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(54) Method for brightening mechanical pulps

(57) The present invention is directed to an improved method for brightening mechanical pulp under neutral or alkaline papermaking conditions. The improvement comprises the steps of: (a) separating neutral or alkaline pulp dilution water into a high-solids stream and a neutral or alkaline low-solids stream; and (b) reusing the neutral or alkaline low-solids stream for pulp dilution purposes prior to a bleaching process.

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Description

Background

[0001] This invention relates generally to a method for brightening mechanical pulp.

[0002] Paper pulp typically is subjected to a brightening process prior to paper making. The presence of transition metal ions in paper pulp is known to be detrimental to the brightening process. Chelation techniques, also known as Q stage techniques, have been used to remove transition metal ions from pulp, thereby enhancing brightness levels. Y. Ni et al., Pulp & Paper Canada, vol. 98, T285 (1998). Treatment of pulp with sodium hydrosulfite prior to chelation, known as the Q_y stage technique, is believed to improve chelation of metals, thereby further enhancing pulp brightness. However, this technique is less effective at higher pH values, such as those encountered when precipitated calcium carbonate ("PCC") is used as a filler in a pulp and paper mill.

[0003] The problem addressed by this invention is to find a more effective method for brightening mechanical pulp at high pH values.

Statement of Invention

[0004] The present invention is directed to an improved method for brightening mechanical pulp under neutral or alkaline paper making conditions. The improvement comprises the steps of: (a) separating neutral or alkaline pulp dilution water into a high-solids stream and a neutral or alkaline low-solids stream; and (b) reusing the neutral or alkaline low-solids stream for pulp dilution purposes prior to a bleaching process.

Detailed Description

[0005]

Figure 1 is a graph showing the effect of differing levels of hydrosulfite on brightness at varying consistency levels.

Figure 2 is a graph showing the effect of white water components on brightening with 1.2% sodium hydrosulfite.

Figure 3 is a graph showing the effect of temperature on brightness at 60 minutes retention and 3.5% consistency and at varying hydrosulfite levels.

Figure 4 is a graph showing the effect of temperature on brightness at 10 minutes retention and 3.5 % consistency and at varying hydrosulfite levels.

Figure 5 is a graph showing the effect of retention time on brightness at 80°C and 3.5% consistency and at varying hydrosulfite levels.

Figure 6 is a graph showing the effect of retention time on brightness at 70°C and 3.5% consistency and at varying hydrosulfite levels.

[0006] Dilution water (i.e. cloudy white water) typically is added to mechanical pulp prior to a bleaching step. In an integrated pulp and paper mill, the dilution water is a recycled stream from the paper making operations. In acid-based mills, the dilution water typically is at a pH from 4 to 5, and contains impurities such as pulp fines, suspended and dissolved solids, fillers and transition metal ions. In a neutral to alkaline paper making environment, i.e., one that utilizes PCC as a filler, the dilution water is at a pH from 6 to 8, and contains impurities such as pulp fines, suspended calcium carbonate, and transition metal ions. Of these impurities, transition metals can be especially troublesome as they can catalyze the decomposition of bleaching chemicals resulting in reduced bleaching efficiency and lower brightness levels. They also tend to increase brightness reversion and thus further contribute to lowering the brightness of bleached pulp. Both reductive and oxidative bleaching chemicals are affected by transition metals. The most commonly used oxidative bleaching chemical is hydrogen peroxide. Reductive bleaching chemicals typically are aqueous reducing agents, including, e.g., dithionite anion, also known as hydrosulfite, borohydrides and bisulfites, and formamidine sulfinic acid.

[0007] The present inventors have determined that use of cloudy white water from neutral to alkaline processes for dilution of pulp decreases the brightness level attainable with reducing agents, such as hydrosulfite. According to this invention, the neutral or alkaline cloudy white water used by the industry for the dilution of pulp prior to a bleaching process can be separated into a high-solids-containing as well as a low-solids-containing stream for treatment to improve the aforementioned bleach process. Separation of the cloudy white water is achieved using any of the methods well-known in the pulp industry for separation of solids, including, e.g., retaining fines on a paper machine wire, processing through a saveall or a clarifier, and flotation or filtration devices. The levels of solids in the low- and high-solids streams are determined by the initial level of solids in the cloudy white water and the method of separation. The amount of solids in the high-solids stream is not critical because this stream can be handled by solids or slurry handling equipment at a variety of solids contents. The high-solids stream can be as much as 30%, or even 40% solids and still be handled as a stream. Moreover, when the high-solids stream is separated by filtration, it is a wet filter cake, which may have an extremely high solids content. The low solids stream contains no more than 5000 ppm of solids, preferably no more than 2000 ppm, more preferably no more than 1000 ppm, still more preferably no more than 500 ppm, still more preferably no more than 250 ppm, and most preferably no more than 100 ppm.

[0008] According to this invention, the use of the low solids stream under neutral or alkaline conditions (pH 6 to 8) minimizes the adverse effects on the brightness of the resulting pulps. The Examples demonstrate that the reduction of the amount of solids in the cloudy white water significantly lowers the levels of transition metals and other impurities in the low solids stream and thereby improves the efficiency of bleaching. Preferably, the pH of the dilution water is from 6.5 to 7.5.

[0009] In one aspect of this invention, the low-solids stream is introduced into a bleaching step. In another aspect of this invention, the low-solids stream is added to the mechanical pulp entering a paper making machine. In one aspect of this invention, the high-solids stream is treated with at least one chelant and at least one reducing agent to produce a treated high-solids stream. Suitable chelants include, e.g., DTPA, STPP, EDTA, and phosphorus-containing chelants, e.g., phosphonate- and phosphonic-acid chelants. In one aspect of this invention, the treated high-solids stream from the process is added to the mechanical pulp entering a paper making machine. In another aspect of this invention, the treated high-solids stream is introduced into a bleaching step. In another aspect of this invention, an untreated high-solids stream is added to the mechanical pulp entering a paper making machine.

[0010] Chemical treatment of the high solids stream recovered from cloudy dilution water from neutral or alkaline processes according to the method of this invention allows recycling of the solids without adverse effects on brightness of the resulting paper and pulps. Without being bound by theory, it is believed that addition of a reducing agent to the solids recovered from the pulp dilution water reduces the valences of the transition metal ions. The reduced valences in turn result in better chelation of transition metals, and treated solids that typically have reduced levels of transition metals, and thus can be introduced into the bleaching and paper making process without adversely affecting pulp brightness.

[0011] It is preferred that the reducing agent is dithionite anion, i.e., hydrosulfite anion. Examples of other reducing agents are borohydride ion and bisulfite ion. Most preferably, the reducing agent is sodium hydrosulfite generated from treatment of sodium bisulfite with sodium borohydride, the latter preferably in the form of a strongly basic aqueous solution, e.g., the product containing 12% sodium borohydride and 40% sodium hydroxide, and sold by Rohm and Haas Company under the name Borol™ solution. Sodium dithionite produced in this manner is known as Borol™-solution-generated hydrosulfite ("BGH").

Examples

Example 1: Effect of Process Conditions on BGH Brightening

[0012] Pulp and white water used in this study were obtained from a North American mill. The pulp was a chemothermomechanical pulp (cTMP), which was collected after the secondary refiners and prior to the latency chest. The Precipitated Calcium Carbonate (PCC) containing white water (WW) was collected just prior to dilution at the latency chest. Studies were conducted to determine the effect on BGH bleached pulp brightness levels of the following four process variables: retention time, bleaching temperature, and bleaching consistency using either PCC-containing white water (WW) or deionized (DI) water for dilution of the pulp slurry. The hydrosulfite dosage (hydro) was 0-24 lbs./ton BGH at a pH of 10. The raw data for these experiments can be seen in Table 1. Temperatures are in °C (Temp.), retention times are in minutes, consistency ("Consist.") in weight % of pulp in the pulp slurry, deionized water had a pH of 6.5 and PCC-containing white water a pH of 7.5, and brightness is given as a percentage ISO. The pulp was cTMP with a pH of 7.1. Initial pH, (before hydrosulfite addition) and final pH (after hydrosulfite addition and after retention time) are also tabulated for each experiment.

Table 1:

cTMP Bleaching Results

Initial pH	Hydro (lb/ton)	Final pH	Time (min.)	Temp. (°C)	Consist. (%)	Water Type	Bright. (% ISO)
6.9	0	6.8	60	80	3.5	WW	47.4
6.9	8	6.7	60	80	3.5	WW	52.3
6.9	16	6.8	60	80	3.5	WW	54.5

Table 1: (continued)

cTMP Bleaching Results							
Initial pH	Hydro (lb/ton)	Final pH	Time (min.)	Temp. (°C)	Consist. (%)	Water Type	Bright. (% ISO)
6.9	24	6.8	60	80	3.5	WW	55.5
6.5	0	6.5	60	80	3.5	DI	50.4
6.5	8	6.6	60	80	3.5	DI	56.5
6.5	16	6.7	60	80	3.5	DI	57.8
6.5	24	6.7	60	80	3.5	DI	59.9
6.9	0	6.9	60	70	3.5	WW	46.9
6.9	8	6.9	60	70	3.5	WW	51.9
6.9	16	6.9	60	70	3.5	WW	52.8
6.9	24	6.9	60	70	3.5	WW	54.4
6.5	0	6.5	60	70	3.5	DI	49.8
6.5	8	6.7	60	70	3.5	DI	55.3
6.5	16	6.8	60	70	3.5	DI	57.4
6.5	24	6.7	60	70	3.5	DI	58.8
6.9	0	6.8	10	80	3.5	WW	47.1
6.9	8	6.8	10	80	3.5	WW	50.9
6.9	16	6.8	10	80	3.5	WW	52.7
6.9	24	6.7	10	80	3.5	WW	53.2
6.5	0	6.5	10	80	3.5	DI	50.2
6.5	8	6.6	10	80	3.5	DI	55.0
6.5	16	6.5	10	80	3.5	DI	56.9
6.5	24	6.6	10	80	3.5	DI	57.8
6.9	0	6.9	10	70	3.5	WW	47.4
6.9	8	6.9	10	70	3.5	WW	50.2
6.9	16	6.8	10	70	3.5	WW	51.8
6.9	24	6.9	10	70	3.5	WW	52.3
6.5	0	6.5	10	70	3.5	DI	50.0
6.5	8	6.6	10	70	3.5	DI	53.6
6.5	16	6.7	10	70	3.5	DI	55.7
6.5	24	6.7	10	70	3.5	DI	56.1
7.1	0	7.1	10	80	6.5	WW	47.9
7.1	8	7.0	10	80	6.5	WW	52.5
7.1	16	7.0	10	80	6.5	WW	54.1
7.1	24	6.9	10	80	6.5	WW	55.2
6.8	0	6.8	10	80	6.5	DI	49.7
6.8	8	6.8	10	80	6.5	DI	54.8
6.8	16	6.8	10	80	6.5	DI	56.2

Table 1: (continued)

cTMP Bleaching Results							
Initial pH	Hydro (lb/ton)	Final pH	Time (min.)	Temp. (°C)	Consist. (%)	Water Type	Bright. (% ISO)
6.8	24	6.7	10	80	6.5	DI	56.0
7.2	0	7.2	10	80	10	WW	47.9
7.2	8	6.7	10	80	10	WW	52.7
7.2	16	6.5	10	80	10	WW	54.0
7.2	24	6.5	10	80	10	WW	56.1
6.9	0	6.9	10	80	10	DI	49.1
6.9	8	6.5	10	80	10	DI	53.5
6.9	16	6.3	10	80	10	DI	55.3
6.9	24	6.3	10	80	10	DI	56.1

[0013] Figures 1-6 depict the effect on bleached brightness of various combinations of the process conditions investigated. Figure 1 shows the effect of bleaching consistency and the type of dilution water used on BGH bleached pulp brightness. Traditionally, it has been difficult to obtain a brightness increase at higher consistencies in laboratory-scale studies, although mill experience has shown that brightness increases with increasing consistency. This is believed to be due to the difficulty in effectively mixing pulp and chemicals at medium consistency in the laboratory. Therefore, the fact that the present study showed that the brightness of bleached pulp decreased with increasing consistency when the pulp was diluted with deionized water was not surprising. However, the fact that the brightness of bleached pulp increased with increasing consistency when the pulp was diluted with PCC-containing white water was unexpected. Without being bound by theory, it is believed that PCC-containing white water has a large negative effect on brightness. The decrease in that negative effect at higher bleaching consistency, where there is less PCC-containing white water present because less water is used for dilution relative to low consistency bleaching, has a positive effect on brightness. This positive effect is larger than the negative effect from increased consistency that is usually observed due to poor mixing for laboratory scale bleaching. Table 2 summarizes the averaged effect of changes in consistency, temperature and retention time on brightness in pulp diluted with either deionized water (DI) or PCC-containing vhite water (WW). The average brightness gains were calculated by taking the average of the brightness gains throughout the response curve of Figure 1, i.e., from 8 to 24 pounds of BGH per ton of pulp.

Table 2:

Effect of Changes in Process Conditions on Average Brightness Gains			
Process Condition	Change	DI	WW
Consistency	3.5 to 10.0	-1.8	+1.9
Temperature	70°C to 80°C	+1.4	+1.0
Retention Time	10 min to 60 min	+1.8	+1.8

[0014] Table 3 shows the effect of changing from DI water to PCC-containing white water at two different BGH levels:

Table 3:

Effect on Brightness of Changing from DI to PCC White Water	
BGH Level	Change in Brightness
8 lbs./ton	-3
24 lbs./ton	-5

[0015] Table 4 shows the maximum absolute brightness level achieved with each process variable combination tested.

Table 4:

Maximum Absolute Brightness Level Obtained				
Time	Temp.	Consistency	Brightness with DI water	Brightness with PCC water
60	80	3.5	59.9	55.6
60	70	3.5	58.8	54.4
10	80	3.5	57.8	53.2
10	70	3.5	56.1	52.3
10	80	6.5	56.0	55.2
10	80	10.0	56.1	56.2

[0016] These results demonstrate that the use of PCC-containing white water for pulp dilution has a negative effect on BGH brightening. However, these results also suggest that this effect is mitigated to some degree by adjustment of process conditions, for example, by increasing the bleaching consistency.

Example 2: Fines (solids) Removal and Reuse of Low-Solids White Water

[0017] Figure 2 compares the BGH-bleached pulp brightness of pulp diluted with DI water, PCC-containing white water, the filtrate of PCC-containing white water, and fines that were removed by filtration of PCC-containing white water and re-suspended in DI water. The results show that the removal of solids and reuse of low solids white water for bleaching purposes minimizes the adverse effects of BGH brightening under alkaline or neutral conditions. The results also show that it is the fines portion, which consists of actual pulp fines, undissolved solids, and transition metals in the white water that is responsible for most of the brightness loss. Based on these results, further testing of the fines portion of PCC containing white water was undertaken and is summarized in the following examples.

[0018] Results of transition metal analysis of the pulp, the white water filtrate, and the fines are shown in Table 5.

Table 5:

Metals Concentration (in ppm) for cTMP & PCC-Containing White Water Portions						
	Al	Ca	Cu	Fe	Mg	Mn
Pulp	17	1760	0.9	40	190	111
PCC Fines High solids	822	96200	7	667	587	183
PCC WW Low solids	2	217	0.1	1.2	9	2

[0019] By far the largest concentration of metal is 96,200 ppm of calcium, almost 10%, in the fines portion of the white water. This high level results from the presence of precipitated calcium carbonate (PCC) in the white water. It is believed that the white water is detrimental to BGH brightening because the white water introduces large amounts of impurities to the pulp slurry. The high iron concentration is detrimental to hydrosulfite brightening. The high manganese concentration is also of concern, especially in the case of peroxide brightening. Manganese is well known as a catalyst for decomposition of peroxide.

Example 3: Fines Treatment and Re-use

[0020] To reduce the transition metal concentrations, fines were treated by the Qy process. The fines first were treated with 0.1% BGH and then with 0.5% diethylenetriaminepentaacetic acid (DTPA). Experiments were conducted at a pH of 5.5, a consistency of 3.0%, and a temperature of 50°C for 30 minutes. The Qy treatment is believed to be more effective than the Q treatment, i.e., use of only chelant, because reduction of transition metal valence state by BGH renders the transition metal ions more amenable to chelation. The Qy treatment allows higher brightness levels when using hydrogen peroxide as a brightening agent. Table 6 shows the results from Q and Qy treatments on the fines portion of PCC-containing white water.

Table 6:

Metal Levels After Q or Qy Treatment of Fines From PCC-Containing White Water						
(levels in ppm, unless otherwise indicated)						
	Al	Ca (%)	Cu	Fe	Mg	Mn
Q	807	8.23	4.3	668	336	76.1
Qy	726	6.84	3.3	638	312	61.2
Control	821	9.99	3.4	667	504	165

[0021] The results demonstrate that the Qy process enhanced removal of transition metals from the fines portion of PCC white water.

[0022] Table 7 shows the results from Qy treatment on the pulp portion with BGH and DTPA, and from Q treatment with DTPA alone. The metal levels are given in ppm.

Table 7:

Treatment of cTMP Pulp by Q and Qy Methods							
Treatment	DTPA, %	BGH, %	Al	Cu	Fe	Mg	Mn
Q	0.5	-	21	0.7	24	130	9
Q	0.13	-	13	0.8	43	133	48
Qy	0.5	0.1	14	0.7	18	123	6
Qy	0.13	0.1	11	1.1	19	120	44
Control	0	0	17	0.9	40	190	111

[0023] The table demonstrates that good results are obtained for reduction of manganese and iron, both of which are associated with poor brightening with BGH and hydrogen peroxide. Although the difference in manganese concentration is small, Qy treatment produces a lower level of manganese than Q treatment. For iron, the results are more readily apparent. Even at the lower level of DTPA, the iron level is substantially lower for the Qy treatment. It is important to note that this pulp sample was taken at the secondary refiner outlet, prior to addition of mill white water. In reality, the pulp entering the bleach plant would have higher levels of metals from the PCC-containing white water dilution.

[0024] Table 8 shows the results from brightening with BGH the treated pulp described in Table 7. Brightness (B) is given in % ISO, and levels of iron and manganese in ppm. These results demonstrate that at relatively low initial levels of transition metals in pulp, the Qy treatment produces a higher brightness pulp. Thus, Qy treatment would be more effective on pulps with higher initial transition metal concentrations.

Table 8:

BGH Brightening of Q and Qy Treated cTMP				
	BGH, %	Fe	Mn	B
0.5% DTPA (Q)	1.2	24	9	58.3
0.13% DTPA (Q)	1.2	43	48	57.2
0.5% DTPA + 0.1% BGH (Qy)	1.2	18	6	58.5
0.13% DTPA + 0.1% BGH (Qy)	1.2	19	44	57.4

[0025] Tables 9 and 10 show the results of hydrogen peroxide brightening of pulps treated as shown in Table 7. Peroxide (H_2O_2) bleaching was carried out with a sodium hydroxide dosage of 1.5% for 3% peroxide and 2.0% for 5% peroxide. The sodium silicate dosage was 2.5%, magnesium sulfate dosage was 0.05%, the consistency was 12.0%, the temperature was 80°C and the bleaching time was 2 hours. The results for % ISO brightness (B) demonstrate that the pulps receiving the Qy treatment display a greater brightness enhancement along with a higher residual peroxide level than those subjected to Q treatment. Transition metal levels are given in ppm, with other measurements given as per cent values.

Table 9:

Hydrogen Peroxide (P) Brightening of Q and Qy treated cTMP (5.0 % H_2O_2)					
	H_2O_2	Fe	Mn	B	Residual Peroxide
0.5% DTPA (Q)	5.0	24	9	72.9	9.2
0.13% DTPA (Q)	5.0	43	48	71.6	6.3
0.5% DTPA + 0.1% BGH (Qy)	5.0	18	6	73.5	15.1
0.13% DTPA + 0.1% BGH (Qy)	5.0	19	44	71.9	8.4

Table 10:

Hydrogen Peroxide Brightening of Q and Qy Treated cTMP (3.0 % H_2O_2)					
	H_2O_2	Fe	Mn	B	Residual Peroxide
0.5% DTPA (Q)	3.0	24	9	69.5	7.6
0.13% DTPA (Q)	3.0	43	48	67.0	4.3
0.5% DTPA + 0.1% BGH (Qy)	3.0	18	6	69.6	13.2
0.13% DTPA + 0.1% BGH (Qy)	3.0	19	44	67.8	8.1

Claims

1. An improved method for brightening mechanical pulp under neutral or alkaline paper making conditions; said improvement comprising steps of:

(a) separating neutral or alkaline pulp dilution water into a high-solids stream and a neutral or alkaline low-solids stream; and
(b) reusing the neutral or alkaline low-solids stream for pulp dilution purposes prior to a bleaching process.

2. The method of claim 1 in which said high-solids stream is treated with at least one chelant and at least one reducing agent to produce a treated high-solids stream.

3. The method of claim 2 in which the neutral or alkaline pulp dilution water and the neutral or alkaline low-solids stream have a pH from 6 to 8.

4. The method of claim 3 in which the treated high-solids stream is added to mechanical pulp entering a paper making machine.

5. The method of claim 3 in which the treated high-solids stream is introduced into a bleaching step.

6. The method of claim 3 in which the pulp dilution water contains suspended calcium carbonate.

7. The method of claim 6 in which said at least one reducing agent comprises dithionite anion.

8. The method of claim 1 in which the low-solids stream is added to mechanical pulp entering a paper making machine.

9. The method of claim 8 in which the neutral or alkaline pulp dilution water and the neutral or alkaline low-solids stream have a pH from 6 to 8.

10. The method of claim 1 in which the high-solids stream is added to mechanical pulp entering a paper making machine.

Fig. 1

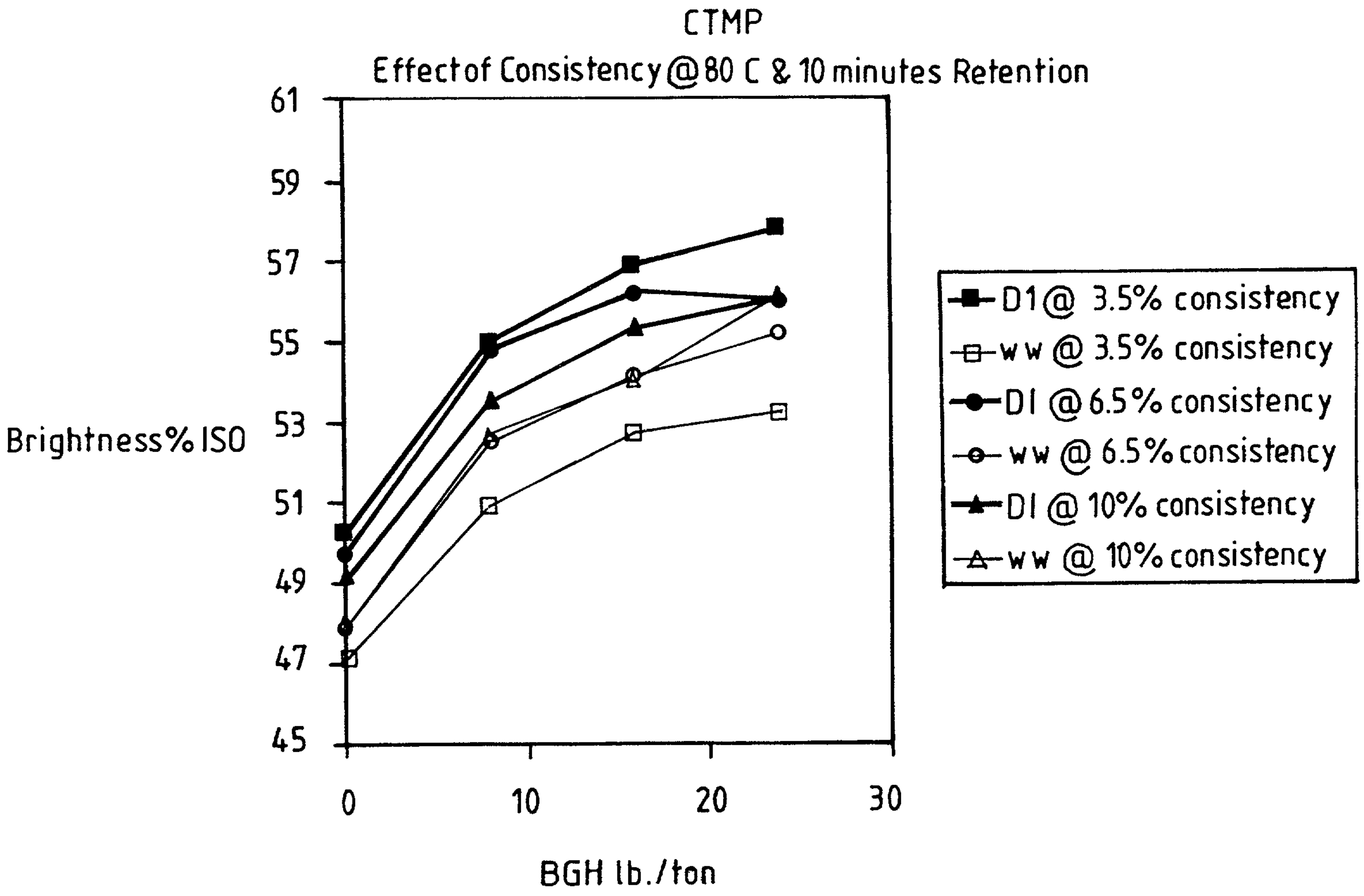

CTMP
Effect of Consistency @ 80 C & 10 minutes Retention
Brightness% ISO
61
59
57
55
53
51
49
47
45
0
10
20
30
BGH lb./ton
■ D1 @ 3.5% consistency
□ ww @ 3.5% consistency
● DI @ 6.5% consistency
○ ww @ 6.5% consistency
▲ DI @ 10% consistency
△ ww @ 10% consistency

Fig. 2

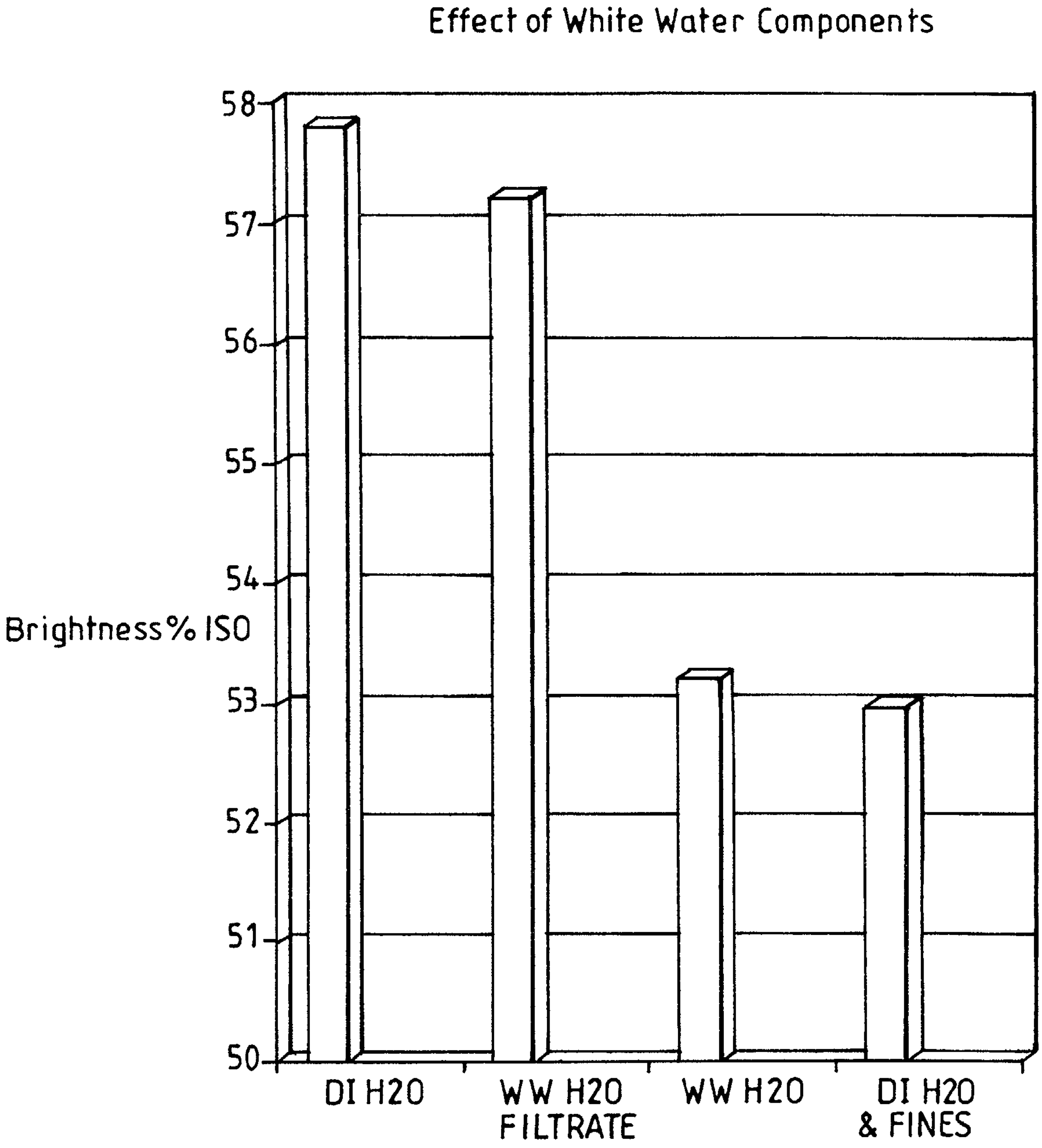
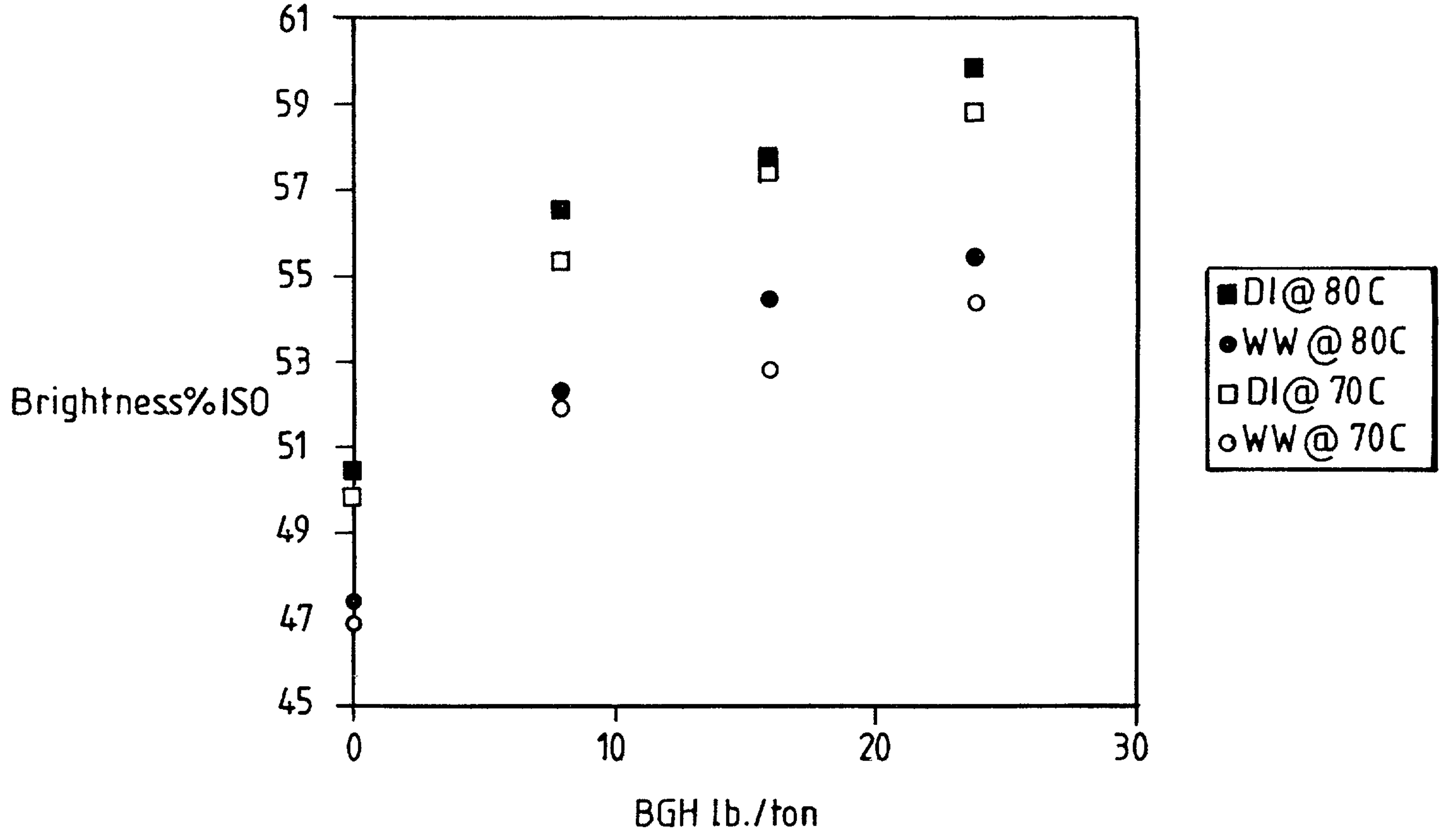
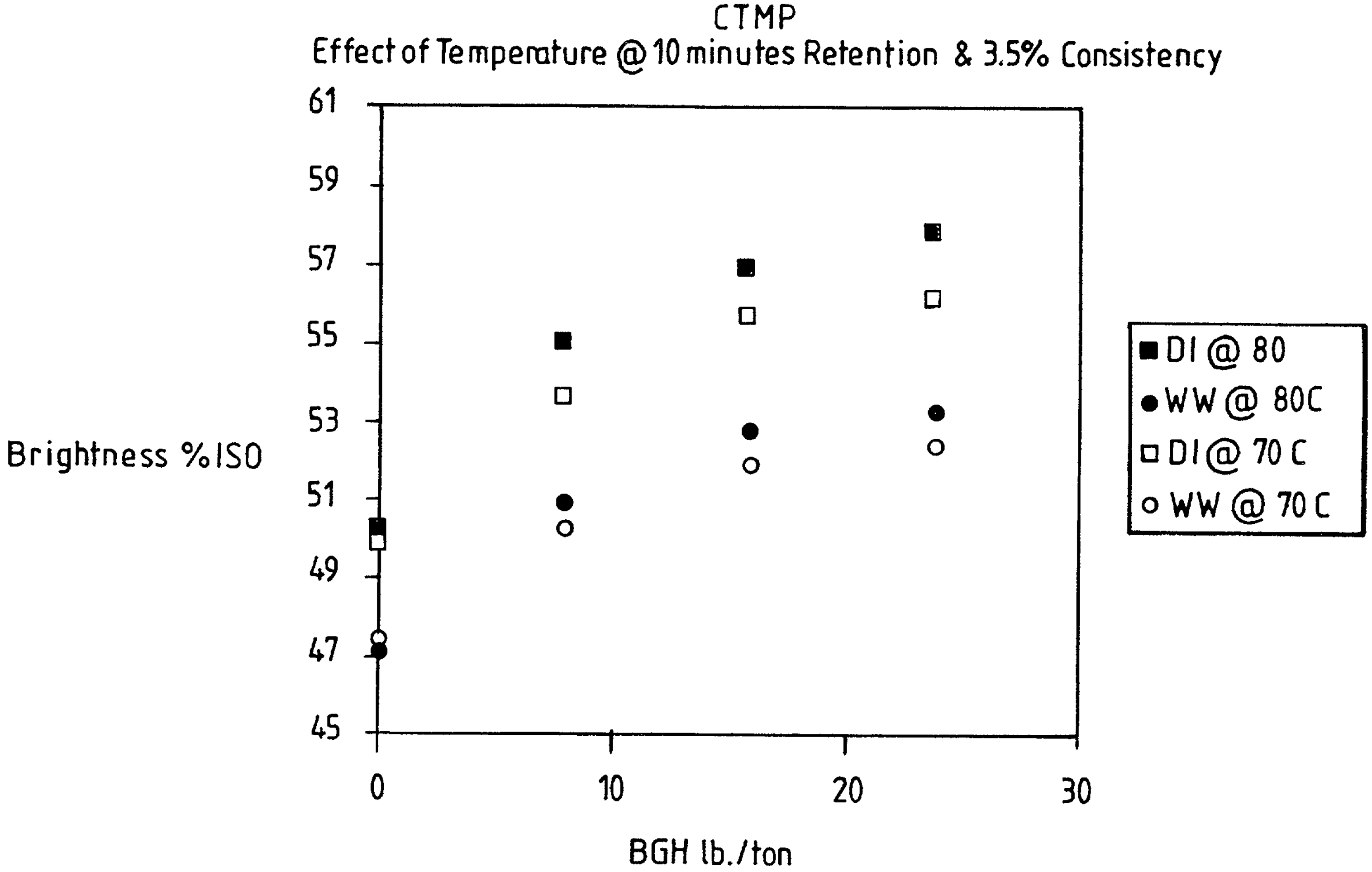

Effect of White Water Components
Brightness % ISO
58
57
56
55
54
53
52
51
50
DI H2O
WW H2O FILTRATE
WW H2O
DI H2O & FINES

Fig. 3



CTMP
Effect of Temperature@60 minutes Retention & 3.5% Consistency

Fig. 4



CTMP
Effect of Temperature @ 10 minutes Retention & 3.5% Consistency

Fig. 5

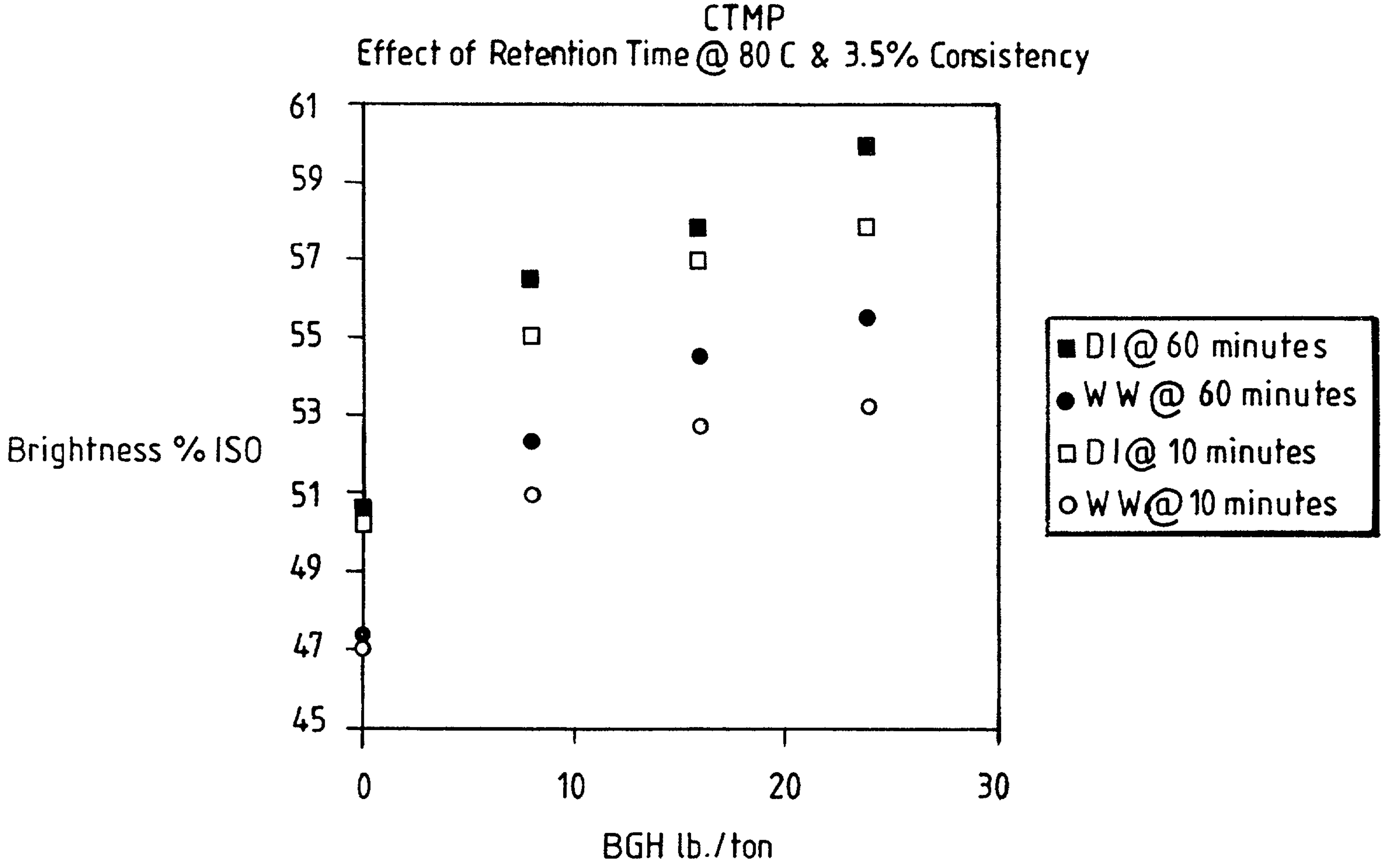
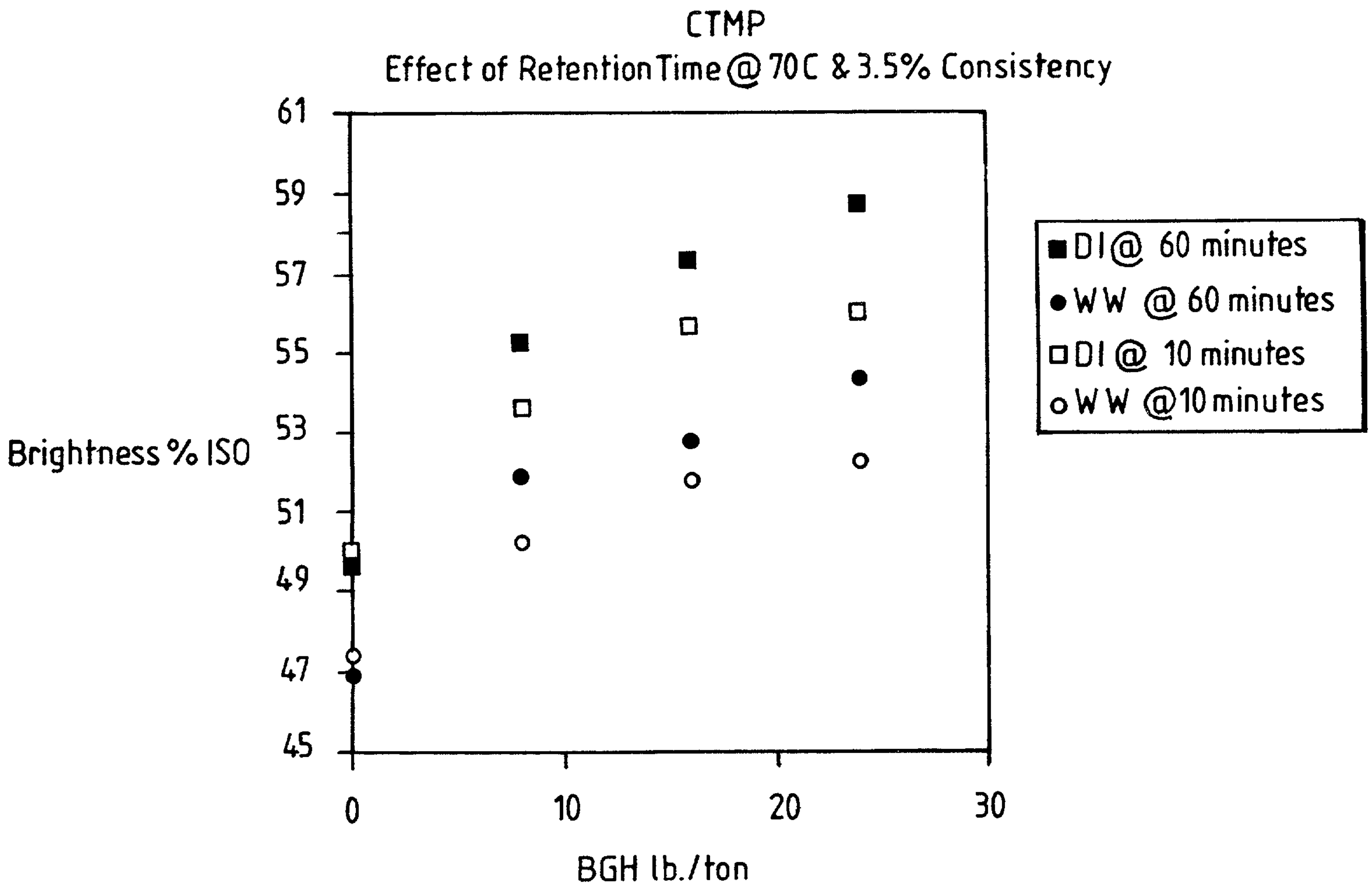

CTMP
Effect of Retention Time @ 80 C & 3.5% Consistency
Brightness % ISO
61
59
57
55
53
51
49
47
45
0
10
20
30
BGH lb./ton
■ DI @ 60 minutes
● W W @ 60 minutes
□ D I @ 10 minutes
○ W W @ 10 minutes

Fig. 6



CTMP
Effect of Retention Time @ 70C & 3.5% Consistency

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 25 3048

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 90 11403 A (HYMAC LTD) 4 October 1990 (1990-10-04) * figure IA *	1-10	D21C9/10
A	CA 1 328 714 A (MAC MILLAN BLOEDEL LTD) 26 April 1994 (1994-04-26) * figures 1,2 *	1-10	
A	WO 00 53844 A (BENGTSSON SVERKER ;HOLMEN AKTIEBOLAG (SE); WANCKE STAAHL CHARLOTTE) 14 September 2000 (2000-09-14) * figure 1 *	1-10	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	29 August 2002	Naeslund, P

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