HIGH-CONSISTENCY PEROXIDE BLEACHING FOR CHEMICAL PULPS

One step towards chlorine-free bleaching

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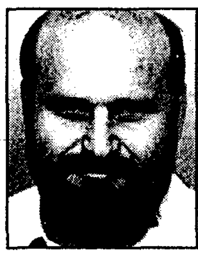

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INCREASING ENVIRONMENTAL restrictions are requiring a reduction in the use of chlorine-containing bleaching agents, mainly of chlorine gas. There are several approaches to this goal, including changes in the cooking process and the effluent treatment.

The majority of publications available at that time dealt with sulphite pulps [1, 2, 3, and 4], or the reinforcement of the oxygen stage with peroxide, e.g. [5] and [6], to name but two. Limited data were available dealing with a separate peroxide stage in kraft pulp bleaching [7, 8, 9 and 10].

The aim of the present study is to optimize the peroxide bleaching stage, which will probably be an important stage in reaching the final brightness in a chlorine-free bleaching sequence. The influence of bleaching consistency, temperature, retention time, caustic soda, silicate and diethylene triamine penta acetate (DTPA) on the final brightness, kappa number and strength properties was investigated using O_2-delignified softwood kraft pulp.

EXPERIMENTAL

A softwood pulp sample was taken from a kraft mill after the washer in the first O_2-delignification stage. The sample was split into small quantities and frozen. Samples had been taken out of the freezer one to four days prior to running the actual bleaching experiments. This procedure slightly reduces the bleachability (usually less than 1% ISO) and has some small effect on strength properties. It ensures the availability of fairly uniform pulp samples over the whole testing period, lasting several weeks.

Since the samples had been taken after a wash press, at a consistency of approximately 35%, no further dewatering was necessary in the laboratory. The pulp was divided into portions of 50 and 100 g bone-dry (bd), fluffed and mixed with the bleaching liquor for 10 minutes in a laboratory-scale kneader-type mixer. Mixing of kraft pulp in the laboratory appeared to be more difficult than mixing mechanical pulps.

The samples were then sealed in plastic bags and bleached under isothermic conditions in a water bath. Small quantities of the pulp were removed hourly to analyze the pH, brightness and residual peroxide. At the end of the bleaching time, residual peroxide was destroyed using sodium bisulphite, and kappa number and strength properties were measured according to the following European standards:

- Freeness: Zellcheming v/7/61
- Burst: DIN 53 141
- Tensile: DIN 53 112
- Tear: DIN 53 128
- Kappa number: DIN 54 357

Samples were beaten for 10 and 38 minutes in a Jokro beater to determine the strength properties.

All data for chemical charges and consistencies given in this paper refer to bone-dry pulp. Figures on hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH) are based on pure chemi-

TABLE I. PULP CHARACTERISTICS OF THE SAMPLE USED FOR PEROXIDE BLEACHING.

Wood species:	spruce, pine
Addition of O_2:	20 kg/t
Brightness:	34.5% ISO
Kappa number after digester:	32 ±2
Kappa number after O_2 stage:	17.8
Viscosity:	1280 dm²/kg
Freeness:	750 mL CSF
Breaking length:	2.6 km
Tear index:	11.5 mN m²/g
Burst index:	1.6 kPa m²/g

TABLE II. PARAMETERS OF THE D-STAGE.

ClO_2 addition (available chlorine):	4.5%
Consistency:	10%
Time:	2 hours
Temperature:	70°C
Initial brightness:	34.5% ISO
Final brightness:	45.5% ISO
Initial kappa number:	17.8
Final kappa number:	9.5

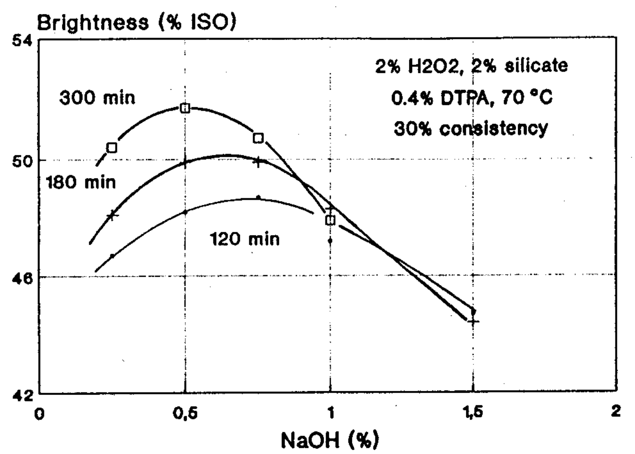

FIG. 1. OPTIMIZATION OF CAUSTIC SODA AT 70°C AND 30% BLEACHING CONSISTENCY.

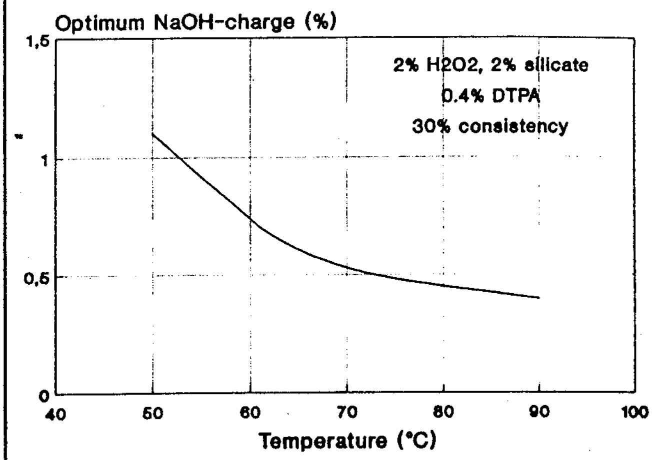

FIG. 2. OPTIMUM CAUSTIC CHARGE AS A FUNCTION OF THE TEMPERATURE.

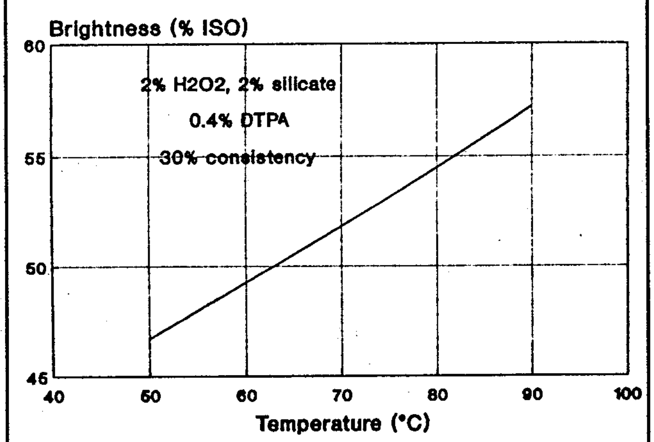

FIG. 3. INFLUENCE OF TEMPERATURE ON FINAL BRIGHTNESS.

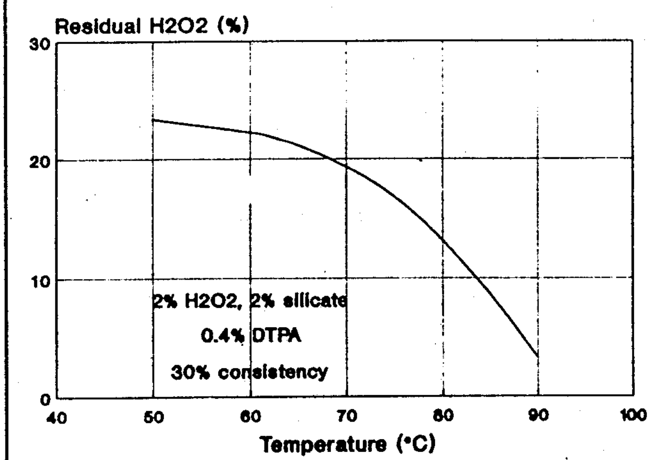

FIG. 4. INFLUENCE OF TEMPERATURE ON RESIDUAL PEROXIDE.

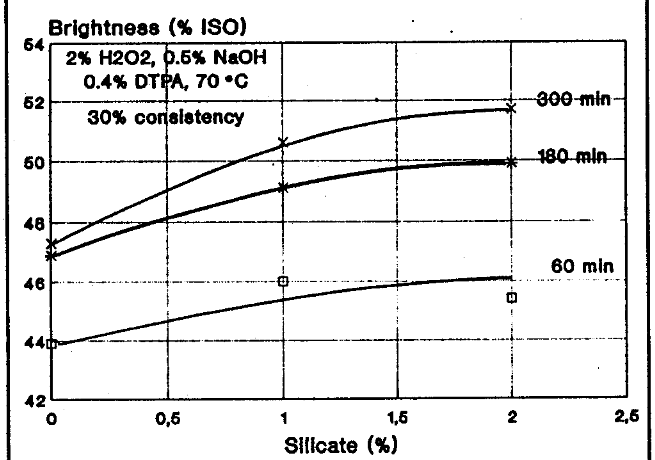

FIG. 5. INFLUENCE OF SILICATE DOSAGE.

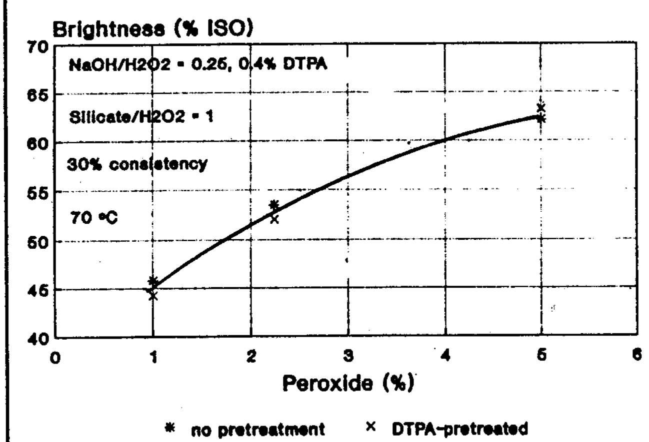

FIG. 6. PRE-TREATMENT WITH DTPA PRIOR TO BLEACHING.

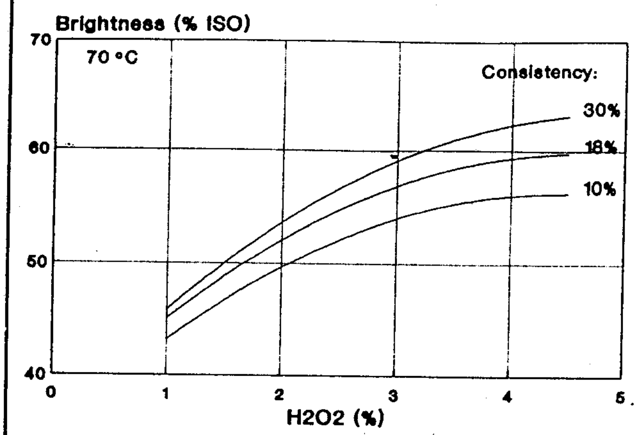

FIG. 7. INFLUENCE OF PEROXIDE CHARGE AND BLEACHING CONSISTENCY. CURVES WERE CALCULATED WITH A SECOND-ORDER MATHEMATICAL MODEL.

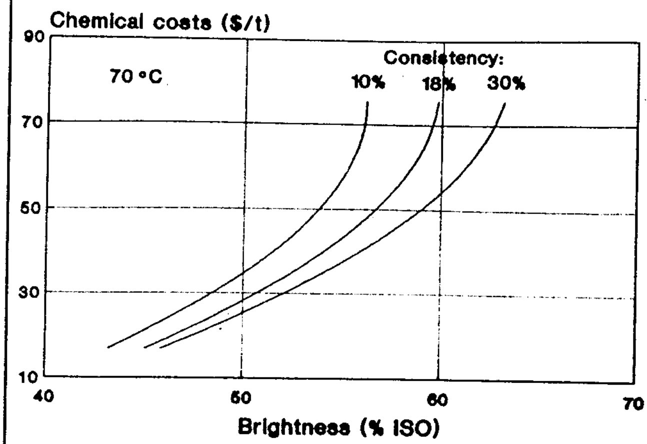

FIG. 8. CHEMICAL COSTS FOR A PEROXIDE BLEACHING STAGE.

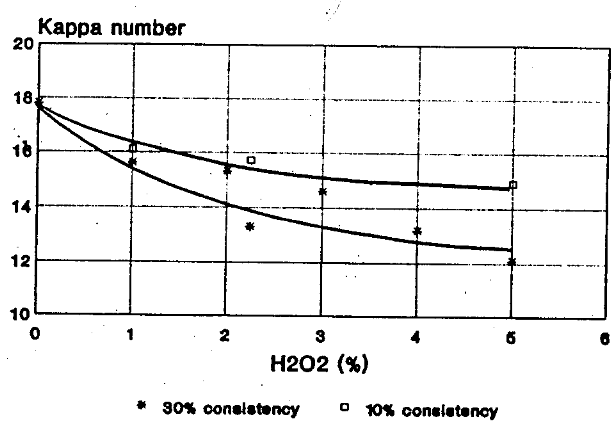

FIG. 9. REDUCTION OF KAPPA NUMBER DURING PEROXIDE BLEACHING.

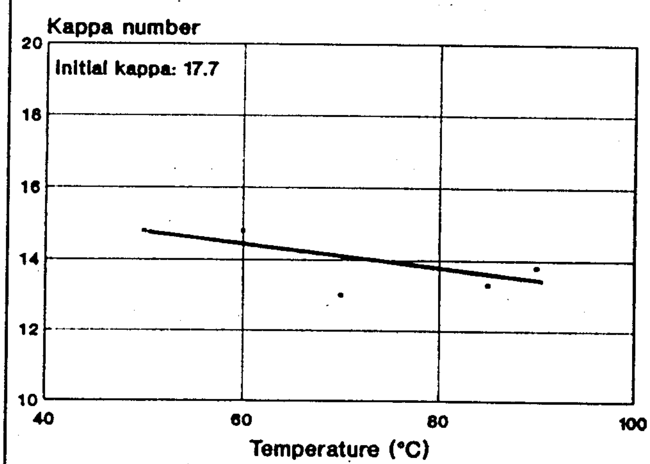

FIG. 10. KAPPA NUMBER VERSUS BLEACHING TEMPERATURE.

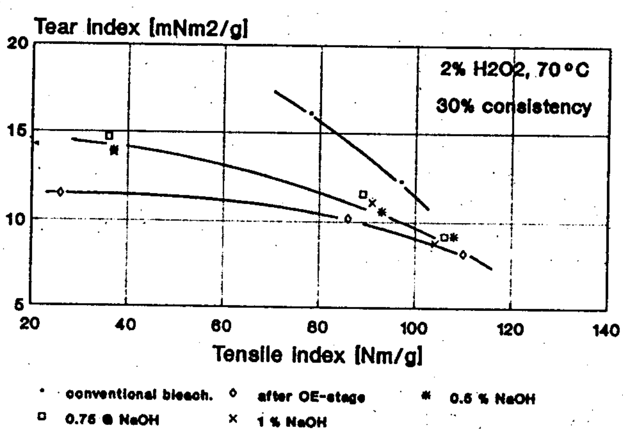

FIG. 11. TEAR/TENSILE AS A FUNCTION OF CAUSTIC CHARGE.

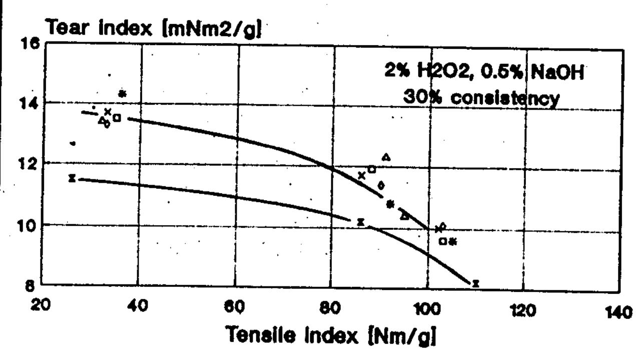

FIG. 12. TEAR/TENSILE AS A FUNCTION OF BLEACHING TEMPERATURE.

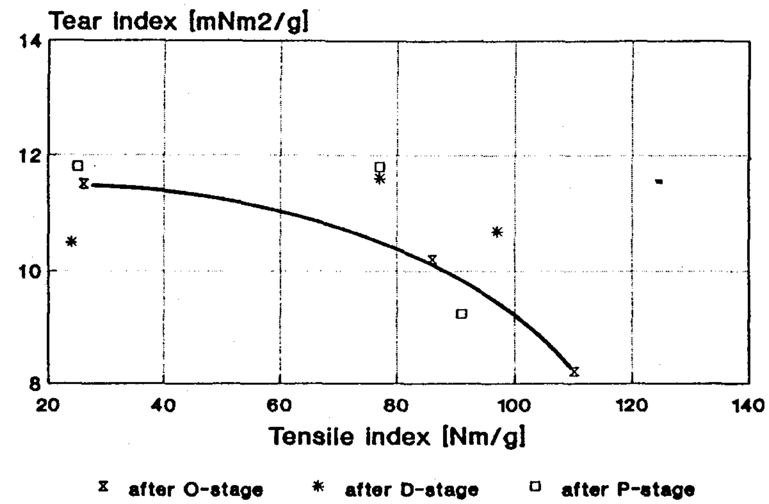

FIG. 13. STRENGTH PROPERTIES OF MULTI-STAGE BLEACHED PULP.

cals (100%), for silicate on the commercially available product with 38° Bé and for DTPA, on usual commercial grades.

TEST RESULTS

Table I shows some characteristic data on the pulp sample after the O_2-delignification stage.

The optimum caustic dosage was determined in a first series of tests using a constant H_2O_2 charge of 2%, Fig. 1. The best bleaching results were obtained at a ratio of $NaOH:H_2O_2$ of only 0.25. This is considerably lower than found in the literature for sulphite pulp [1].

The bleaching reaction lasted five hours until no further significant brightness increases were achieved. With shorter retention times, the level of optimum caustic dosage increased, however the final brightnesses obtained were 2 to 4% lower. At optimum conditions, some 20 to 25% of the peroxide applied was left.

Similar optimization work was done at other temperatures. Figure 2 shows the optimum caustic charges in the temperature range of 50 to 90°C. At 90°C, the optimum bleaching time dropped from five to four hours.

High temperatures significantly increased the final brightness obtainable, Fig. 3. The bleaching temperature of 90°C boosted the final brightness to 57% ISO with a peroxide charge of only 2%. This is a brightness increase of close to 23% ISO.

At the same time, the amount of residual peroxide dropped to less than 5%, Fig. 4.

If, in the future, it is possible to bleach kraft pulps without any chlorine, most of the washing liquor in the bleach plant can be recirculated to the brown stock washer and the evaporation plant, counter-current to the pulp. In this case, silicate-free bleaching is not an option, as it is with mechanical pulps. It becomes essential with chlorine-free chemical pulp bleaching sequences.

The final brightness dropped by more than 4% ISO when no silicate was added to the bleaching liquor, Fig. 5. At the same time, the amount of residual peroxide was reduced close to the limit of detectability.

Pre-treatment of the pulp with a chelating agent (DTPA) at a pH of 7 showed no effect on the final brightness, Fig. 6., not even on the residual peroxide. This is an indication of adequate washing in the mill. DTPA was added to the bleaching liquor in all tests.

When investigating the influence of peroxide and bleaching consistency, statistical design of tests was done and the results were incorporated into a second-order mathematical model, Fig. 7. The caustic soda and silicate were kept at a constant ratio to H_2O_2. All tests were carried out at 70°C.

Similar to mechanical pulp bleaching, significant influence of consistency was measured. At a given final brightness, 25 to 35% chemicals can be saved when comparing 10 and 30% bleaching consistency. The maximum brightness increase was 30% ISO.

Figure 8 shows the cost of bleaching chemicals, calculating $1400/t of peroxide and 20% additional costs for auxiliary chemicals. The cost is higher than when using conventional bleaching agents, but up to a brightness of 55 to 60% ISO high-consistency bleaching has acceptable chemical costs.

Fibre properties: The kappa number was reduced by up to 30% in the peroxide stage, Fig. 9. Higher consistencies yielded slightly better delignification as did higher bleaching temperatures, Fig. 10.

The strength properties could be improved compared to those of the O_2-delignified pulp, but were lower than in a conventional bleaching process. No significant influence of caustic soda, peroxide, consistency and temperature could be measured. Of the numerous test data, the tear/tensile diagrams for various NaOH charges and bleaching temperatures are shown in Fig. 11 and 12.

TABLE III. BLEACHING CONDITIONS OF P-STAGE, AFTER O-D.

H_2O_2 addition:	2%
No silicate added	
pH:	11.2
Time:	2 hours
Temperature:	70°C
Consistency:	30%
Initial brightness:	45.5% ISO
Final brightness:	78.7% ISO

Multi-stage bleaching: Although the main objective of the tests was to optimize the H_2O_2 bleaching stage, some tests were run to check the chemicals required for bleaching pulp to higher brightnesses. The pulp was pre-bleached in the laboratory using chlorine dioxide (ClO_2). The main characteristics are shown in Table II.

The bleachability in the peroxide stage using the O-D pre-bleached pulp was better than in the O-P sequence. Table III summarizes the bleaching conditions of the P-stage. A final brightness of 79% ISO could be obtained with a peroxide charge of only 2%.

The strength properties were hardly changed compared to those after the O-D-stage, however they were significantly poorer than those of pulp bleached in a conventional sequence (Fig. 13, Fig. 11).

CONCLUSION

The following results were obtained in laboratory-scale peroxide bleach tests using O_2-delignified softwood kraft pulp:

- Brightness increases up to 30% ISO were possible in one P-stage;
- High-consistency bleaching saved up to 35% chemicals when comparing with 10% bleaching consistency;
- The best bleaching results were obtained with high temperature, low caustic charge and addition of silicate.
- The kappa number could be reduced by 30%. High consistency and high temperatures resulted in slightly better delignification;
- Strength properties were improved during H_2O_2 bleaching;
- A three-stage bleaching sequence, O-D-P, achieved 79% final brightness.

A great deal of test work has yet to be done to optimize complete bleaching sequences, including the high-consistency peroxide stage.

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Résumé: Des essais de blanchiment ont été effectués en laboratoire avec de la pâte kraft de bois résineux délignifiée au O_2 afin d'établir les conditions optimales de consistance, de température, de durée de retention, ainsi que d'addition de soude caustique et de silicate. L'influence sur la blancheur, l'indice Kappa et les caractéristiques de resistance a été mesurée. De plus, une séquence de blanchiment O-D-P a été mise à l'essai.

Abstract: Laboratory-scale bleach tests were performed with O_2-delignified softwood kraft pulp in order to investigate optimum conditions with regard to consistency, temperature, retention time, caustic and silicate. The influence on brightness, kappa number and strength properties was measured. In addition, an O-D-P bleaching sequence was tested.

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