions between decomposition products from hydrogen peroxide and reactive structures, e.g. phenols, within the pulp.[1] Although suppressed as noted above such a decomposition seems nevertheless to take place under normal bleaching conditions. It was further suggested that the decomposition of hydrogen peroxide occurs by a chain mechanism in which phenolic lignin structures participate and that this continues as long as phenols (and other suitable substrates) are available in the fibres. For the bleaching of mechanical pulps this type of reaction seems to be a necessary prerequisite in order to reach the highest brightness levels.

In the presence of transition metal ions like those of manganese or iron the decomposition of hydrogen peroxide to oxygen via hydroxyl radicals and superoxide ions is strongly enhanced. Such a system is still able to oxidize the pulp constituents but with far less selectivity for lignin since the concentration of reactive radical intermediates is increased. At the same time the bleaching capacity decreases as a result of a rapidly decreasing concentration of hydrogen peroxide.

The hypothesis that hydrogen peroxide participates in two completely different sets of reactions with lignin, viz. elimination of chromophores via nucleophilic attack by hydroperoxy anions and oxidative degradation of phenolic lignin structures caused by decomposition products from hydrogen peroxide, suggests that alkaline hydrogen peroxide could be used as an efficient lignin-degrading bleaching agent for kraft (and sulfite) pulps. Although the lignin content is much lower than in mechanical pulps, the residual lignin in kraft pulps contains a large number of free phenolic units.[7] In general such structures are more reactive than carbohydrates towards the radical intermediates formed from hydrogen peroxide.[8] Thus a fairly selective removal of lignin may be expected to occur if the chain decomposition of hydrogen peroxide can be controlled at a suitable (low) rate.

In the present paper it is demonstrated that, analogously to mechanical pulp bleaching, an efficient removal of transition metal ions from chemical pulps prior to bleaching is an absolute prerequisite for an efficient utilization of hydrogen peroxide. Furthermore it is shown that the bleaching should be carried out at a high bleaching-pH, at a high temperature and with a short bleaching time. Under such conditions it is possible to utilize the chain decomposition of hydrogen peroxide for removal of the major portion of the residual lignin in a kraft pulp without decreasing the pulp viscosity to an unacceptable level. At the same time a substantial increase in pulp brightness can be obtained.

RESULTS AND DISCUSSION

In a preliminary experiment a pine kraft pulp with a kappa number of 35 was bleached at 85°C with 4 % hydrogen peroxide (% on o.d. pulp) and with an alkali charge corresponding to a starting pH = 12.0 in the bleaching liquor. After 20 min the pH had increased to 12.2, no residual hydrogen peroxide could be detected and the kappa number of the pulp was 25. A similar bleaching experiment, carried out after a pretreatment of the pulp with diethylenetriaminepentaacetic acid (DTPA) gave an almost identical result but with a pulp brightness of 39 % ISO compared with 32 % in the former case. In a third experiment the pulp was pretreated with DTPA and bleached with 4 % hydrogen peroxide in the presence of sodium silicate. The bleaching temperature was 60°C, the time 120 min and the starting pH = 11.5; thus the conditions resembled those usually employed in the bleaching of mechanical pulps. The final pH in the bleaching liquor had also increased in this case and no residual hydrogen peroxide could be analysed. The kappa number of the resulting pulp was 24 and the brightness was 39 % ISO.

These results indicate that, despite treatment with a powerful chelating agent, the pulp contains a considerable amount of transition metal ions able to catalyze a decomposition of hydrogen peroxide. Most of the radicals formed i.e. hydroxyl radicals and superoxide ions react further with the formation of oxygen which in the open bleaching system used (see Experimental) has only a limited influence on the delignification and increase in brightness (cf. Ref. 1). In order to obtain meaningful results it was therefore necessary to find a more powerful method of pretreatment to remove the transition metal ions from the pulp prior to bleaching.

Recently a method has been described in which transition metal ions in wood chips are effectively removed by the combined action of sodium sulfite and DTPA.[9] In the present work this mixture was used and optimized for the pretreatment of kraft pulps. After such a treatment under optimum conditions only small amounts of transition metal ions remain in the pulp (Table 1).

It can be assumed that the transition metal ions present in the original wood are converted to insoluble sulfides and/or hydroxides during the course of a kraft cook and that they are thus strongly retained in the fibres. By the action of bisulfite ions the metal hydroxides (sulfides) are reduced and dissolved. In the absence of DTPA the solubilized metal ions can be expected to be chelated with lignin and carbohydrate structures, whereas in the presence of DTPA (or any other strong chelating agent) DTPA-metal ion complexes are formed. These can subsequently be eliminated from the pulp by washing.

In order completely to eliminate transition metal ions from kraft pulps and thus achieve an optimal stability of hydrogen peroxide in a subsequent bleaching stage it was found necessary to optimize the pretreatment stage with respect to pH, temperature and the charge of sulfite. As can be seen in Fig. 1 the pH in the

TABLE 1

Content of Transition Metal Ions (Mn and Fe) in an Unbleached Kraft Pulp from Pine (Kappa Number = 35) after Treatment with DTPA (0.2 % on O.D. Pulp) and/or Sodium Bisulfite (3 % as SO_2 on O.D. Pulp).

Treatment	Mn (ppm)	Fe (ppm
—	127	48
DTPA (25°C)	45	48
$NaHSO_3$(90°C)	27	12
$NaHSO_3$/DTPA (25°C)	26	28
$NaHSO_3$/DTPA (90°C)	1	10

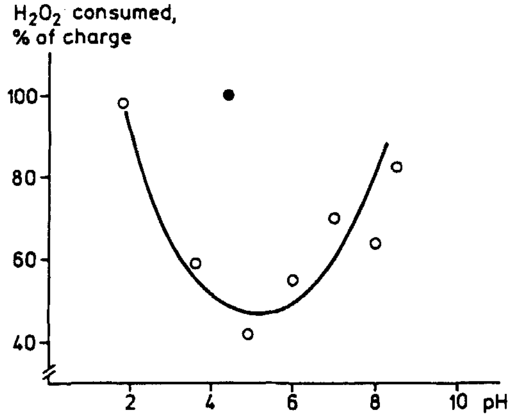

FIGURE 1. Consumption of hydrogen peroxide in the bleaching stage as a function of pH during the pretreatment with sodium bisulfite and DTPA (o). ● = no DTPA present. Pretreatment conditions: 5 % (as SO_2) sodium bisulfite, 0.2 % DTPA, 90°C, 60 min. Bleaching conditions: 4 % H_2O_2, 5.8 % NaOH (pH = 12.5), 90°C, 15 min.

pretreatment liquor had a pronounced effect on the consumption of hydrogen peroxide in a subsequent standardized hydrogen peroxide bleaching stage. A distinct minimum in the consumption was obtained when the pretreatment was carried out at pH $\sim$ 5. As expected, a similar curve with a minimum at about pH = 5 was obtained when the decrease in pulp viscosity after bleaching was plotted against pH of the pretreatment liquor (Fig. 2). From the results presented in Table 1, Fig. 1 and Fig. 2 it is also obvious that a pretreatment involving sodium bisulfite alone does not lead to a complete removal of transition metal ions from the pulp and that this in turn leads to inferior results in the subsequent bleaching stage.

As indicated in Table 1 an increased temperature in the sulfite/DTPA pretreatment stage is also necessary if metal ions are to be efficiently eliminated from the pulp. Fig. 3 shows that the consumption of hydrogen peroxide is markedly reduced when the pretreatment temperature is increased above 80°C. The pretreatment time was found to have only a minor influence on the consumption of hydrogen peroxide if the pretreatment was carried out at 90°C for at least 10 min.

Under constant conditions with respect to pH, time, temperature and charge of DTPA, pretreatment with different amounts of sodium sulfite gave rise to slightly different amounts of consumed hydrogen peroxide in the bleaching stage (Fig. 4). For charges above 1 % (as SO_2 on o.d. pulp) the differences were however negligible.

It can be concluded that transition metal ions present in kraft pulps play a decisive role for the performance of a subsequent hydrogen peroxide bleaching stage. Furthermore these ions are removed from the pulp only with difficulty using a combination of a reducing agent and a strong chelating agent under carefully selected conditions.

In a series of bleaching experiments the influence of the type of pretreatment (i.e. the residual amounts of transition metal ions present in the pulp) on the brightness, kappa number,

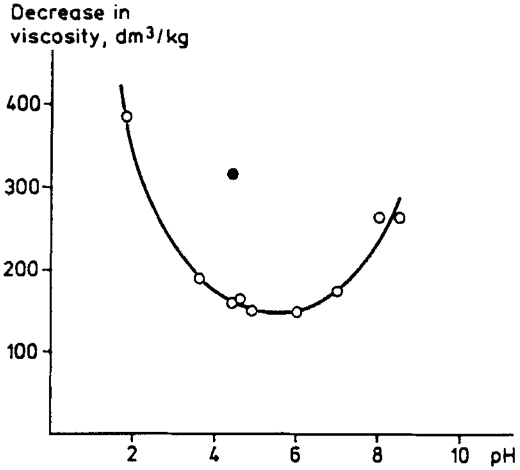

FIGURE 2. Decrease in viscosity after bleaching as a function of pH during the pretreatment with sodium bisulfite and DTPA (o). ● = no DTPA present. Pretreatment and bleaching conditions as in Fig. 1.

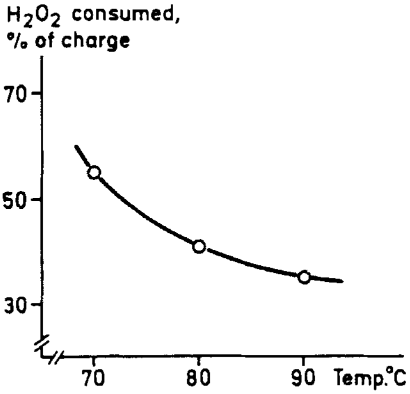

FIGURE 3. Consumption of hydrogen peroxide in the bleaching stage as a function of temperature during the pretreatment with sodium bisulfite and DTPA. Pretreatment conditions: 3 % (as SO_2) sodium bisulfite, 0.2 % DTPA, pH = 4.5, 20 min. Bleaching conditions as in Fig. 1.

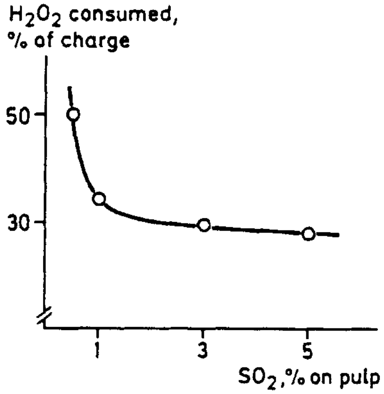

FIGURE 4. Consumption of hydrogen peroxide in the bleaching stage as a function of the charge of sodium bisulfite (as SO_2) in the pretreatment. Pretreatment conditions: 0.2 % DTPA, pH = 4.5, 90°C, 60 min. Bleaching conditions as in Fig. 1.

peroxide consumption and pulp viscosity after hydrogen peroxide bleaching was investigated. Furthermore some experiments were carried out in order to evaluate the importance of bleaching time, bleaching temperature and charge of alkali (expressed as starting pH in the bleaching liquor). Under otherwise identical conditions the charge of alkali had a pronounced effect on the resulting brightness and kappa number after bleaching (Fig. 5). A strong increase in brightness with increasing pH accompanied by a decrease in kappa number was obtained for pH values below ∿ 12. A linear dependency of brightness on temperature was obtained when the other parameters were held constant (Fig. 6). The major part of the bleaching experiments were therefore carried out at pH = 12.5 and 90°C.

An increase in bleaching time resulted as expected in an increase in brightness and a decrease in kappa number after bleaching. However, since the amount of residual transition metal ions in the pulp determines the amount of hydrogen peroxide present during bleaching, long bleaching times could only be applied when the pulp was essentially free of metal ions. This effect is illustrated in Fig. 7 where it can be seen that when

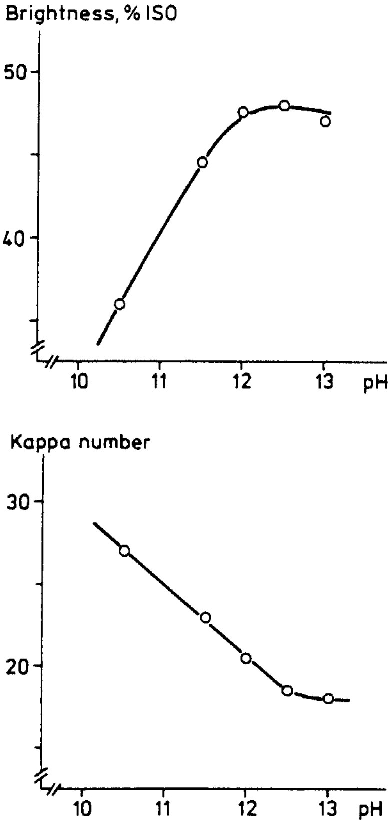

FIGURE 5. Pulp brightness and kappa number after bleaching with hydrogen peroxide in the presence of various amounts of sodium hydroxide. Pretreatment conditions: 3 % (as SO_2) sodium bisulfite, 0.2 % DTPA, pH = 4.5, 25°C, 15 min. Bleaching conditions: 4 % H_2O_2, 90°C, 10 min.

the pulp contains a certain amount of manganese and iron ions (cf. Table 1) the bleaching virtually stops after 15 min or less under the conditions used due to a shortage of hydrogen peroxide in the bleaching liquor. On the other hand, a complete removal of the metal ions prior to bleaching makes it possible to extend the bleaching time considerably and thus to increase the brightness further.

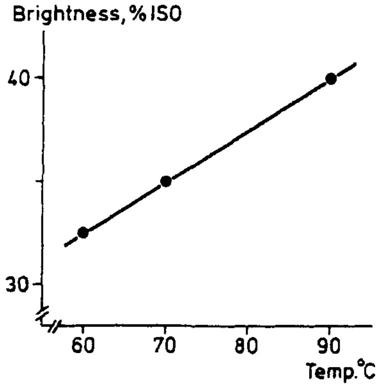

FIGURE 6. Pulp brightness after bleaching with hydrogen peroxide at various temperatures. Pretreatment conditions as in Fig. 5. Bleaching conditions: 4 % H_2O_2, 1.5 % NaOH (pH = 11.0), 10 min.

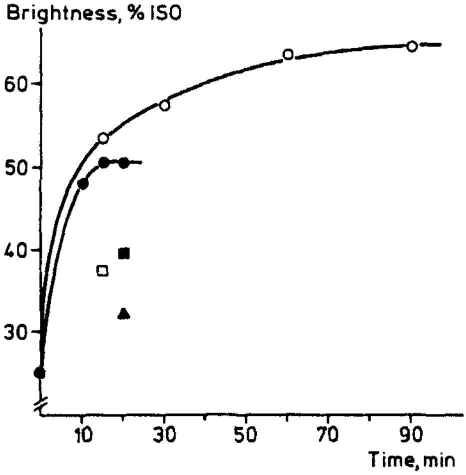

FIGURE 7. Pulp brightness after bleaching with hydrogen peroxide for various times. Pretreatment conditions: ▲ = no pretreatment, □ = 5 % (as SO_2) sodium bisulfite, pH = 4.5, 90°C, 60 min; ■ = 0.2 % DTPA, pH = 8.0, 25°C, 15 min; ● = 3 % (as SO_2) sodium bisulfite, 0.2 % DTPA, pH = 4.5, 25°C, 15 min; o = 3 % (as SO_2) sodium bisulfite, 0.2 % DTPA, pH = 4.5, 90°C, 20 min. Bleaching conditions: 4 % H_2O_2, 5.8 % NaOH (pH = 12.5), 90°C.

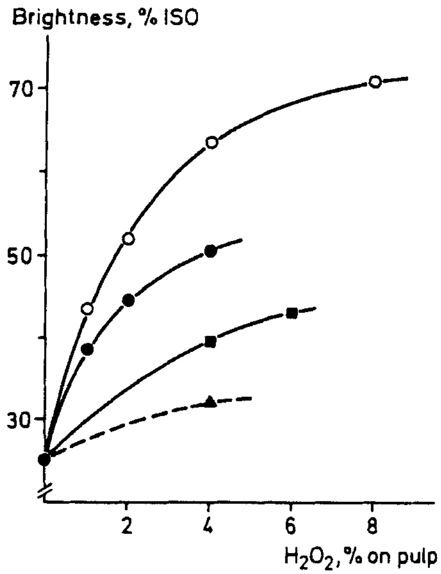

FIGURE 8. Influence of the pretreatment conditions on the pulp brightness after bleaching with various amounts of hydrogen peroxide. Pretreatment conditions and symbols as in Fig. 7. Bleaching conditions: pH = 12.5, 90°C, 60 min (o), 20 min (▲, ■, ●).

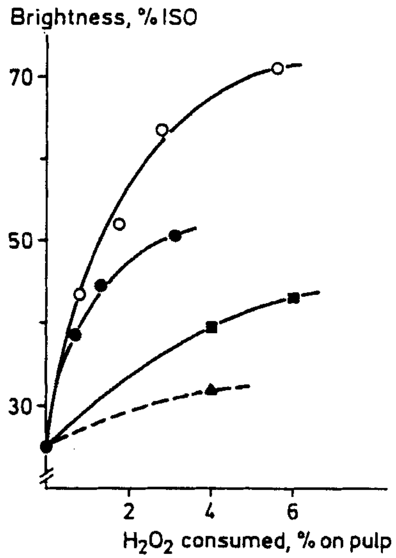

FIGURE 9. Influence of the pretreatment conditions on the consumption of hydrogen peroxide during bleaching. The same bleaching experiments as in Fig. 8.

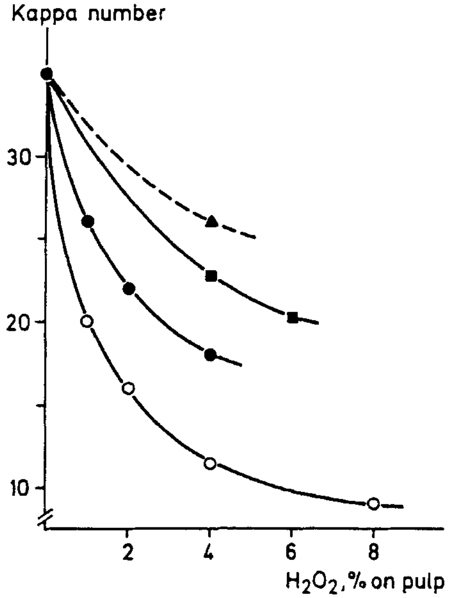

FIGURE 10. Influence of the pretreatment conditions on the kappa number after bleaching with various amounts of hydrogen peroxide. The same bleaching experiments as in Fig. 8.

A corresponding dependence of the brightness gain on the content of transition metal ions could be seen when the pulp was bleached with different amounts of hydrogen peroxide. As can be seen in Fig. 8 and Fig. 9 different pretreatments led to large differences in bleachability and consumption of hydrogen peroxide. In a similar way, the reduction in kappa number was affected (Fig. 10) by the different amounts of hydrogen peroxide present during bleaching. It should be noted that most of the oxygen formed via decomposition of hydrogen peroxide escapes reaction with the pulp components due to the experimental technique used.

The brightness gain and the kappa number reduction obtained when kraft pulps were oxidized with hydrogen peroxide seem to be interrelated as long as a certain amount of residual hydrogen peroxide is available in the bleaching liquor. At any given brightness a corresponding kappa number was reached irrespective of the

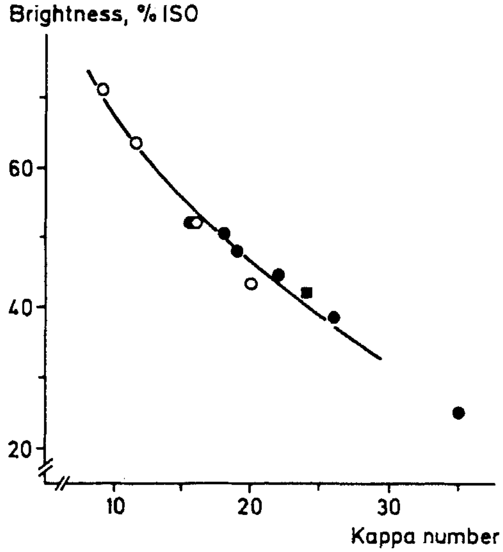

FIGURE 11. Pulp brightness vs kappa number after bleaching with hydrogen peroxide for different pretreatments. Symbols as in Fig. 7.

type of pretreatment and thus of the amount of transition metal ions present in the pulp (Fig. 11). The viscosity - kappa number relationship on the other hand, i.e. the selectivity between polysaccharide and lignin oxidation turned out, as expected, to be largely affected by the pretreatment. At a given kappa number, pulps with large differences in viscosity were obtained (Fig. 12).

From the results described above it is quite obvious that as long as transition metal ions are present in the pulp, hydrogen peroxide can be used only to achieve a fairly limited delignification (and brightness increase). Furthermore such a bleaching stage actually leads to the formation of a considerable amount of oxygen via decomposition of hydrogen peroxide (cf. Refs. 10,11). If, on the other hand, the transition metal ions are removed completely, a substantial increase in brightness accompanied by a similar decrease in lignin content can be achieved. In contrast to the bleaching of mechanical pulps, however, the bleaching conditions

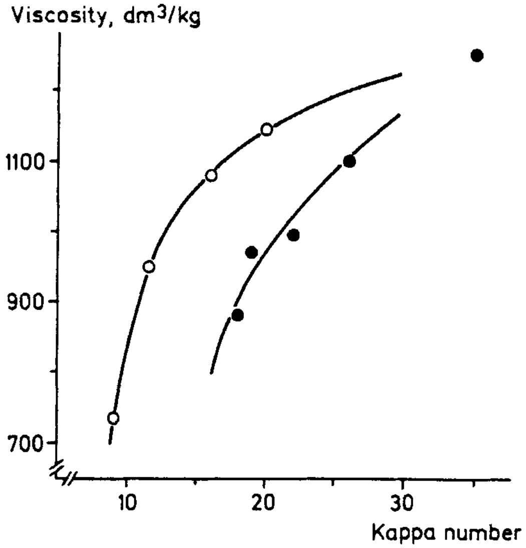

FIGURE 12. Pulp viscosity vs kappa number after bleaching with hydrogen peroxide for different pretreatments. Symbols as in Fig. 7.

must be selected in such a way that the delignification is facilitated. This can be done by increasing the temperature and alkali charge. Under such conditions a decomposition of hydrogen peroxide takes place at a rate suitable to give a comprehensive oxidation of (phenolic) lignin units while leaving the carbohydrates fairly intact. Since, however, the lignin content in the pulp fibres is much lower than the content of carbohydrates, it is obvious that even a slight increase in the rate of decomposition of hydrogen peroxide can lead to an increased attack on the polysaccharides and thus to a drop in pulp viscosity (cf. Fig. 12). Furthermore, the selectivity between lignin and carbohydrate degradation can be expected to be dependent upon the amount of free phenolic structures in the pulp since these are in general more reactive towards hydroxyl radicals compared to other structural units expected to be found in the fibres. In a recent work it has been demonstrated that the amount of free phenolic structures in lignin varies greatly during the course of a kraft cook. For softwood pulps with kappa numbers in the range of ∿ 50-20, however, the amount (for a given amount of pulp) seems to decrease almost linearly with decreasing kappa number.[12] Therefore delignification with hydrogen peroxide (or oxygen) can be expected to be more selective when applied to pulps with a high initial content of lignin (cf. Refs. 11,13) than when applied to low kappa number pulps.

The delignification (and bleaching) of a kraft pulp with hydrogen peroxide involves a decomposition of hydrogen peroxide into hydroxyl radicals and superoxide ions as the initial reaction.[2,14] This reaction is strongly accelerated in the presence of transition metal ions, whether "free" or chelated.[3,15-17] The hydroxyl radicals formed react further either with themselves, with superoxide ions, with hydrogen peroxide or with organic substrates. In these reactions hydrogen peroxide, oxygen, superoxide ions or organic radicals are formed respectively, all with very high rates of reaction.[8] The most important reaction of the superoxide ions seems to be the dismutation into hydrogen peroxide and oxygen.[18] Although it is comparatively slow at high pH-values,[19] this reaction seems to proceed rapidly in the presence of acidic hydrogens (like those from hydrogen peroxide).[20] Moreover, the reaction has been shown to be catalysed by certain metal ions and metal complexes like Fe(III)-EDTA.[21,22] The reaction between a hydroxyl radical (or manganese(III)) and a phenolic lignin structure[23,24] leads to the formation of a phenoxy radical which subsequently adds either oxygen or a superoxide ion.[3] In this reaction a hydroperoxide is formed together with a new radical species or alternatively a hydroxyl ion. (Some important reactions thought to be responsible for the formation of hydroperoxides are outlined in Fig. 13.) In subsequent reaction steps the hydroperoxide intermediates formed react further with the participation of hydrogen peroxide and alkali leading to lignin fragmentation as well as to bleaching.[25-28] A corresponding set of reactions can also be envisaged in the degradation of carbohydrates by alkaline hydrogen peroxide (cf. Ref. 29).

$$\begin{aligned}
2\,H_2O_2 + HO^- &\longrightarrow HO\cdot + O_2\cdot^- + 2\,H_2O \\
HO\cdot + H_2O_2 + HO^- &\longrightarrow O_2\cdot^- + 2\,H_2O \\
HO\cdot + R{-}H &\longrightarrow R\cdot + H_2O \\
2\,O_2\cdot^- + 2\,H_2O &\longrightarrow O_2 + H_2O_2 + 2\,HO^- \\
R\cdot + O_2 + H_2O &\longrightarrow R{-}OOH + HO\cdot \\
R\cdot + O_2\cdot^- + H_2O &\longrightarrow R{-}OOH + HO^-
\end{aligned}$$

FIGURE 13. Decomposition of hydrogen peroxide and further reactions between the decomposition products and organic substrates (R-H) leading to the formation of organic hydroperoxides.

The results obtained in this work further support the earlier hypothesis that hydrogen peroxide bleaching involves two sets of reactions with lignin (see above). In contrast to the bleaching of mechanical pulps, however, the major part of the brightness increase in a kraft pulp requires a simultaneous degradation of the residual lignin. It therefore seems likely that the chromophoric structures in kraft pulps to a large extent involve condensed phenolic units containing methylene quinone and quinone moieties (cf. Refs. 30-32). Such structures should only be degraded with difficulty by nucleophilic agents in alkaline media (e.g. hydroperoxy anions) due to the presence of phenolate anions as part of the conjugated system (cf. Ref. 5).

CONCLUSIONS

Alkaline hydrogen peroxide can be used to increase substantially the brightness of kraft pulps. In order fully to utilize the bleaching power of hydrogen peroxide the content of transition metal ions must, however, be reduced to extremely low levels. Since kraft pulps, unlike mechanical pulps, contain transition metal ions which are strongly retained in the fibres, a pretreatment of the pulp with a chelating agent alone is not sufficient. Treatment with chelating agent in combination with sodium bisulfite is more powerful and under such conditions most of the metal ions can be removed from the pulp.

The bleaching of kraft pulps with hydrogen peroxide requires a simultaneous dissolution of lignin. This dissolution is assumed to be due to an oxidative degradation starting with phenolic lignin units and involving degradation products from hydrogen peroxide. For kraft pulps this type of reaction seems to play a dominant rôle. In the bleaching of mechanical pulps, on the other hand, most of the brightness increase can be attributed to the elimination of various conjugated carbonyl structures by the action of hydroperoxy anions. These reactions proceed with only minor amounts of material being dissolved.

The use of a hydrogen peroxide bleaching stage in the production of various types of bleached kraft pulps could be advantageous from an environmental as well as from a process equipment point of view. The high cost of hydrogen peroxide may, however, be prohibitive. Despite this disadvantage hydrogen peroxide may find expanded use as a bleaching agent for kraft pulps in particular for products with limited brightness requirements.

EXPERIMENTAL

An industrial kraft pulp from pine (Pinus silvestris) with brightness 25 % ISO, kappa number 35.3 and intrinsic viscosity 1265 dm^3/kg was used. The quantities of manganese and iron in the pulp samples were analysed by atom absorption spectrophotometry.

The pulp sample (15 g of o.d. pulp) was disintegrated for 3 min at room temperature in 500 ml of distilled water or in distilled water containing sodium bisulfite and/or DTPA (for amounts, see text). After 15 min the pulp was filtered and washed (until free of sulfite). For samples treated with sodium bisulfite and DTPA at elevated temperatures the pulp was disintegrated in water as above, filtered and placed in a polyethylene bottle. Pulp and water were heated to the desired temperature and mixed with the bleaching chemicals giving a final pulp consistency of 10 %. After the chosen reaction time (see text) the pulp was filtered and washed with distilled water. The consumption of sulfite was checked by iodimetric titration of the filtrate and found to be

TABLE 2

The Amount of Sodium Hydroxide Required to Reach a Certain pH in the Bleaching Liquor in the Presence of Various Amounts of Hydrogen Peroxide.

pH	H_2O_2, %	NaOH, %
11.5	2.0	1.3
11.5	4.0	2.5
12.5	1.0	2.4
12.5	2.0	3.3
12.5	4.0	5.8
12.5	8.0	10.4

10 % of the charge or less (cf. Ref. 33) in all cases except for treatments carried out at pH = 3 or below.

In the bleaching experiments, the pretreated and washed pulp sample was placed in a polyethylene bottle and preheated to the desired temperature together with water and magnesium sulfate (0.05 % on o.d. pulp). Hydrogen peroxide and sodium hydroxide (amounts, see Table 2) dissolved in a little water were added and thoroughly mixed with the pulp giving a final pulp consistency of 10 %. After the chosen bleaching time the pulp was filtered and washed with distilled water, buffer solution (citrate-phosphate buffer, pH = 5) and distilled water. The filtrate was analysed for residual hydrogen peroxide by iodometric titration.

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