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(54) **Chemical pulp bleaching**

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Description

This invention relates to a process for bleaching kraft or sulfite wood pulp to enhance its brightness, to improve brightness stability and generally to improve the physical properties of the pulp.

Wood pulp can be produced by numerous different processes which can be classified under the broad headings of mechanical, chemical and hybrid processes. Among the chemical processes are the kraft process wherein the wood chips or the like are treated at elevated temperature and alkaline pH with sodium sulfide, sodium hydroxide and sodium carbonate, and the sulfite process wherein the wood chips are treated at acid pH, again at elevated temperature, with sodium and magnesium bisulfites. The process of the present invention has been found to be particularly advantageous in relation to pulps produced by these chemical processes, but is not limited to any particular type of wood pulp.

Hitherto, different chemical bleaching processes have been used for different types of wood pulp, and in the past these have generally comprised treatments with various combinations of chlorine, chlorine dioxide, sodium hydroxide and sodium hypochlorite. For example kraft pulp has conventionally been treated with chlorine followed by two successive cycles of sodium hydroxide and chlorine dioxide. Sulfite pulp on the other hand has been treated successively with chlorine, sodium hydroxide, sodium hypochlorite and chlorine dioxide.

Because of the pollution risks associated with the use of chlorine, and in particular the risk to the ozone layer, in recent years ways have been studied to replace chlorine in such bleaching treatments and ultimately to replace chlorine compounds as well. To this end, various combinations of oxidising agents have been tried and in particular oxygen itself, ozone and hydrogen peroxide have been used in various combinations.

Kassepi et al (TAPPI) Pulping Conf, (Toronto) Proc, 327-340 (Oct 1992) disclose the effect of ozonisation on kraft-oxygen (K-O) and kraft oxygen-peroxide (K-OP) pulps. The K-OP pulps generally responded better to ozone bleaching than K-O pulps. It was found that too high an ozone concentration gave rise to carbohydrate degradation and decreased viscosity of the pulp.

According to Patt et al *Holzforschung* 45 (Suppl) 87-92 (September 1991), ozone can be used effectively in both pre-bleaching and final bleaching but both lignins and carbohydrates tend to be attacked. Carbohydrate degradation has to be suppressed by preacidification of the pulp, low-temperature bleaching, slow addition of ozone to the pulp and proper mixing. Under these conditions, an ozone concentration of 0.1% can reduce the pulp kappa number by one unit.

Numerous similar studies have been carried out in recent years.

WO-A-92/07139 describes a method for preserving the mechanical strength properties of chemical paper pulp comprising two steps using a peroxygenated reagent, the first of which is carried out in an acidic medium while the second is carried out in an alkaline one treatment with a reducing compound being inserted therebetween.

The present invention consists in a process for bleaching kraft or sulfite wood pulp which comprises treating the pulp first with at least one oxidising agent and then with a reducing agent, characterised in that the oxidising agent comprises alkaline hydrogen peroxide or ozone and the reducing agent comprises sodium borohydride.

There can thus be provided a pulp bleaching process, preferably totally chlorine free, which gives a pulp of high and stable brightness without adversely affecting the physical properties of the pulp and in particular without degrading the polysaccharides or reducing the viscosity of the pulp.

A further oxidising treatment may optionally be carried out after the treatment with the reducing agent. This is preferably done with hydrogen peroxide and sodium hydroxide.

The various bleaching stages are preferably all carried out at alkaline pH, for which purpose an alkaline metal hydroxide such as sodium hydroxide may be added.

Brightness may be further enhanced by the use of enzymes such as xylanase and chelants such as ethylene diamine tetraacetic acid (EDTA) or, more preferably, diethylene triamine pentaacetic acid (DTPA).

The sodium borohydride is preferably used in alkaline solution, and a particularly advantageous form is an aqueous solution of 10 to 25 wt.% of sodium borohydride and 15 to 45 wt.% of sodium hydroxide. One commercially available solution of this type comprises 12% of sodium borohydride and 40% of sodium hydroxide, and is supplied by Morton International, Inc under the trade mark Borol. Another such solution developed more recently comprises 20% of sodium hydroxide and 20% of sodium borohydride.

Further objects and advantages of the invention will become apparent from the following detailed description and examples.

The accompanying drawings illustrate results obtained in some of the examples. In the drawings:

FIGS. 1 and 2 illustrate the brightness gains obtained with varying borohydride addition rates in Example 1;

FIG. 3 illustrates the relationship between tensile strength and beating degree for treated and untreated kraft pulps in Example 2;

FIG. 4 illustrates the relationship between tear index and beating degree for the pulps of Example 2;

FIGS. 5 and 6 illustrate the brightness gains obtained in Example 3;

For simplicity, the various different treatment steps which can be used in accordance with the invention are given the following letter codes:

D	C10 ₂	Not used in the most preferred embodiments which are totally chlorine-free.
EOP		Alkaline extraction, enhanced with peroxide and oxygen.
ER		Alkaline extraction, enhanced with sodium borohydride.
O	Oxygen, O ₂	Preferred concentration 2-5% based on oven-dried pulp (ODP). Typically about 3% may be used with NaOH, at a preferred concentration of 2.0-3.0%.
P	Hydrogen Peroxide H ₂ O ₂	Preferred concentration 2.0-3.0% on ODP. Generally used with NaOH at a preferred concentration of 2.0-3.0%. Preferred temperature about 70°C.
OP	O ₂ /NaOH/H ₂ O ₂	
OPN	O ₂ /NaOH/H ₂ O ₂ /Nitrilamine	
Q	Chelant	EDTA or, more preferably DTPA, at preferred concentration of 0.2 to 0.6% on ODP.
R	Sodium Borohydride	Preferably in the form of the Borol solution described above, concentration 0.5-2.0% on ODP.
X	Enzyme treatment	Preferably with xylanase, optionally together with a chelant.
Y	Sodium hydrosulfite	Preferably generated <i>in situ</i> by reaction of sodium bisulfite with an aqueous borohydride/sodium hydroxide solution.
Z	Ozone, O ₃	Preferred addition rate 0.2-1.0% on ODP, depending on the kappa number of the incoming pulp. Treatment temperature preferably less than 50°C.

The following bleaching sequences in accordance with the invention have been found particularly advantageous:

OZRD;
OZRP;
OXPRP;
OXPR;
OQPR;
OQPRP;
(OP) (OP_N) ZRP

The following processes are preferred for bleaching particular types of pulp:

SULFITE PULP (SOFTWOOD OR HARDWOOD)

ECF Processes (free of elemental chlorine):

OZRD OZRDY
OZDR

TCF Processes (totally chlorine-free)

OZPR
ZPR OZRP QPR
ZRP (EOP) PR
OZRPY

KRAFT PULP (SOFTWOOD OR HARDWOOD)

ECF Processes:

D(EOP)D(ER)D OZR(EOP)D
D(EOP)D(ER)DY

TCF Processes:

O(OP)ZRP
OZRP O(OP)ZRPY
OZPR
OQPR OXPR OZRPY

In the following examples concentrations are based on ODP (oven-dried pulp) unless otherwise stated.

EXAMPLE 1

Totally chlorine free (TCF) bleaching process sequences OXPR and OXPRP were carried out on kraft pulp of NCC pine.

The oxidative bleaching sequence was as follows:

O: O₂ at 3%, NaOH at 2.0-2.5%;
X: Xylanase;
P: H₂O₂ at 2.0 to 3.0%, NaOH at 2.0 to 3.0%, DTPA at 0.4%.

The pulp was taken out after SO₂ addition after the last peroxide stage and had a pH value of 4.5 and a consistency of 31.8%. The initial ISO brightness was 73.9% but was not stable and varied between 70.9 and 71.8% several days later. The pulp was diluted down to 10% consistency with distilled water and a series of reductive bleaching trials was carried out at 70°C, for a retention time of 60 minutes in each case.

The trials were conducted using sodium borohydride, alone and in combination with sodium bisulfite and with hydrogen peroxide.

A 2% wt. aqueous borohydride solution (NaBH₄:NaOH ratio 3:10, pH = 12.8) and 4% wt. NaHSO₃ solution (pH = 4.2) were prepared for the treatment. Aging tests were conducted according to TAPPI standard method (4 hrs at 105°C).

Aqueous solutions of 11.5% H₂O₂ and 10% NaOH were used for the peroxide bleaching. A 32% DTPA solution considered as 100% was diluted with distilled water to a 1% solution to be used for the peroxide stage.

After the pH adjustment to 4.5 with 1% H₂SO₄, handsheets were prepared.

The trials were performed with 20g samples in sealed polyethylene bags plunged into an agitating water bath.

The first series of the trials was conducted with different amounts of alkaline borohydride solution (NaBH₄ 12%, NaOH 40%, water 48%). The bleaching conditions and the results are listed in Table 1 below and the brightness response versus the NaBH₄ solution addition rate is illustrated in Figure 1, which also illustrates the brightness after aging. Figure 1 shows that the brightness response is increased very fast by adding the borohydride solution to 0.6%. A further increasing of chemical charge to 1% can achieve 0.5% brightness extra. A maximum brightness gain of 2.6% ISO points can be achieved by adding 1% of the borohydride solution.

TABLE 1

RUN N°	NaBH ₄ / NaOH Solution	pH		BRIGHTNESS		Δ-BRIGHTNESS	
		%/o.d.pulp	Initial	Final	Before aging % ISO	After aging % ISO	Before aging % ISO
blank*	-	4.5	4.5	73.9	72.8	0.0	0.0
1	0.2	9.1	5.6	74.3	73.0	0.4	0.2
2	0.4	10.2	9.3	74.9	74.0	1.0	1.2
3	0.6	11.0	11.0	76.0	74.8	2.1	2.0
4	0.8	11.5	11.4	76.4	75.1	2.5	2.3
5	1.0	11.8	11.5	76.5	75.3	2.6	2.5

* The brightness of the blank sample was determined immediately after receiving the pulp sample.

The brightness reversion of the untreated kraft pulp was 1.1 points. The reductive treatment with sodium borohydride solution can offer a relatively stable brightness gain, if one compares the brightness gain before and after aging.

The second series of the trials was performed with 1% of the borohydride solution and subsequently with 1% hydrogen peroxide with and without washing between these two stages. As reference, the pulp was also bleached with 1% hydrogen peroxide alone. The bleaching conditions and the results are compiled in Table 2. The combined treatment

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was carried out for 180 min. and the peroxide-only treatment for 240 min.

A treatment with 1% hydrogen peroxide can increase the final brightness by 3.6 points. A reductive treatment with 1% of the borohydride solution increases the brightness by 3 points. A subsequent peroxide bleaching can increase the brightness by 2.8 points more.

5 The brightness response is slightly reduced (0.2 points) if the pulp is not washed between the borohydride solution stage and the peroxide stage. For the mill practice, this combination is very interesting, because the mill can not only save the investment cost for the washer, but also use residual NaOH of the borohydride solution.

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TABLE 2

RUN N°	STAGE	CHEMICALS (% / o.d. pulp)				pH		BRIGHTNESS (% ISO)		Δ -BRIGHTNESS (% ISO)	
		NaBH ₄ /NaOH solut.	H ₂ O ₂	NaOH	DTPA	Initial	Final	Before aging	After aging	Before aging	After aging
blank 6	P	- -	- 1.0	- 1.0	- 0.3	4.5 12.5	4.5 12.4	71.8 75.4	71.5 74.9	- 3.6	- 3.4
blank 7	R / P without washing	- 1.0 -	- - 1.0	- - 0.45	- - 0.3	4.5 11.7 11.4	4.5 10.8	70.9 73.9 76.5	70.7 73.3 75.5	- 3.0 5.6	- 2.6 4.8
8	R / P with washing	1.0 -	- 1.0	- 0.85	- 0.3	11.9 11.9	11.1 11.0	76.7	75.7	5.8	5.0

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Constant bleaching conditions:		
	R-Stage	P-Stage
Temperature, °C	70	70
Consistency, %	10	10
Time, min.	60	180 (n°6) 240 (n° 7-8)
Consumption of H ₂ O ₂ , %	-	49.8 (n°6) 64.2 (n°7) 61.6 (n°8)

The third series of the bleach trials was carried out with sodium bisulfite as a reference and a combination of sodium bisulfite and the sodium borohydride solution. The addition rate of NaHSO₃ was kept constant by 1.5%/o.d. pulp, while the NaBH₄ addition rate was varied between 0.1% and 0.5%. The treatment rates and brightness gains are given in Table 3.

TABLE 3

RUN N°	CHEMICAL (% / o.d. pulp)		pH		BRIGHTNESS (% ISO)		Δ-BRIGHTNESS (% ISO)	
	NaBH ₄ /NaOH solution	NaHSO ₃	Initial	Final	Before aging	After aging	Before aging	After aging
blank*	-	-	4.5	4.5	73.9	72.8	-	-
9 (ref.)	-	1.5	4.2	3.7	74.2	72.7	0.3	-0.1
10	0.1	1.5	4.5	3.7	74.0	72.9	0.1	0.1
11	0.2	1.5	5.2	4.2	74.9	73.6	1.0	0.8
12	0.3	1.5	5.6	4.5	75.0	73.8	1.1	1.0
13	0.4	1.5	6.0	4.7	75.3	74.2	1.4	1.4
14	0.5	1.5	6.5	5.4	75.8	74.6	1.9	1.8

* The brightness of the blank pulp sample was determined immediately after receiving the pulp sample.

Constant bleaching conditions	
Temperature	70°C
Time	60 min.
Consistency	10 %

Sodium bisulfite is a weak reductant. A reductive treatment of the TCF bleached kraft pulp with 1.5% NaHSO₃ can increase the final brightness by 0.3 points. A combination of sodium bisulfite and alkaline borohydride solution can improve the bleaching efficiency to gain 1.9 brightness points. In comparison with adding 0.6% borohydride solution only, little synergistic bleaching effect is obtained by adding two reductants serially. This has already been established in the case of mechanical pulp and deinked pulp. The reason might be due to the lower residual lignin content of the bleached chemical pulp. The brightness gains before and after aging are illustrated in Figure 2 which shows that the brightness stability of the treated only with 1.5 NaHSO₃ pulp is inferior to that of the combination of NaHSO₃ and borohydride solution.

EXAMPLE 2 (reference)

To investigate the physical properties of the reductive treated pulp, 100g oven dry pulp as used in Example 1 were treated with 1% of an alkaline NaBH₄ solution having the composition of the Borol solution described above. The reaction time was prolonged to 90 min. to compensate for the difficult mixing of the pulp at the medium consistency of 10% in the laboratory. The treatment temperature was 70°C as in Example 1, with an initial pH of 11.8 and a final pH of 11.6

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The yield of the borohydride treated pulp was 99.7% and the final brightness before and after aging was 74.6% and 73.3% ISO respectively. The physical properties of the untreated and treated pulps are set out in Tables 4 and 5 respectively. In comparison with the untreated TCF bleached pulp, the beating energy as well as the strength properties, especially tensile strength and burst index of the borohydride treated pulp, were positively influenced, whereas the tear index of the treated and untreated pulps remained at the same level, as can be seen from Figures 3 and 4.

The optical properties, i.e. opacity, absorption coefficient and light-scattering coefficient of the borohydride-treated pulp were reduced slightly due to the higher final brightness of the treated pulp (2.8 points higher). The viscosity of the borohydride treated pulp was increased from 748 dm³/kg to 762 dm³/kg. This can explain the improvement of the strength properties after the borohydride treatment.

Kappa number and all strength properties were determined according to ZELLCHEMING standards. Brightness, viscosity and light-scattering, were tested according to SCAN-C 11:75, SCAN-CM : 88 AND SCAN-C 27:76, respectively.

TABLE 4

	BEATING DEGREE									
	1	2	3	4	5	1 interpolat.	2 interpolat.	3 interpolat.		
BEATING DEGREE [°SR]	15.8	17.0	20.3	30.3	53.0	20.0	25.0	30.0		
BEATING TIME [min]	0	15	30	45	60	29	37	45		
SPEC. VOLUME (bulk) [cm³/g]	1.49	1.25	1.21	1.17	1.12	1.21	1.19	1.17		
BREAKING LENGTH [km]	4.13	7.90	8.79	9.29	9.65	8.72	9.03	9.28		
BURSTING PRESSURE [kPa]	263	446	466	459	469	465	463	459		
BURSTING PRESSURE 75 g [kPa]	235	420	444	440	456	442	442	440		
BURSTING PRESSURE 80 G [kPa]	251	448	474	470	486	472	472	440		
TEARING RESISTANCE [cN]	214.5	127.5	122.1	108.8	99.6	122.6	115.8	109.1		
STRENGTH FACTOR	9.42	10.03	10.36	10.05	9.81	10.33	10.21	10.06		
TENSILE-INDEX [Nm/g]	40.5	77.4	86.1	91.1	94.6	85.5	88.5	91.0		
TEAR-INDEX [mN.m²/g]	25.6	16.0	15.5	13.8	12.9	15.6	14.7	13.9		
BURST-INDEX [kPa.m²/g]	3.1	5.4	5.8	5.7	6.0	5.8	5.8	5.7		
ABSORPTION COEFFICIENT [m³/kg]	0.47	0.47	0.53	0.51	0.60	0.53	0.52	0.51		
OPACITY, 80 g/m² [%]	82.0	72.1	71.4	70.1	69.0	71.4	70.8	70.1		
LIGHT-SCATTERING COEFF. [m²/kg]	28.9	18.4	17.5	16.5	15.4	17.5	17.0	16.5		
BRIGHTNESS [% ISO]	71.8									
CUEN VISCOSITY [dm³/kg]	748									
KAPPA N°	5.4									

TABLE 5

BEATING DEGREE									
	1	2	3	4	5	1 interpolat.	2 interpolat.	3 interpolat.	
BEATING DEGREE [°SR]	16.0	18.0	23.5	32.5	52.0	20.0	25.0	30.0	
BEATING TIME [min]	0	15	30	45	60	20	33	41	
SPEC. VOLUME (bulk) [cm³/g]	1.48	1.20	1.15	1.15	1.10	1.18	1.15	1.15	
BREAKING LENGTH [km]	4.31	8.16	8.50	9.48	10.24	8.28	8.67	9.21	
BURSTING PRESSURE [kPa]	289	428	491	465	549	450	486	472	
BURSTING PRESSURE 75 g [kPa]	256	404	467	448	532	427	463	453	
BURSTING PRESSURE 80 G [kPa]	273	431	498	477	568	455	494	483	
TEARING RESISTANCE [cN]	223.6	121.2	108.6	107.0	98.0	116.6	108.4	107.4	
STRENGTH FACTOR	9.82	9.94	9.61	10.07	10.02	9.80	9.69	9.95	
TENSILE-INDEX [Nm/g]	42.3	80.1	83.4	93.0	100.4	81.2	85.0	90.3	
TEAR-INDEX [mN.m²/g]	26.4	15.3	13.8	13.6	12.6	14.7	13.7	13.6	
BURST-INDEX [kPa.m²/g]	3.3	5.2	6.1	5.9	6.9	5.5	6.1	6.0	
ABSORPTION COEFFICIENT [m³/kg]	0.44	0.38	0.38	0.40	0.44	0.38	0.38	0.39	
OPACITY, 80 g/m² [%]	82.2	69.8	68.1	66.3	65.2	69.2	67.8	66.8	
LIGHT-SCATTERING COEFF. [m²/kg]	29.2	17.5	16.2	15.3	14.3	17.0	16.1	15.6	
BRIGHTNESS [% ISO]	74.6								
CUEN VISCOSITY [dm³/kg]	762								
KAPPA N°									

EXAMPLE 3

Bleaching trials similar to those of Example 1 but using a sequence OQPR were carried out on 20g samples of spruce kraft pulp. The O and P stages were as in Example 1 and the Q stage was carried out with EDTA. The pulp was taken out after SO₂ addition, at a pH value of 5.5.

The treatment conditions were the same as those of Example 1. The pH value of the pulp was adjusted to 5.5 with 0.1% H₂SO₄ before handsheets were prepared for brightness determination. The initial ISO brightness of the untreated pulp was 75.6% before aging and 74.2% after aging for 4 hours at 105°C.

The first series of the trials was performed by adding the alkaline borohydride solution only. The addition rate of this solution was varied between 0.2% to 1%.

Another series of the bleach trials was carried out with a serial combination of sodium bisulfite and the borohydride solution. The addition rate of NaHSO₃ was kept constant at 1.5%/o.d. pulp, while the borohydride solution addition rate was varied between 0.2% to 0.6%.

2% alkaline borohydride solution and 4% sodium bisulfite solution were prepared daily.

The results are shown in Table 6 and illustrated in Figures 5 (NaBH₄ solution only) and 6 (NaBH₄/bisulfite).

The maximum achieved brightness response was 3.6% ISO points by adding 0.6% of the NaBH₄ solution. A further increase of the amount of NaBH₄ solution reduced the bleaching efficiency of this solution, most probably because the high alkalinity of the solution causes a negative alkaline darkening effect.

The use of 1.5% sodium bisulfite as a reference improved the brightness response by 1.3 brightness points.

A combination of sodium bisulfite and alkaline NaBH₄ solution could increase the brightness gain by 3 points (see Fig. 6) but concerning the brightness response, there was little evidence of the synergistic bleaching effect of adding two reductants, which has been observed when bleaching mechanical and deinked pulp.

TABLE 6

RUN N°	CHEMICAL		pH		BRIGHTNESS (% ISO)		BRIGHTNESS INCREASE VERSUS BLANK (% ISO)		BRIGHTNESS REVERSION (% ISO)
	NaBH ₄ / NaOH sol. %	NaHSO ₃ %	Initial	Final	Before aging	After aging	Before aging	After aging	
Blank	-	-	5.5	5.5	75.6	74.2	0	0	1.4
1	0.2	-	10.6	8.9	77.1	75.7	1.5	1.5	1.4
2	0.4	-	11.4	11.0	78.8	76.7	3.2	2.5	2.1
3	0.6	-	11.6	10.6	79.2	77.3	3.6	3.1	1.9
4	0.8	-	11.8	11.5	79.1	77.0	3.5	2.8	2.1
5	1.0	-	11.9	11.2	78.7	76.2	3.1	2.0	2.5
6 (ref.)	-	1.5	4.8	4.0	76.9	75.0	1.3	0.8	1.9
7	0.2	1.5	4.8/5.7	4.7	78.2	76.5	2.6	2.3	1.7
8	0.3	1.5	4.8/6.7	5.8	78.4	77.0	2.8	2.8	1.4
9	0.4	1.5	4.8/6.2	5.0	78.2	76.4	2.6	2.2	1.8
10	0.5	1.5	4.8/7.1	5.9	78.6	76.6	3.0	2.4	2.0
11	0.6	1.5	4.8/7.4	6.5	78.5	76.6	2.9	2.4	1.9

Constant conditions	
Temperature	70 °C
Time	60 min.
Consistency	10 %
Pulp sample	20 g oven dry pulp

The aging test was conducted for 4 hours at 105°C, according to the TAPPI-method. The brightness of the untreated and reductively treated pulps decreased after the aging.

Fig 5 and 6 show the brightness reversion varies between 1.4 and 2.5 points. The brightness reversion of the OP bleached pulp was 1.4 points. The brightness reversion of the reductively treated pulps varied between 1.4 and 2.5%

ISO. However the final brightness of reductively treated pulps (after aging) was still 2.8 - 3.1 points higher than the final brightness of untreated pulp.

EXAMPLE 4 (reference)

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To investigate the physical properties after the reductive treatment, 100g o.d. pulp as used in Example 3 were treated with 1% of the Borol NaBH_4 solution described above. The results before treatment are listed in Table 7 and those after are listed in Table 8. The conditions were the same as in Example 2 and the pH was 11.7 before and after treatment. The physical properties were measured as in Example 2.

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The yield of the borohydride-treated pulp was 99.8% and the final brightness was 78.5% ISO before aging and 77.8% after. In comparison with the untreated kraft pulp, the beating energy as well as the strength properties of the borohydride-treated pulp were not influenced significantly.

Due to the higher final brightness, the optical properties like opacity, absorption coefficient and light-scattering coefficient were reduced a little. The viscosity of the treated pulp was increased slightly as expected.

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The variations of tear index and tensile strength with beating degree were similar to those obtained in Example 2 (see Figs. 3 and 4).

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TABLE 7

	1. BEATING	2. BEATING	3. BEATING	4. BEATING	5. BEATING	1. Inter- polated BEATING DEGREE	2. Inter- polated BEATING DEGREE	3. Inter- polated BEATING DEGREE
BEATING DEGREE [°SR]	14.5	15.5	22.5	35.0	52.0	20.0	25.0	30.0
BEATING TIME [min]	0	15	30	45	60	25	33	39
SPEC. VOLUME [cm ³ /g]	1.69	1.31	1.24	1.20	1.15	1.27	1.24	1.22
DRAWING LENGTH [mm]	2.94	6.91	8.32	9.09	8.88	7.82	8.47	8.78
BURSTING PRESSURE [kPa]	181	402	449	466	439	432	453	459
BURSTING PRESS 75g [kPa]	157	377	425	456	428	408	431	444
BURSTING PRESS 80g [kPa]	167	402	453	486	456	435	460	473
TEARING RESISTANCE [cN]	216.8	158.9	138.5	117.9	117.4	145.8	134.4	126.1
STRENGTH FACTOR	7.98	10.48	10.73	10.35	10.21	10.64	10.66	10.50
TEXSILE INDEX [Nm/g]	28.8	67.8	81.5	89.1	87.0	76.6	83.1	86.1
TEAR INDEX [mN·m ² /g]	25.0	19.9	17.5	14.9	15.3	18.3	16.9	15.9
HURST INDEX [kPa·m ² /g]	2.0	5.0	5.7	5.9	5.4	5.4	5.7	5.8
ABSORPTION COEFF. [m ² /kg]	0.37	0.33	0.38	0.37	0.39	0.36	0.38	0.37
OPACITY, 60 g/m ² [%]	81.5	71.0	69.5	67.4	67.7	70.0	69.1	68.2
LIGHT-SCAT. COEFF. [m ² /kg]	29.0	19.1	17.3	16.5	16.1	17.9	17.1	16.8
BRIGHTNESS [% ISO]	75.6							
CORE-VISCOSITY [dm ³ /kg]	716.0							

TABLE 8

	1. BEATING DEGREE	2. BEATING DEGREE	3. BEATING DEGREE	4. BEATING DEGREE	5. BEATING DEGREE	1. Inter- polated BEATING DEGREE	2. Inter- polated BEATING DEGREE	3. Inter- polated BEATING DEGREE
BEATING DEGREE	14.0	15.5	22.5	38.5	51.0	20.0	25.0	30.0
BEATING TIME	0	15	30	45	60	25	32	37
SPEC. VOLUME	1.64	1.29	1.21	1.18	1.15	1.24	1.20	1.19
BREASTING LENGTH	2.78	7.67	8.30	9.18	9.14	8.08	8.44	8.71
BURSTING PRESSURE	176	426	456	497	462	445	462	475
BURSTING PRESS. 150	156	395	436	466	448	421	441	450
BURSTING PRESS. 800	166	422	465	497	478	450	470	480
TZARING RESISTANCE	220.8	150.9	130.1	125.4	118.0	137.6	129.4	127.9
STRENGTH FACTOR	7.84	10.76	10.40	10.73	10.39	10.52	10.45	10.55
TENSILE INDEX	27.3	75.2	81.4	90.0	89.6	79.2	82.7	85.4
TZAR INDEX	26.1	18.7	16.6	16.0	15.3	17.3	16.5	16.3
BURST INDEX	2.0	5.2	5.7	6.2	5.9	5.5	5.7	5.9
ABSORPTION COEFF.	0.26	0.25	0.33	0.36	0.33	0.30	0.33	0.34
OPACITY. 80 g/m ²	79.8	69.0	68.0	67.7	65.9	68.3	67.9	67.9
LIGHT-SCAT. COEFF.	28.9	18.2	17.0	16.0	15.8	17.4	16.8	16.5
BRIGHTNESS	78.5							
CUTZ-VISCOSITY	719.0							

EXAMPLE 5

Reductive bleaching trials using sequences OQPR and OQPRP were carried out on samples of kraft hardwood (birch) pulp, the oxidative sequence being carried out as in Example 3. The pulp samples came from Sweden. The kappa number after the cooking process was 15 and 10 after the O-stage. The residual kappa number of the OQP bleached pulp was determined as 5.4 in the laboratory.

The trials were conducted by using the Borol NaBH₄ solution described above, directly or in combination with

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hydrogen peroxide. Two pulps, namely wet pulp (ledge) and pulp sheet, with an initial brightness of 79.7% ISO and 81.6% ISO were used for the laboratory bleach trials.

A first series of the trials was performed by adding the NaBH₄ solution to both pulp samples. The addition rate was varied between 0.2% and 1.2% (the solution contains 12% wt NaBH₄, 40% wt NaOH and 48% wt H₂O).

The second series of the bleach trials was done by adding 1% peroxide or 0.5-1% NaBH₄ solution and 1% peroxide with and without washing between these two stages.

The bleach trials were performed in sealed PE-bags plunged into an agitating water bath.

The following conditions were applied:

Temperature	70°C
Consistency of pulp	10% (15% for R-stage)
Time	60 min for NaBH ₄ and combination stage 240 min for peroxide stage
Sample weight	10 g and 100 g o.d. pulp

A 2% wt NaBH₄ solution (Borol, described above, pH = 12.8) was prepared freshly each time for the treatment. Aging tests were conducted according to TAPPI standard method (4 hrs at 105°C). The results are shown in Table 9.

TABLE 9

RUN N°	CHEMICAL	pH		BRIGHTNESS (% ISO)		BRIGHTNESS INCREASE VS. BLANK (% ISO)		BRIGHTNESS REVERSION (% ISO)
	NaBH ₄ sol. (%/pulp)	Initial	Final	Before aging	After aging	Before aging	After aging	
WET PULP (ledge)								
Blank	-	6.4	6.0	79.7	78.6	0	0	1.1
1	0.2	10.8	9.7	81.4	79.4	1.7	0.8	2.0
2	0.4	11.3	10.0	82.9	81.0	3.2	2.4	1.9
3	0.6	11.6	10.4	82.4	80.8	2.7	2.2	1.6
4	0.8	11.9	10.6	82.9	80.9	3.2	2.3	2.0
5	1.0	12.0	10.8	83.0	81.0	3.3	2.4	2.0
6	1.2	12.1	11.8	82.2	80.8	2.5	2.2	1.4
PULP SHEET								
Blank	-	6.9	6.5	81.6	79.9	0	0	1.7
7	0.2	10.6	9.4	83.0	80.2	1.4	0.3	2.8
8	0.4	10.9	10.4	83.6	81.0	2.0	1.1	2.6
9	0.6	11.1	10.8	83.9	81.5	2.3	1.6	2.4
10	0.8	11.4	10.9	84.0	81.7	2.4	1.8	2.3
11	1.0	11.5	11.2	84.1	82.0	2.5	2.1	2.1

Constant conditions	
Temperature	70°C
Time	60 min
Consistency	10%
Pulp sample	10 g oven dry pulp

The second series of the laboratory bleach trials was carried out with peroxide as well as with a combination of the NaBH₄ solution and peroxide. The bleaching conditions and the results are listed in Table 10. The physical properties

of the treated and untreated pulp are listed in Tables 11 to 13.

1% H_2O_2 can increase the brightness of 2.6 points. Reductive treatments with 0.5 and 1% of the $NaBH_4$ solution increased the brightness response of 2.1 and 2.8 points respectively. Subsequently the pulps were bleached with 1% H_2O_2 . The final brightness was 85.1% ISO and 85.4% ISO respectively. If the pulp was not washed between the R-stage and the P-stage, the brightness response was reduced by 0.2 and 0.4 points.

With respect to the viscosity, the initial pulp had a viscosity of $770 \text{ dm}^3/\text{kg}$. After the $NaBH_4$ treatment, the viscosity of the pulp was increased to $800 \text{ dm}^3/\text{kg}$. But the viscosity of the pulp dropped again to $756 \text{ dm}^3/\text{kg}$ after the P-stage. In comparison with peroxide bleaching the viscosity difference was not significant.

The yield of the peroxide treated and with the combination of $NaBH_4$ solution and peroxide treated pulp ranged between 99.8-99.7%.

TABLE 10

RUN N°	STAGE	CHEMICALS (%o.d. pulp)				pH		BRIGHTNESS (% ISO)		Δ -BRIGHTNESS (% ISO)	
		NaBH ₄ sol.	H ₂ O ₂	NaOH	DTPA	Initial	Final	Before aging	After aging	Before aging	After aging
BLANK		-	-	-	-			81.6	79.9	-	-
30	P	-	1	1	0.4	11.7	10.7	84.2	82.5	2.6	2.6
31	R	0.5	-	-	-	11.0	10.3	83.7	81.7	2.1	1.8
	P without washing	-	1	0.8	0.4	11.4	11.0	84.9	83.3	3.3	3.4
32	R	1.0	-	-	-	11.5	10.7	84.4	82.5	2.8	2.6
	P without washing	-	1	0.65	0.4	11.4	11.2	85.0	83.1	3.4	3.2
33	R	0.5	-	-	-	11.0	10.3	83.7	81.7	2.1	1.8
	P with washing	-	1	0.8	0.4	11.5	10.8	85.1	83.0	3.5	3.1
34	R	1	-	-	-	11.5	10.7	84.4	82.5	2.8	2.6
	P with washing	-	1	0.8	0.4	11.6	11.0	85.4	83.3	3.8	3.4

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Constant bleaching conditions:		
	R-Stage	P-Stage
Temperature, °C	70	70
Consistency, %	15	10
Time, min.	60	240
Consumption of H ₂ O ₂		45.2 (N° 30)
		64.2 (N° 31)
		67.0 (N° 32)
		63.0 (N° 33)
		77.3 (N° 34)

TABLE 11

	1. BEATING DEGREE	2. BEATING DEGREE	3. BEATING DEGREE	4. BEATING DEGREE	5. BEATING DEGREE	1. Interpolat. BEATING DEGREE	2. Interpolat. BEATING DEGREE	3. Interpolat. BEATING DEGREE
BEATING DEGREE	18.0	24.0	31.5	40.5	64.0			
BEATING TIME	0	15	30	45	60			
SPEC. VOLUME	1.48	1.21	1.24	1.23	1.13			
BREAKING LENGTH	3.64	8.32	8.83	9.17	9.71			
BURSTING PRESSURE	149	388	378	396	442			
BURSTING PRESS. 75g	142	370	370	384	439			
BURSTING PRESS. 80g	151	395	395	410	468			
TEARING RESISTANCE	72.2	87.2	97.3	106.7	77.9			
STRENGTH FACTOR	5.13	8.52	9.27	9.89	8.70			
TENSILE INDEX	35.7	81.6	86.6	89.9	95.2			
TEAR INDEX	9.2	11.1	12.7	13.9	10.3			
BURST INDEX	1.9	4.8	4.8	5.0	5.7			
ABSORPTION COEFFICIENT	0.22	0.21	0.22	0.21	0.28			
OPACITY, 80 g/ m ²	81.0	71.6	71.1	69.1	63.2			

TABLE 11 (continued)

	1. BEATING DEGREE	2. BEATING DEGREE	3. BEATING DEGREE	4. BEATING DEGREE	5. BEATING DEGREE	1. Interpolat. BEATING DEGREE	2. Interpolat. BEATING DEGREE	3. Interpolat. BEATING DEGREE
LIGHT-SCAT. COEFFICIENT [m ² /kg]	33.8	21.3	19.6	18.6	13.9			
BRIGHTNESS [% ISO]	≈ 81.6							
CUEN- VISCOSITY [dm ² /kg]	770							
KAPPA N° [-]	5.4							

TABLE 12

	1. BEATING DEGREE	2. BEATING DEGREE	3. BEATING DEGREE	4. BEATING DEGREE	5. BEATING DEGREE	1. Interpolat. BEATING DEGREE	2. Interpolat. BEATING DEGREE	3. Interpolat. BEATING DEGREE
BEATING DEGREE	18.0	24.0	33.0	42.3	65.5	20.0	25.0	30.0
BEATING TIME	0	15	30	45	60	5	17	25
SPEC. VOLUME	1.45	1.24	1.24	1.24	1.11	1.38	1.24	1.24
BREAKING LENGTH	3.80	8.63	90.6	9.55	9.59	5.41	8.67	8.92
BURSTING PRESSURE	169	380	412	388	434	239	384	401
BURSTING PRESS. 75g	159	359	398	378	426	226	363	385
BURSTING PRESS. 80 g	170	382	425	403	454	241	387	411
TEARING RESISTANCE	54.3	85.6	93.5	105.5	85.5	64.7	86.4	90.9
STRENGTH FACTOR	4.54	8.59	9.21	10.04	9.06	5.89	8.66	9.00
TENSILE INDEX	37.3	84.6	88.9	93.7	94.0	53.1	85.0	87.4
TEAR INDEX	6.8	10.8	12.1	13.6	11.2	8.1	10.9	11.6
BURST INDEX	2.1	4.7	5.2	5.0	5.5	2.9	4.7	5.0
ABSORPTION COEFF.	0.16	0.16	0.15	0.16	0.22	0.16	0.16	0.15
OPACITY. 80 g/m ²	79.1	70.7	68.9	67.2	64.9	76.3	70.5	69.5

TABLE 12 (continued)

	1. BEATING DEGREE	2. BEATING DEGREE	3. BEATING DEGREE	4. BEATING DEGREE	5. BEATING DEGREE	1. Interpolat. BEATING DEGREE	2. Interpolat. BEATING DEGREE	3. Interpolat. BEATING DEGREE
LIGHT-SCAT. COEFF.	33.3	21.4	19.6	18.3	14.5	22.2	2.2	13.1
BRIGHTNESS	85.1							
CUEN- VISCOSITY	756							
KAPPA N°	[-]							

TABLE 13

	1. BEATING DEGREE	2. BEATING DEGREE	3. BEATING DEGREE	4. BEATING DEGREE	5. BEATING DEGREE	1. Interpolat. BEATING DEGREE	2. Interpolat. BEATING DEGREE	3. Interpolat. BEATING DEGREE
BEATING DEGREE	18.0	25.8	33.5	45.0	71.8	20.0	25.0	30.0
BEATING TIME	0	15	30	45	60	4	14	23
SPEC. VOLUME	1.50	1.24	1.22	1.23	1.05	1.44	1.26	1.23
BREAKING LENGTH	3.85	8.38	9.02	9.36	10.47	5.02	7.94	8.73
BURSTING PRESSURE	163	391	382	389	448	222	369	386
BURSTING PRESS. 75g	154	368	367	378	443	209	347	367
BURSTING PRESS. 80 g	165	392	392	404	473	223	370	392
TEARING RESISTANCE	63.8	98.3	93.1	95.1	81.9	72.7	95.0	95.4
STRENGTH FACTOR	4.95	9.08	9.16	9.43	9.26	6.02	8.68	9.12
TENSILE INDEX	37.7	82.2	88.5	91.8	102.6	49.2	77.9	85.6
TEAR INDEX	8.1	12.3	11.9	12.2	10.8	9.2	11.9	12.1
BURST INDEX	2.0	4.8	4.7	5.0	5.8	2.7	4.5	4.8
ABSORPTION COEFF.	0.17	0.16	0.17	0.17	0.37	0.17	0.16	0.17
OPACITY. 80 g/m ²	79.8	70.9	67.8	68.0	62.4	77.5	71.8	69.2

TABLE 13 (continued)

	1. BEATING DEGREE	2. BEATING DEGREE	3. BEATING DEGREE	4. BEATING DEGREE	5. BEATING DEGREE	1. Interpolat. BEATING DEGREE	2. Interpolat. BEATING DEGREE	3. Interpolat. BEATING DEGREE
LIGHT-SCAT. COEFF.	33.6	21.0	18.7	17.7	11.7	30.3	22.2	19.8
BRIGHTNESS	84.2							
CUEN- VISCOSITY	748							
KAPPA N°								

With an increasing chemical addition rate of NaBH₄ solution to 1%/o.d. pulp, a brightness gain between 2.5 and 3.3% ISO was achieved. A further increase of the NaBH₄ solution addition rate did not improve the bleaching efficiency due to the high alkalinity of the NaBH₄ solution.

After the aging test (4 hours at 105°C), a higher brightness loss on the pulp sheet than on the wet pulp was determined. The reason was that the latter pulp had already lost its brightness before the bleach performance. However we were able to increase the final brightness (after aging) of the pulp with 2.1%-2.4% ISO by using 1% of the NaBH₄ solution.

In the combined treatment, total brightness increases of 3.5 and 3.8% ISO were gained by using 0.5 and 1% of alkaline NaBH₄ solution in R-stage and 1% H₂O₂ in P-stage. The brightness response was reduced slightly to 3.3-3.4% ISO if the pulp was not washed between R- and P-stage.

By applying 1% H₂O₂ for the final bleaching stage, a brightness gain of 2.6 points was achieved, which was 0.9-1.2% ISO lower than with the combination.

The physical properties of the P and RP treated pulps did not change in comparison with the untreated pulp.

The optical properties, i.e. opacity, absorption coefficient and light-scattering coefficient of the P and RP treated pulps were reduced slightly due to the higher final brightness of the treated pulps.

EXAMPLE 6

Bleaching sequences with and without a borohydride treatment stage were carried out to compare the brightness level and viscosity of the resulting pulp. One pulp sample was subjected to the bleaching sequence (OP) (OP_N) ZRP with the results shown in Table 14.

TABLE 14

Stage No.	Treatment Step	Residual kappa No.	Brightness % ISO	Viscosity dm ³ /kg
O	Unbleached	15	28	886
1	OP (O ₂ , NaOH, H ₂ O ₂)	4.5	50.7	765
2	OP _N (O ₂ , NaOH, H ₂ O ₂ , nitrilamine)	2.9	63.7	734
3	Z (O ₃ at 0.2%)	1	80.7	639
4	R (1% Borol at 70°C)	-	83	680
5	P (1%H ₂ O ₂ , 1% NaOH at 70°C)	-	87.3	662

A second sample was subjected to steps 1 to 3 and 5 in Table 14, the R stage 4 being omitted. The resulting brightness was also 87.3% ISO, but the viscosity was only 568 dm³/kg. Thus, the process of the invention gave an equivalent brightness level to that achieved with oxidative bleaching only, but with a much lower viscosity loss. Indeed, it can be seen from Table 14 that the NaBH₄ bleaching stage itself gives a substantial gain in viscosity.

Claims

1. A process for bleaching kraft or sulfite wood pulp which comprises treating the pulp first with at least one oxidising agent and then with a reducing agent, characterised in that the oxidising agent comprises alkaline hydrogen peroxide or ozone and the reducing agent comprises sodium borohydride.
2. A process as claimed in claim 1 wherein the sodium borohydride is used in an aqueous alkaline solution.
3. A process as claimed in claim 2 wherein said aqueous solution comprises 10 to 25 wt.% of sodium borohydride and 15 to 45 wt.% of sodium hydroxide.
4. A process as claimed in claim 3 wherein said aqueous solution comprises about 12% sodium borohydride and about 40% sodium hydroxide and is used in an amount of 0.5 to 2.0% based on oven dried pulp (ODP).
5. A process as claimed in any preceding claim wherein a further oxidation treatment is carried out after the treatment with said reducing agent.

6. A process as claimed in claim 5 wherein said further oxidising treatment is carried out using hydrogen peroxide.
7. A process as claimed in any preceding claim wherein said treatments with oxidising and reducing agents are carried out at alkaline pH.
8. A process as claimed in any preceding claim wherein said pulp is treated with an enzyme to enhance brightness.
9. A process as claimed in claim 8 wherein said enzyme is xylanase.
10. A process as claimed in any preceding claim wherein said pulp is treated with a chelant to enhance brightness
11. A process as claimed in claim 10 wherein said chelant is diethylenetriamine pentaacetic acid (DTPA).

Patentansprüche

1. Verfahren zum Bleichen von Kraft- oder Sulfitholzstoff, bei dem man den Holzstoff zunächst mit wenigstens einem Oxidationsmittel und dann mit einem Reduktionsmittel behandelt, dadurch gekennzeichnet, daß das Oxidationsmittel alkalisches Wasserstoffperoxid oder Ozon und das Reduktionsmittel Natriumborhydrid umfassen.
2. Verfahren nach Anspruch 1, bei dem das Natriumborhydrid in einer wäßrigen alkalischen Lösung verwendet wird.
3. Verfahren nach Anspruch 2, bei dem die wäßrige Lösung 10 bis 25 Gew.% Natriumborhydrid und 15 bis 45 Gew.% Natriumhydroxid umfaßt.
4. Verfahren nach Anspruch 3, bei dem die wäßrige Lösung etwa 12 % Natriumborhydrid und etwa 40 % Natriumhydroxid umfaßt und in einer Menge von 0,5 bis 2,0 %, bezogen auf ofentrockenen Holzstoff (ODP), verwendet wird.
5. Verfahren nach einem der vorausgehenden Ansprüche, bei dem eine weitere Oxidationsbehandlung nach der Behandlung mit dem Reduktionsmittel durchgeführt wird.
6. Verfahren nach Anspruch 5, bei dem die weitere Oxidationsbehandlung unter Verwendung von Wasserstoffperoxid durchgeführt wird.
7. Verfahren nach einem der vorausgehenden Ansprüche, bei dem die Behandlungen mit Oxidations- und Reduktionsmitteln bei alkalischem pH-Wert durchgeführt werden.
8. Verfahren nach einem der vorausgehenden Ansprüche, bei dem der Holzstoff mit einem Enzym behandelt wird, um die Helligkeit zu verbessern.
9. Verfahren nach Anspruch 8, bei dem das Enzym Xylanase ist.
10. Verfahren nach einem der vorausgehenden Ansprüche, bei dem der Holzstoff mit einem chelatbildenden Mittel behandelt wird, um die Helligkeit zu verbessern.
11. Verfahren nach Anspruch 10, bei dem das chelatbildende Mittel Diethylentriaminpentaessigsäure (DTPA) ist.

Revendications

1. Procédé de blanchiment de pâte de bois kraft ou au sulfite qui comprend de traiter la pâte d'abord avec au moins un agent oxydant et ensuite avec un agent réducteur, caractérisé en ce que l'agent oxydant comprend du peroxyde d'hydrogène alcalin ou de l'ozone et l'agent réducteur comprend du borohydrure de sodium.
2. Procédé selon la revendication 1, où on utilise le borohydrure de sodium dans une solution alcaline aqueuse.
3. Procédé selon la revendication 2, où ladite solution aqueuse comprend 10 à 25 % en poids de borohydrure de

sodium et 15 à 45 % en poids d'hydroxyde de sodium.

5 **4.** Procédé selon la revendication 3, où ladite solution aqueuse comprend environ 12 % de borohydrure de sodium et environ 40 % d'hydroxyde de sodium et on l'utilise en une quantité de 0,5 à 2,0 % par rapport à la pâte séchée à l'étuve (ODP).

5. Procédé selon l'une quelconque des revendications précédentes où on réalise un autre traitement d'oxydation après le traitement avec ledit agent réducteur.

10 **6.** Procédé selon la revendication 5, où on réalise l'autre traitement oxydant en utilisant le peroxyde d'hydrogène.

7. Procédé selon l'une quelconque des revendications précédentes, où on réalise lesdits traitements avec des agents oxydants et des agents réducteurs à des pH alcalins.

15 **8.** Procédé selon l'une quelconque des revendications précédentes où on traite ladite pâte avec une enzyme pour améliorer la blancheur.

9. Procédé selon la revendication 8, où ladite enzyme est la xylanase.

20 **10.** Procédé selon l'une quelconque des revendications précédentes, où on traite ladite pâte avec un agent chélatant pour améliorer la blancheur.

11. Procédé selon la revendication 10, où ledit agent chélatant est l'acide diéthylènetriaminepentaacétique (DTPA).

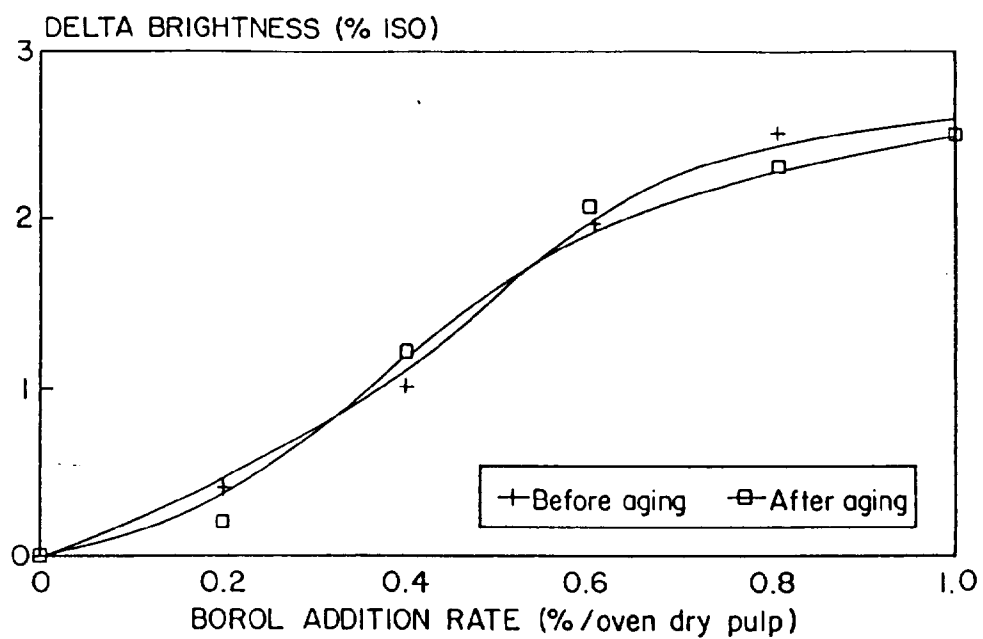


FIG. 1

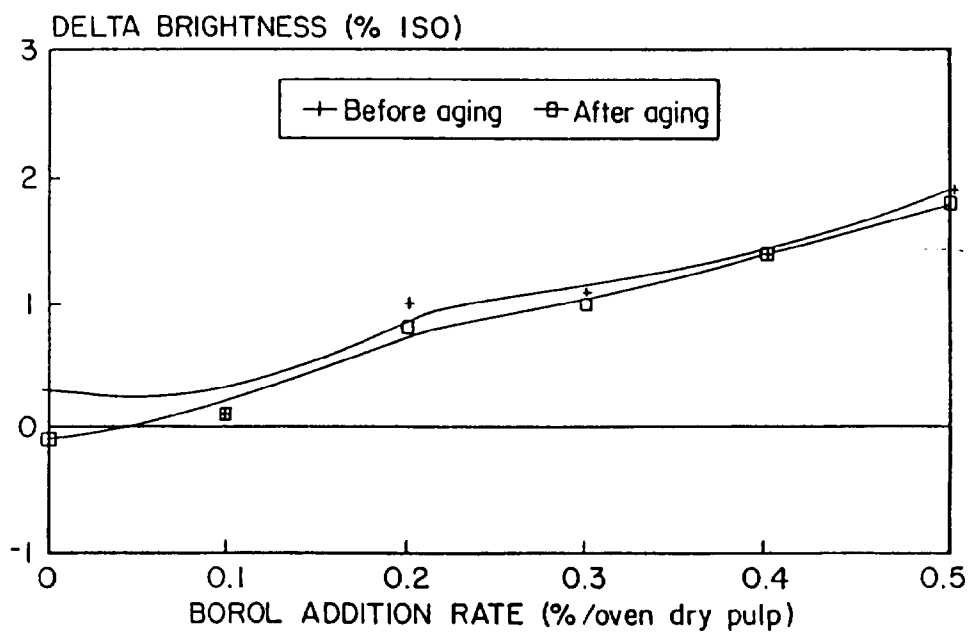


FIG. 2

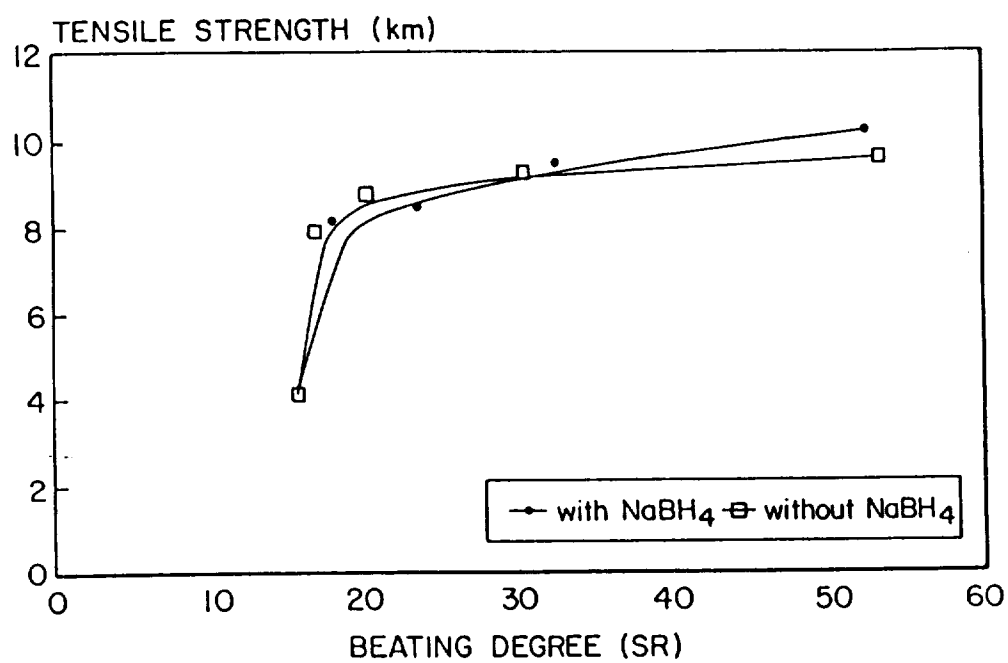


FIG. 3

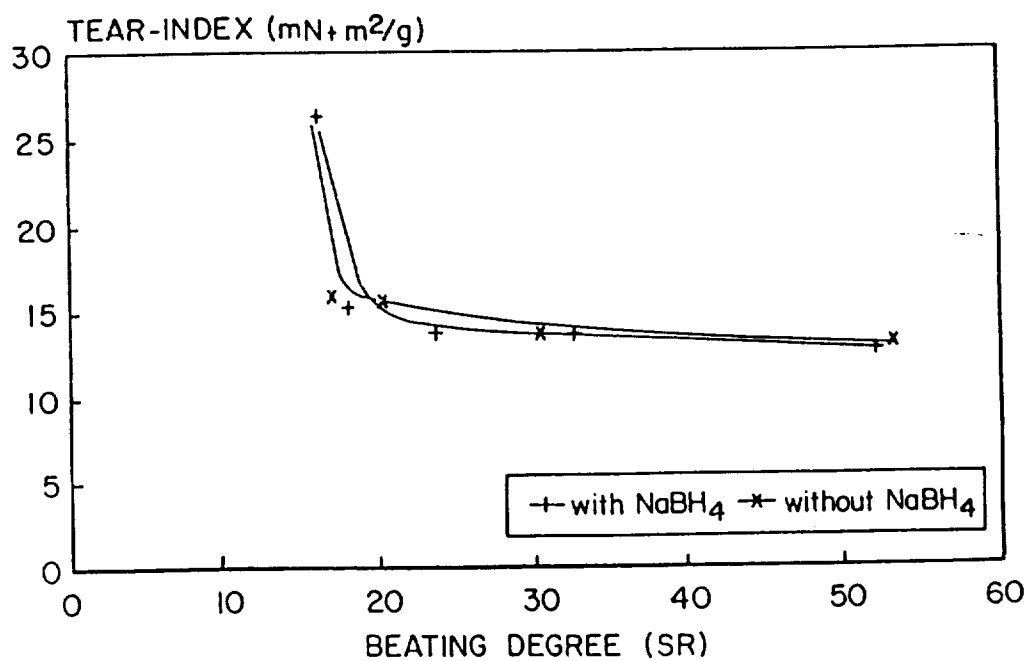


FIG. 4

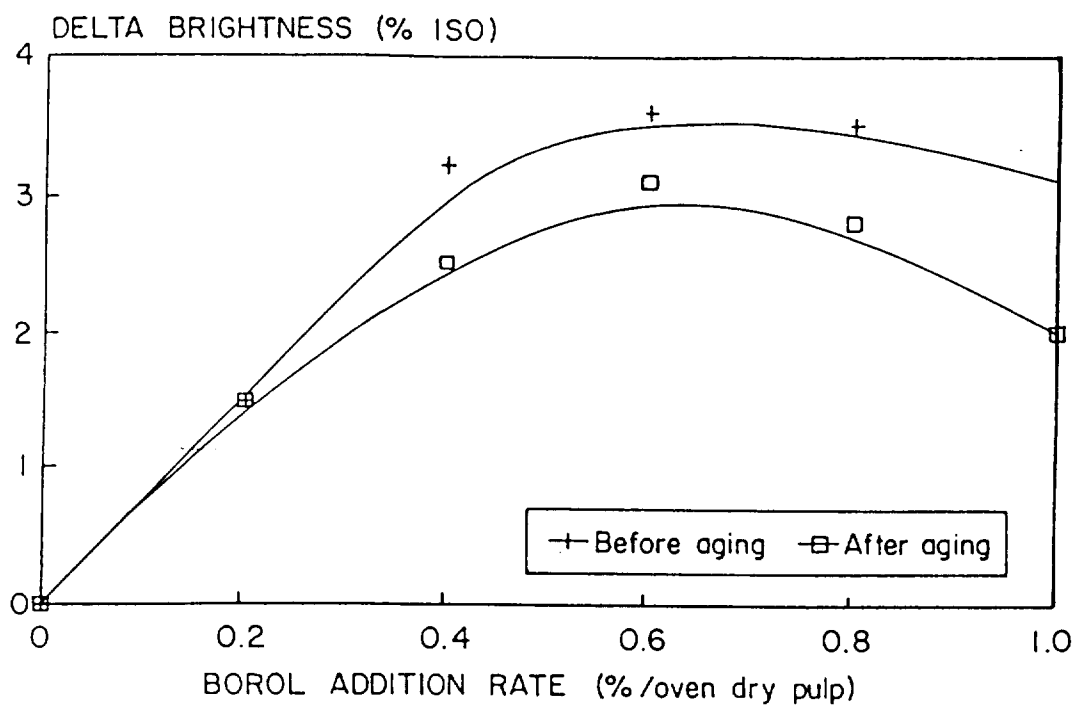


FIG. 5

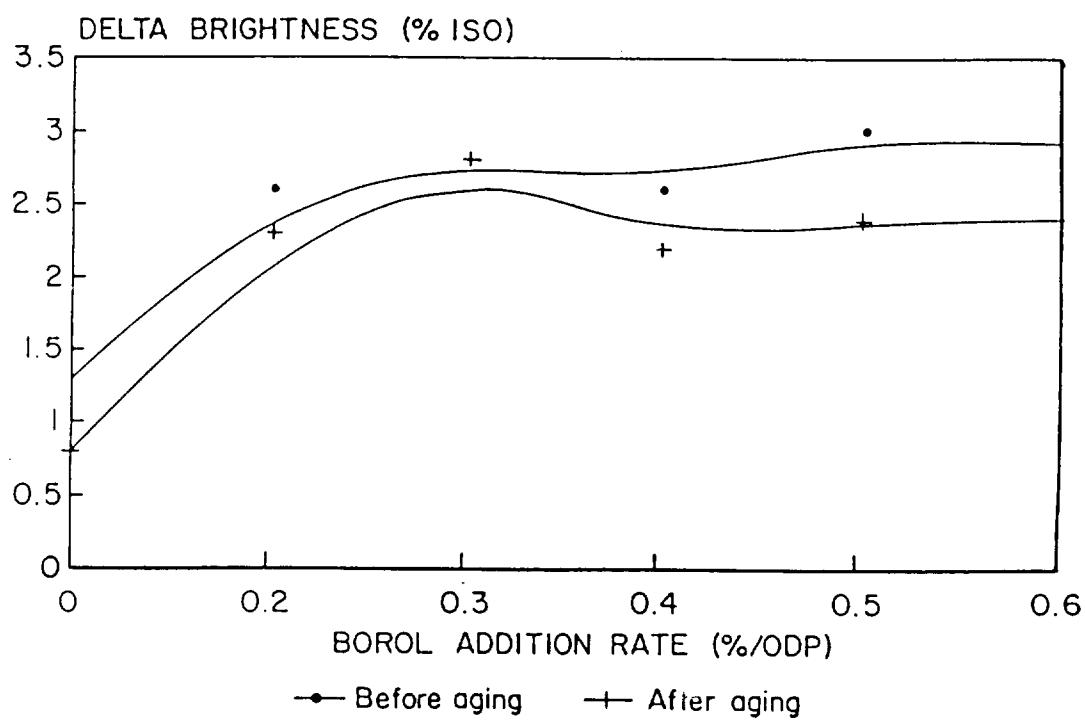


FIG. 6