Bleaching of thermomechanical pulp with sodium perborate

SUZANNE VARENNES, CLAUDE DANEAULT, AND MARTIN PARENTEAU

ABSTRACT

The possibility of using sodium perborate for bleaching thermomechanical pulp was investigated. The effects of sodium perborate concentration, temperature, bleaching time, and pulp consistency, and the influence of stabilizing and chelating agents on the final paper brightness were examined. A comparative study was made on the pulp-bleaching efficiencies of sodium perborate and hydrogen peroxide. The experimental data indicated that the use of sodium perborate resulted in pulp brightness, tensile, tear, and burst strengths almost similar to those of the pulps bleached with hydrogen peroxide.

IN RECENT YEARS, THE PULP AND paper industry has been faced with a series of challenges presented by environmental considerations and product economy. High-yield pulps have become increasingly popular since the past decade. The major motivation to use these pulps in the pulp and paper industry is the increasing pulp demand. Another objective is to conserve wood resources. For these reasons, the interest for bleaching thermomechanical pulp (TMP) has increased considerably. Unfortunately, the level of brightness and the brightness stability of these pulps are blocking the possibility for new markets, particularly in the printed paper applications. Presently, the most effective and most widely used bleaching agents are hydrosulfite and hydrogen peroxide. These agents, applied in one stage, are limited in their ability to bleach mechanical pulp from softwood to no more than 70–80 ISO brightness *(1, 2)*. Therefore, technical development on bleaching could improve the situation. The development of alternative bleaching methods is needed to obtain a pulp with higher brightness and brightness stability.

Besides hydrogen peroxide and hydrosulfite, another oxidizing agent, sodium perborate, can be used. Sodium perborate is manufactured by chemical means, and it is used extensively as a component in detergents and in the preparation of washing and disinfecting agents. Chupka *et al. (3)* have conducted laboratory studies on the use of sodium and potassium perborates for bleaching softwood kraft pulp. They compared the physico-chemical and mechanical properties of the bleached pulp with those bleached with hydrogen peroxide, and concluded that it is more advantageous to bleach kraft pulp with potassium perborate than hydrogen peroxide. In the present study, the possibility of bleaching softwood TMP with sodium perborate is investigated.

More specifically, this work deals with the investigation of sodium perborate as a bleaching agent for TMP. Effects of sodium perborate concentration, temperature, retention time, and pulp consistency, and the influence of stabilizing and chelating agents on the final brightness of bleached pulp are reported. The cost estimation of the perborate bleaching process is presented.

EXPERIMENTAL

For this study, we used unbleached thermomechanical softwood pulp from the Kruger mill in Trois-Rivières; the initial pulp brightness was 60% ISO.

Sodium perborate tetrahydrate (99.6%), magnesium sulfate (99%), sodium hydroxide (97%), and diethylenetriamine pentaacetate (DTPA) (40%) were obtained from Omega Chemicals. Sodium silicate (41°Be solution) and hydrogen peroxide (35%) were supplied by Anachemia Chemicals.

Before the bleaching process, the pulp is pretreated with 0.4% DTPA for 15 min at 60°C to eliminate undesirable heavy-metal ions. The pulp consistency was 3% in this stage. Then, the pretreated pulps were dewatered to 20% consistency and stored in closed polyethylene bags at 4°C until further use.

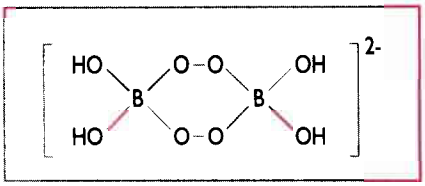
The general procedure for sodium perborate bleaching used in this investigation is as follows. The bleach liquor of perborate, consisting of 3% sodium silicate, 0.05% magnesium sulfate, 0.4% DTPA, and a desired amount of sodium perborate, was mixed in a sufficient amount of demineralized water to dissolve the perborate. The bleach liquor was transferred to a plastic bag containing 10 g of oven-dried (o.d.) pulp, sealed, and placed in a water bath. The bag remained in the constant-temperature water bath for 15–120 min. Once the bleaching was completed, the mixture was filtered, and a filtrate sample was obtained; this sample was used for residual peroxide determination. Peroxide residuals were measured by iodometric titration. The pulp was neutralized to pH 5.5, and handsheets were made for brightness testing according to TAPPI Test Method T 452 om-92.

For a hydrogen peroxide–bleached pulp, we proceeded as follows. We used 0.05% magnesium sulfate and 3% of sodium silicate (41°

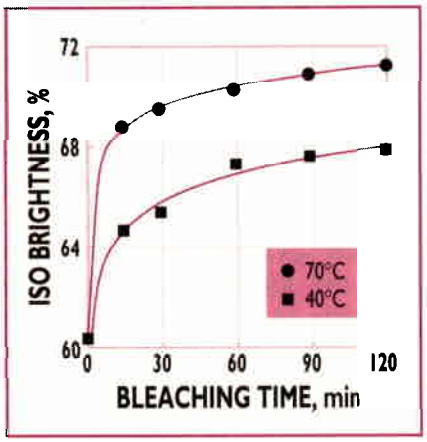
Perborate, %	Silicate, %	$MgSO_4$, %	DTPA, %	Final brightness, %	Final pH	H_2O_2 consumed, %
6.5*	0	0	0	66.9	8.5	1.9
6.5	3	0.05	0.4	70.3	8.5	1.1

*The equivalence is 2.2% in hydrogen peroxide. Bleaching conditions: pulp consistency 10%, temperature 70°C, time 1 hour. Unbleached TMP brightness: 60% ISO.

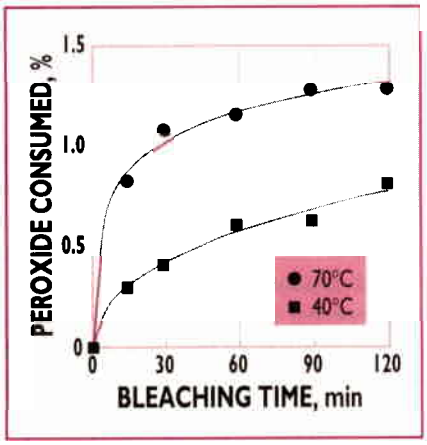
I. Effects of stabilizing and chelating agents on perborate bleaching response



1. Formula of sodium perborate



2. ISO brightness as a function of bleaching time at two different temperatures. Bleaching conditions: pulp consistency 10%, sodium perborate 6.5%.



3. Effect of temperature on peroxide consumption at various bleaching times for the TMP bleaching with sodium perborate. Bleaching conditions: pulp consistency 10%, sodium perborate 6.5%.

Be) to help stabilize the hydrogen peroxide through the formation for peroxysilicates. Then, a 2% hydrogen peroxide solution was added. The pH was set at 11.0 with NaOH, and the consistency was adjusted to 10% with deionized water. The temperature was raised to 70°C and held for 60–120 min. The residual of peroxide was determined by iodometric titration. After bleaching, the mixture was neutralized with sodium metabisulfite at 1% consistency to attain a pH of 5.5. The pulp was washed with deionized water and filtered, and finally handsheets were made for brightness testing.

The chemical formula of sodium perborate is $NaBO_3 \cdot 4H_20$. The crystal structure that is schematically shown in **Fig. 1** has been found to contain $[B_2(O_2)_2(OH)_4]^{2-}$ units with two peroxo groups bridging the tetrahedral boron atoms *(4)*. Sodium perborate decomposes rapidly in an aqueous solution to yield hydrogen peroxide according to Eq. 1 *(5)*:

$$Na_2(H_4B_2O_8) + 4H_20 \rightarrow 2Na[B(OH)_4] + 2H_2O_2 \quad (1)$$

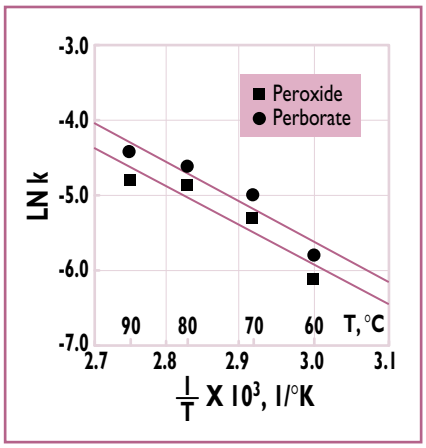
Thus, one mole of sodium perborate liberates two moles of hydrogen peroxide.

From Eq. 1, it was possible to determine the amount of hydrogen peroxide generated in wt. % from a given quantity of sodium perborate. The concentrations of hydrogen peroxide and sodium perborate were determined by iodometric and permanganatometric titrations, respectively. Therefore, to obtain the initial concentration of sodium perborate ($NaBO_3 \cdot 4H_2O$), a sample of the bleach liquor was acidified with H_2SO_4 and titrated with 0.1 *N* $KMnO_4$ *(6)*. The initial sodium perborate content was also measured by iodometric titration *(7)* and reported as concentration of hydrogen peroxide (% o.d. pulp) released in bleached solution and expressed in units of HOOH.

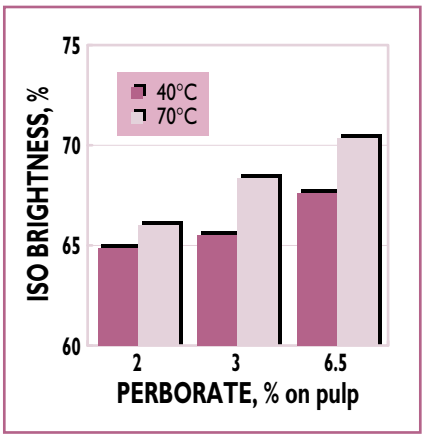
RESULTS AND DISCUSSION

Effects of additives

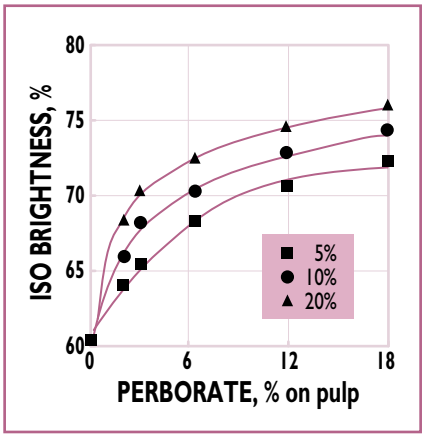
A number of additives, e.g., sodium silicate, magnesium sulfate, and DTPA, have been reported to improve the peroxide bleaching efficiency *(8)*. DTPA formed complexes with the heavy-metal ions and prevented the formation of colored structures. The heavy-metal ions also catalyzed the peroxide decomposition. The reaction of magnesium sulfate ($MgSO_4$) with sodium silicate (Na_2SiO_3) formed a magnesium silicate complex, which could be able to stabilize the peroxide and thus reduce its rate of decomposition. Preliminary experiments were carried out to determine whether Na_2SiO_3, $MgSO_4$, and DTPA had an influence on the final paper bright-



4. Dependence of reaction rate on reaction temperature for sodium perborate and hydrogen peroxide bleaching of TMP. Bleaching conditions: pulp consistency 20%, sodium perborate 6.5%, and hydrogen peroxide 2.2%. Bleaching time: 120 min.



5. Effects of temperature and sodium perborate concentration on final pulp brightness. Bleaching conditions: pulp consistency 10%. Bleaching time: 60 min.



6. Effect of pulp consistency and sodium perborate concentration on final pulp brightness. Bleaching conditions: 70°C. Bleaching time: 60 min.

ness. The concentrations of solutions (Na_2SiO_3, $MgSO_4$, and DTPA) were the same as those in the conventional peroxide bleaching. Results in **Table I** show that the brightness increased from 66.9 to 70.3 when the previously mentioned additives were included. The bleaching trials without stabilizing and chelating agents resulted in a higher consumption of peroxide. Therefore, the formation of a magnesium silicate complex reduced the decomposition of perborate. Hence, in all subsequent experiments, sodium silicate 3%, magnesium sulfate 0.05%, and DTPA 0.4% were added to the bleaching liquor.

Effects of retention time and temperature

Retention time and temperature are interrelated variables. Within the experimental limits, increasing one or both of these parameters can cause improvements in final brightness. Temperature has marked effects on the final brightness **(Fig. 2)** and on the rate of sodium perborate consumption **(Fig. 3)**.

Figure 2 indicates the effect of bleaching time on the final brightness at 40 and 70°C, respectively. Bleaching conditions were 10% pulp consistency, and the sodium perborate concentration was 6.5%. The initial concentration of sodium perborate was calculated in units of HOOH and represents 2.2% solutions of hydrogen peroxide. Over a period of 2 hours, a nonlinear dependence of ISO brightness on bleaching time was observed. After 2 hours of bleaching time, brightness levels of 67 and 71% ISO are obtained at 40 and 70°C, respectively. The bleaching effect observed with sodium perborate essentially results from the oxidation of the residual lignin. The later observation is in agreement with the oxidation caused by the hydroperoxide anion HOO^-, which is formed as a result of peroxide decomposition *(2)*.

In Fig. 3, sodium perborate consumption is expressed in units of HOOH. Figure 3 shows that the peroxide consumptions at 40 and 70°C were 25 and 50%, respectively, for a total bleaching time of 60 min.

A temperature increase allows reducing the bleaching time to obtain a predetermined pulp brightness. A bleaching temperature increase not only enhances the degree of brightening but also increases the amount of peroxide decomposition. To verify the dependence between the rate of decomposition peroxide and the pulp brightness, we determined the decomposition rates of a 2% solution of hydrogen peroxide and a 6.5% solution of sodium perborate, which correspond to 2% in units of HOOH at four different temperatures. The total decomposition time was 120 min, and pulp consistency was 20% for all of these experiments.

Considering a first-order reaction rate for the perborate decomposition, the rate constant can be expressed according to the following equation *(8)*:

$$k = 2.303/t \cdot \log (c_0/c) \qquad (2)$$

where k represents the rate constant and has units of the reciprocal of time, t is the reaction time (min), and c_0 and c are the initial concentration and the concentration at time t, respectively, in g/L.

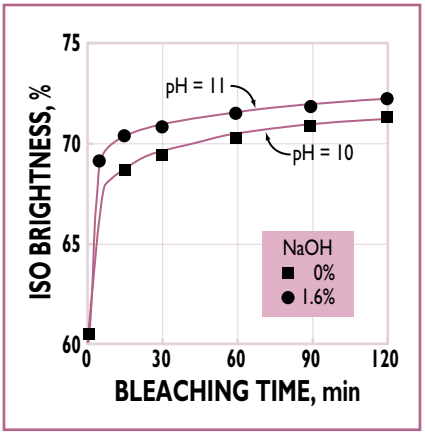
The rate constant depends strongly on temperature and, in most cases, the rate of decomposi-

Bleaching agent	Sodium perborate	Hydrogen peroxide
Concentration, %	6.5	2.2
Pulp consistency, %	10-12	10-12
NaOH concentration, %	0	2.2
Initial pH	10	11
Bleaching time, min	60-90	60-90
Temperature, °C	70	70

II. Bleaching conditions for sodium perborate and hydrogen peroxide bleaching

Property	Unbleached pulp	Sodium perborate	Hydrogen peroxide
NaOH, %	-	-	2.2
Brightness, %	60.4	72.0	72.3
H_2O_2 consumed, %	-	1.1	1.3
Final pH	-	8.6	8.3
Breaking length, km	5.1	5.0	5.0
Burst strength, kPa·m²/g	2.7	2.6	2.7
Tear strength, mN·m²/g	8.3	8.2	8.4
Opacity, %	95.9	90.7	90.4

III. Physical properties of TMP after bleaching with sodium perborate and hydrogen peroxide. Perborate 6.5%, peroxide 2.2%, temperature 70°C,



7. Effect of bleaching solution pH on final pulp brightness. Bleaching conditions: 70°C, pulp consistency 10%. Bleaching time: 60 min.

tion increases with temperature *(9)*. Arrhenius points out that the *k(T)* data for many reactions fit the expression:

$$k = A\, e^{-E_a/RT} \qquad (3)$$

where A is the pre-exponential factor and E_a is the Arrhenius activation energy. Taking logs of Eq. 3, we get:

$$\ln k = \ln A - (E_a/RT) \qquad (4)$$

By plotting the logarithm of the reaction rate against the inverse of the absolute temperature, as shown in **Fig. 4**, the activation energies E_a for decomposition of sodium perborate and hydrogen peroxide were determined. For sodium perborate, the activation energy was calculated to be 44.4 kJ/mol. The activation energy of hydrogen peroxide bleaching was determined to be 44.2 kJ/mol. We found similar values for the activation energy, which is in agreement with the brightness values obtained by bleaching the pulp separately with these two components.

Effect of perborate concentration

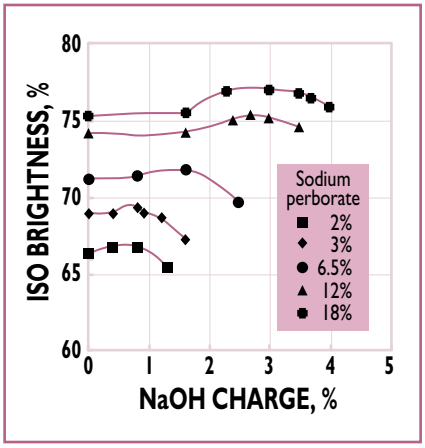
The brightness increase was proportional to the amount of perborate used. **Figure 5** shows the effect of temperature and perborate concentration on final brightness. The pulp consistency was 10%, and the bleaching time was 60 min. The bleaching at high temperature can achieve similar brightness using less chemicals, as shown in Fig. 5. To obtain similar brightness values, we need higher concentrations at low temperature.

Effect of consistency

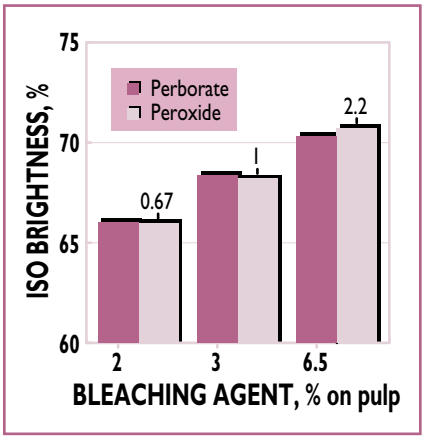
Bleaching experiments on TMP were conducted at different pulp consistencies. In fact, pulp brightness is progressively increased with increased pulp consistency. As indicated in **Fig. 6**, the brightness response of TMP to 6.5% sodium perborate is enhanced by increasing the consistency. The increased perborate consumption that accompanies higher-consistency bleaching enhanced the degree of brightening. The plots in Fig. 6 also show the effect of perborate concentration on final pulp brightness. By increasing the pulp consistency, we need less perborate charge to obtain equivalent brightness. For example, a 20% consistent pulp slurry containing 3% perborate attained the same brightness of about 70% ISO as that obtained by bleaching a 10% consistent pulp with 6% perborate.

Effect of alkalinity

In general, the hydrogen peroxide bleaching is effected at about pH 11 *(10)*. However, in the present investigation, the perborate bleaching could be performed only at a pH of about 10 without alkali addition. Thus, attempts have been made to note the effect of alkali addition on the pulp-bleaching efficiency of perborate. **Figure 7** shows that the



8. Effect of NaOH addition in the bleach liquor on final pulp brightness for different concentrations of sodium perborate. Bleaching conditions: 70°C, pulp consistency 10%. Bleaching time: 90 min.



9. Comparison between sodium perborate and hydrogen peroxide bleached pulp brightness at different bleaching agent concentrations. Bleaching conditions: 70°C, pulp consistency 10%. Bleaching time: 60 min.

Chemical agent	Cost, US$/kg
Sodium silicate (41° Be)	0.1819
Magnesium sulfate	0.3527
Sodium hydroxide to 50%	0.3478
DTPA	1.1243
Hydrogen peroxide to 50%	0.7551
Sodium perborate	0.8047

IV. Cost of the chemical agents *(11)*

addition of 1.6% NaOH in perborate solution increased the pH of this solution to about 11, and the final pulp brightness in the latter case is increased by about 2% ISO. The effect of pH increase on the coordinate b^* was examined. Coordinate b^* is a coefficient that measures the yellow color of the pulp. We found that the value of coordinate b^* in brightness scale remained unchanged with a pH increase from about 10 to 11.

The effect of NaOH concentration on the brightness of TMP for different concentrations of perborate is reported in **Fig. 8.** For very low perborate concentrations, e.g., ≤3%, no positive effect of NaOH concentration on pulp brightness is observed. On the other hand, an increase in the perborate charge to above 3% shows a minor increase in pulp brightness, depending on the concentration of NaOH. Thus, an increase in initial pH from 10 to 11 has a beneficial effect on the pulp brightness. However, continued addition of NaOH in the bleaching solution shows a reversion in the increase of pulp brightness beyond an optimum concentration of NaOH, as illustrated in Fig. 8. The maximum brightness obtained with perborate charge above 3% occurs at pH 11, and the coordinate b^* stays constant.

For a comparative study, we bleached the TMP with hydrogen peroxide. The operating conditions are detailed in **Table II**. The bleaching efficiency and the physical properties (breaking length, burst strength, tear strength, and opacity) of the perborate-bleached pulps were identical to those of the pulps bleached by the conventional hydrogen peroxide process, as reported in **Table III**. The pulp-brightening and bleaching action of the sodium perborate solution is similar to that of the alkaline hydrogen peroxide liquor, which is shown in **Fig. 9**. Thus, sodium perborate can be considered as a nonchlorinated bleaching agent and is useful for the TMP bleaching.

The cost factor of the bleaching process is summarized in **Tables IV and V**. The total cost of the products for the peroxide bleaching is about US$ 59 per metric ton of bleached pulp. In the case of perborate bleaching, the stabilizing and chelating agents and sodium perborate are the only raw materials required. No alkali was needed. Thus, the cost of additives would be about US$ 17.59 per ton of pulp. Including the cost of perborate would bring the total to US$ 62. Although within the scope of the results presented in this paper it is estimated that the cost of perborate bleaching is marginally higher than that of the peroxide bleaching, our future research is oriented toward reducing the cost of perborate bleaching by increasing the perborate bleaching efficiency with bleach activators.

CONCLUSIONS

The results demonstrate that it is possible to bleach TMP with sodium perborate. A sizable gain in brightness and quality of bleached pulp that is comparable to conventional hydrogen peroxide–bleached pulp was obtained. The sodium perborate process allowed us to reach a brightness as high as 75% ISO with the bleaching conditions of pulp consistency 20%, sodium perborate 6.5%, temperature 70°C, and a bleaching time of 120 min.

The pulp brightness is favored by increasing the temperature and/or by increased perborate concentration and pulp consistency. The pH increase from 10 to 11 has a positive

KEYWORDS
Bleaching, borates, boron compounds, brightness, hydrogen peroxide, mechanical pulps, optical properties, physical properties, thermomechanical pulps.

influence on the brightness. The presence of stabilizing and chelating agents in bleach liquor improves the pulp brightness. The action mechanism of perborate indicated that each mole of sodium perborate liberates two moles of hydrogen when dissolved in water. **TJ**

Varennes is a research associate, Daneault is a professor, and Parenteau is a graduate student at Université du Québec à Trois-Rivières, Centre de recherche en pâtes et papiers, C.P. 500, Trois-Rivières, PQ G9A 5H7, Canada.

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Product	CHARGE, %	
	Peroxide	Perborate
Sodium silicate (41°Be)	3	3
Magnesium sulfate	0.05	0.05
Sodium hydroxide	2.2	-
DTPA	0.4	0.4
Hydrogen peroxide	2.2	-
Sodium perborate	-	6.5
Cost, US$/ODMT[b]	58.63	62.43

[a]Brightness = 70% ISO
[b]ODMT = Ovendry metric ton

V. Cost for peroxide and perborate bleaching[a]

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