MILL TRIAL AND COMMERCIAL IMPLEMENTATION OF THE NEW BLEACHING AGENT - THPS

Thomas Q. Hu[1], Trevor Williams[1], John A. Schmidt[2], Brian R. James[3], Roger Cavasin[4], and Drew Lewing[4]
[1]Paprican, 3800 Wesbrook Mall, Vancouver, BC, Canada V6S 2L9 (thu@paprican.ca)
[2]Paprican, 570 boul. St-Jean, Pointe Claire, QC, Canada H9R 3J9
[3]Dept. of Chemistry, UBC, Vancouver, BC, Canada V6T 1Z1
[4]Cytec Canada Inc., P.O. Box 240, Niagara Falls, ON, Canada L2E 6T4

ABSTRACT

We have successfully conducted an 8-day mill trial using tetrakis(hydroxymethyl)phosphonium sulfate (THPS), $[P(CH_2OH)_4]_2SO_4$, as a complementary bleaching agent to sodium hydrosulfite (Y) in the bleaching of spruce stone-ground wood (SGW) pulp. Addition of 1.0 kg THPS/t pulp to the hydrosulfite bleaching provided an average, additional brightness gain of 2.0-2.3 ISO points to the pulp without any process upsets in the bleach plant or on the paper machine. This additional brightness gain, sustained during the subsequent commercial implementation of such a “THPS + Y” bleaching technology, has allowed the mill to reach the brightness target at reasonable cost even during the difficult summer period, and to reduce the consumption of expensive brightness-enhancing additives in the coating color when producing hi-brite LWC papers. Overall estimated cost saving to the mill is in the order of Cdn$250,000 per year.

INTRODUCTION

Industrial bleaching of mechanical pulps is currently achieved by the use of alkaline hydrogen peroxide [1] and/or sodium hydrosulfite (i.e. sodium dithionite) [2]. Alkaline hydrogen peroxide, in the presence of peroxide stabilizers such as sodium silicate and magnesium sulfate, is capable of providing a brightness gain of up to ~25 ISO points to most mechanical pulps. However, alkaline peroxide reduces the pulp yield by 2-5% and produces effluent with high chemical oxygen demand [3] due to oxidative degradation of lignin and hemicelluloses from the fibres.

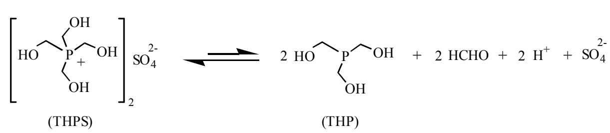
Sodium hydrosulfite is a cheap and selective bleaching agent currently used by 45 mills in Canada and in the US to bleach ~12 million metric tons of mechanical pulps/year. However, hydrosulfite can only provide a maximum brightness gain of ~10 ISO points to most mechanical pulps. In addition, hydrosulfite-bleached pulps are highly unstable; they undergo rapid brightness reversion when they are, for example, diluted with neutral paper machine white water and stored at elevated temperatures. The brightness ceiling and the brightness reversion of hydrosulfite-bleached pulps often make it difficult for mills to achieve the brightness targets for their products when the incoming wood is darker (e.g. during summer months) or when mills wish to produce higher brightness papers.

Several other chemical agents capable of bleaching mechanical pulps have been reported over the past few decades [4-12]. Such bleaching has been achieved with, for example, sodium borohydride [4], thiols [5], formamidine sulfinic acid (FAS) [7], amino boranes [10] or a spirophosporane [11]. None of these agents has been used commercially for the bleaching of virgin mechanical pulps because of their high cost (e.g. sodium borohydride), high toxicity (e.g. thiol), or low bleaching ability (e.g. spirophosphorane). FAS has found applications in the bleaching and/or color stripping of recycled fibres including mixed office waste [13,14].

Recently, Hu, James, and co-workers discovered that H_2O-soluble, tertiary hydroxyalkyl phosphines and quaternary hydroxymethyl phosphonium salts are effective bleaching and brightness stabilizing agents for mechanical pulps [15-20]. These phosphorus (P) compounds have a bleaching power similar to or higher than that of sodium hydrosulfite, but are less sensitive to pH, consistency and elevated temperature [14-19], and produce bleached pulps with higher thermal stability [20].

Among the P-compounds discovered, tetrakis(hydroxymethyl)phosphonium sulfate (THPS), $[P(CH_2OH)_4]_2SO_4$, is the most promising candidate for commercialization because it is extremely water-soluble, air-stable, and is commercially available in large quantities (~10,000 metric tons/annum). Commercial, 75% solution of THPS, prepared from the reaction of phosphine, PH_3, with 4.0 molar equivalents of formaldehyde, HCHO, and 0.5 molar equivalent of sulfuric acid, H_2SO_4 [21], is stable for months in the presence of air. THPS is used to make flame retardants for cotton and cellulose fabrics [22], as an iron-sequestering agent in oil fields [23], as a leather tanning agent, and as an environmentally-friendly biocide for sulfate-reducing bacteria in industrial water-treatment including paper mill white water treatment [24].

Aqueous solutions of THPS are acidic (pH ~3.2) due to the small dissociation of THPS to tris(hydroxymethyl)phosphine (THP), $P(CH_2OH)_3$, formaldehyde, HCHO, and sulfuric acid (Eq. 1) ($pK_d = 12.20$) [25,26]:



(1)

When THPS comes into contact with pulp slurries that have a pH of 5.0 to 7.0, the equilibrium will be shifted to the right and THP will become one of the dominant species in the solutions. THP, capable of undergoing nucleophilic addition to the C=C-C=O units in lignin chromophores such as coniferaldehyde and 2-methoxy-*p*-benzoquinone [27], is likely the active species in THPS bleaching. Although THP can be made from the reaction of PH_3 with 3.0 molar equivalents of HCHO and is cheaper than THPS on the same molar phosphorus basis, it is not produced or used on a commercial scale because of its low stability.

Previously, Hu, James, and co-workers have shown that THPS provides an ISO brightness gain of 7.7 and 10.5 points to a spruce TMP (from 58.2 to 65.9%) and a lodgepole pine TMP (from 54.6 to 65.1%), respectively [17,18]. In this report, we describe a laboratory evaluation and a successful 8-day mill trial of THPS as a complementary bleaching agent to sodium hydrosulfite (Y) in the bleaching of spruce stone-ground wood (SGW) pulp. During the mill trial and subsequent commercial implementation, we combined a commercial THPS solution with the hydrosulfite solution near the bleach tower, and we designated such one-stage bleaching "THPS + Y" bleaching.

METHODS AND MATERIALS

General

Tetrakis(hydroxymethyl)phosphonium sulfate (THPS), $[P(CH_2OH)_4]_2SO_4$, was provided as a 75% solution (pH = ~3.2, specific gravity = 1.41 at 20°C) by Cytec Canada (Niagara Falls, ON, Canada) for both the laboratory bleaching and the mill trial. For the laboratory bleaching, the active THPS concentration was determined based on the procedure for the quantitative determination of tris(2-carboxyethyl)phosphine [28]. Sodium hydrosulfite (Y), $Na_2S_2O_4$, was purchased from Fisher Scientific and its active concentration determined according to TAPPI Test Method T622 cm-01 [29]. Spruce stone-ground wood (SGW) pulp slurry (~4.0% Cs) was taken at the exit of the SGW storage in a Paprican member mill. The pulp slurry was dewatered in the lab to ~20% Cs to allow for accurate Cs determination. The filtrate (pH 5.0) was saved aside in a refrigerator and used for the laboratory bleaching experiments (*see* below) while the pulp was frozen to maintain stable brightness. All chemicals doses used for the lab bleaching are reported in percentage with respect to oven-dried (o.d.) weight pulp.

Laboratory Sodium Hydrosulfite (Y), THPS or "THPS + Y" Bleaching

For Y or THPS bleaching, the dewatered spruce SGW pulp (4.0-20 g o.d.) was combined with a known amount of the saved filtrate and Y (0.2-1.0%) or THPS (0.1-1.0%) in a polyester bag to give a 4.0% Cs pulp slurry. For "THPS + Y" bleaching, Y (0.2-1.0%) was combined with 0.1% THPS in a small amount of the saved filtrate, and added along with a known amount of the saved filtrate to the dewatered spruce SGW pulp (4.0-20 g o.d.) in a polyester bag to give a 4.0% Cs pulp slurry. The bag was sealed with minimal headspace above the pulp slurry, and immersed in a water-bath heated at 65°C for 1.0 h with hand-mixing of the bag after 10 minutes. The polyester bag was cooled in a water-bath to ~20°C. The pulp was diluted with deionized (DI) water to 0.5-1.0% Cs, and the pulp slurry was filtered with the filtrate being recycled once to recover the fines. The same dilution and filtration were then repeated once. Handsheets (200 g/m^2) of the Y-, THPS- or "THPS + Y"-bleached pulps were prepared according to PAPTAC Test Methods (Standard C.5) [30], and their ISO brightness determined in a Technibrite Micro TB-1C instrument (Technidyne Co., New Albany, IN, USA) according to PAPTAC Test Methods, Standard E.1 [31].

Mill Trial of "THPS + Y" Bleaching

THPS (Cytec Canada, Niagara Falls, ON, Canada) was added via an L-shaped, stainless-steel tubing (*see* Fig. 3) to the sodium hydrosulfite addition line ~0.3 m away from the pulp line connecting the unbleached SGW storage tank and the up-flow bleach tower in the ground-wood plant at the mill. The L-shaped stainless-steel tubing was connected with a Nylon tubing (3/8 inches) to a ProMinent SIGMA/1 pump (ProMinent Fluid Controls Ltd. Guelph, ON, Canada) and then to a THPS tote (*see* Fig. 3). The flow rate of THPS was manually adjusted on the pump to give a dosage of 1.0 kg/t pulp (i.e. 0.1% THPS) based on the SGW pulp production rate. The addition rate of sodium hydrosulfite (Y) was controlled at 8.0 kg/t pulp (i.e. 0.8% Y) prior to, during and after the mill trial. Unbleached and bleached pulp slurries were taken manually once every four hours or longer at the exit of the SGW pulp storage tank and at the exit of the down-flow bleach tower, respectively (*see* Sampling Points A and B in Fig. 4). The temperature and the pH of the pulp slurries were measured immediately after sampling. Handsheets (200 g/m^2) of the pulps were prepared according to PAPTAC Test Methods (Standard C.5) [30], and their ISO brightness determined in a Technibrite Micro TB-1C instrument according to PAPTAC Test Methods, Standard E.1 [31].

RESULTS AND DISCUSSION

Trial Background

The mill bleached its spruce SGW pulp (typical ISO brightness = 64-66%, full production rate = ~350 metric tons/day) with 0.8-1.0% sodium hydrosulfite (Y) at 4.0% Cs, pH 5.0 and ~65°C. The bleaching occurred in an up-flow tower followed by a down-flow tower with a combined retention time of 1.0 h. Some of the Y-bleached pulp exiting the down-flow bleach tower was sent to paper machines (PMs) 2 and 3 that were run under acidic papermaking conditions. The rest of the Y-bleached pulp exiting the down-flow bleach tower was dewatered through a twin-wire press to ~35% Cs (to remove the acidic filtrate), diluted with neutral PM 4 white water to 4.0% Cs, and stored in a bleached pulp storage tank at pH ~6.8 and 50°C for up to 6.0 h before being sent to PM 4 to make LWC papers (*see* Fig. 4). Trim bleaching of the stored, Y-bleached pulp going to PM 4 with up to 1.0% sodium hydrosulfite was often needed to meet the ISO brightness target (~70%) of the LWC papers. When producing hi-brite (≥75% ISO brightness) LWC papers or when the ISO brightness of the unbleached SGW pulp was < 63%, the mill usually needed to add expensive brightness-enhancing additives in the coating formulation.

The mill was interested in the possible use of THPS to: 1) achieve the same brightness target with less bleach chemical; 2) overcome the brightness ceiling of Y bleaching so that ~70% ISO brightness target could be achieved when the brightness of the chips/unbleached SGW pulp was low (e.g. in the summer months); and/or 3) reduce the dosage of expensive brightness-enhancing additives when producing hi-brite LWC sheets.

Laboratory Evaluation of THPS and "THPS + Y" Bleaching

We first evaluated the bleach response of the spruce SGW pulp (ISO brightness = 66.2%) to Y and to THPS bleaching, respectively, at 4.0% Cs, pH 5.0 and 65°C in the laboratory. We found that at lower bleach chemical charges, THPS gave slightly higher brightness gain than Y, but at higher charges, THPS gave lower brightness gain than Y (Fig. 1). The lower bleach response of the pulp to THPS than to Y at higher bleach chemical charges was likely due to the incomplete reaction of ≥0.5% THPS with the pulp within 1.0 h at 65°C. Bleaching of the spruce and lodgepole pine TMP pulps to give an ISO brightness gain of 7.7 and 10.5 points, respectively, with THPS was done at 90-130°C for 3.0 h [17,18].

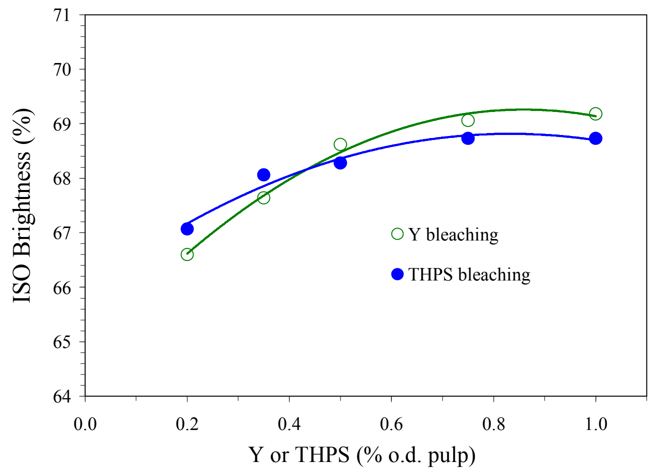


Fig. 1. Bleaching of the SGW pulp (ISO brightness = 66.2%) with sodium hydrosulfite (Y) or THPS at 4.0% Cs, pH 5.0 and 65°C for 1.0 h.

We next studied the bleaching of the spruce SGW pulp with 0.1% THPS and 0.2-1.0% Y combined in one-stage as an attempt to use THPS more effectively. These experiments were done based on the following considerations: 1) because the bleaching reaction of THPS with pulp was slow at 65°C, complete reaction of THPS with pulp over one hour would likely occur only at ≤0.2% THPS; 2) because THPS is more expensive than hydrosulfite, use of 0.1% THPS and perhaps ≥0.5% Y would be more economical; 3) because the bleaching chemistry of THP, the likely active species involved in the bleaching of the pulp with THPS, is different from that of hydrosulfite [27], a combination of THPS and Y might achieve a higher brightness than using either chemical alone; and 4) one-stage, simultaneous use of THPS and Y would be easy to implement in the mill.

The results of our laboratory study are shown in Figure 2 and Table I. Y bleaching was able to provide a maximum ISO brightness gain of 3.0 points to the SGW pulp (from 66.2 to 69.2%). When 0.1% THPS was used by itself to bleach the pulp, an ISO brightness gain of 0.9 point was obtained. Surprisingly, combining 0.1% THPS and Y produced a synergistic bleaching effect on the pulp at ≥0.35% Y and particularly at ≥0.50% Y (Table I). For example, bleaching of the pulp with 0.1% THPS and 1.0% Y produced a synergy of 1.1 ISO points; the synergy equals brightness gain from "0.1% THPS + 1.0% Y" bleaching minus brightness gain from 0.1% THPS bleaching minus brightness gain from 1.0% Y bleaching = 5.0 – 0.9 – 3.0 = 1.1. Because of such a synergy, adding 0.1% THPS to 1.0% Y bleaching provided an additional ISO brightness gain of 2.0 points to the pulp (i.e. the brightness ceiling of Y-bleached pulp was raised by 2.0 ISO points). Without the use of THPS, an increase of Y dosage from 1.0 to 1.5 or 2.0% failed to overcome the brightness ceiling of Y bleaching at a maximum ISO brightness gain of 3.0 points (Table I).

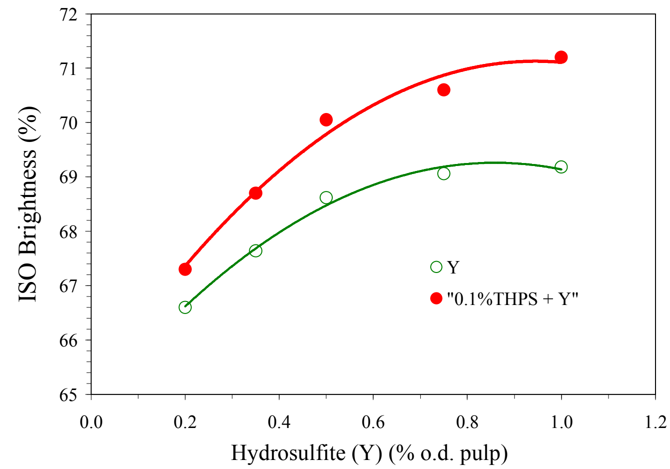


Fig. 2. Bleaching of the SGW pulp (ISO brightness 66.2%) with sodium hydrosulfite (Y) or "0.1% THPS + Y" at 4.0% Cs, pH 5.0 and 65°C for 1.0 h.

TABLE I. RESULTS FROM LABORATORY BLEACHING OF THE SGW PULP[a] WITH HYDROSULFITE (Y) AND/OR THPS

THPS (%)	Y (%)	ISO Brightness (%)	ΔBrightness (ISO point)	Synergy[b] (ISO point)
0.1	-	67.1	0.9	-
-	0.35	67.6	1.4	-
0.1	0.35	68.7	2.5	0.2
-	0.5	68.6	2.4	-
0.1	0.5	70.1	3.9	0.6
-	0.75	69.1	2.9	-
0.1	0.75	70.6	4.4	0.6
-	1.0	69.2	3.0	-
0.1	1.0	71.2	5.0	1.1
-	1.5	68.8	2.6	-
-	2.0	69.1	2.9	-

[a]ISO brightness of the unbleached SGW pulp = 66.2%; [b]Synergy = $\Delta Brightness_{(THPS + Y)}$ - $\Delta Brightness_{(THPS)}$ - $\Delta Brightness_{(Y)}$.

In separate studies, we have found that whether and how much synergy can be achieved with "THPS + Y" bleaching depends on the sodium hydrosulfite formulation, the pulp type, the temperature profile (preheating vs. no preheating) of the pulp immediately before the addition of the bleach chemical, the efficiency of air removal, and the bleaching pH. We have also found that one-stage, "THPS + Y" bleaching with a weight ratio of Y/THPS ≥6.0 removes the formaldehyde formed from the dissociation of THPS to THP through the reaction of formaldehyde with Y or bisulfite (a by-product of Y bleaching). The removal of formaldehyde from the bleaching system is important because formaldehyde is an irritant for the respiratory tract.

Mill Trial of "THPS + Y" Bleaching

Encouraged by the laboratory "THPS + Y" bleaching results, a mill trial of adding 1.0 kg THPS/t pulp (i.e. 0.1% THPS) to the Y bleaching of the SGW pulp was conducted in June 2005. The objectives of the mill trial were: 1) to quantify the additional brightness gain provided with 1.0 kg THPS/t pulp; and 2) to determine whether the addition of THPS to the Y bleaching would cause any process upsets in the bleach plant or on the paper machine.

For the mill trial, an L-shaped, stainless-steel tubing was connected to the sodium hydrosulfite (Y) addition line ~0.3 m away from the pulp line connecting the SGW storage tank and the up-flow bleach tower (Fig. 3). This L-shaped, stainless-steel tubing was connected with a Nylon-tubing to a ProMinent SIGMA/1 pump and then to the THPS tote (~1.4 tons of THPS on 100% basis). The addition rate (0.0 or 1.0 kg/t pulp) of THPS was controlled manually on the SIGMA pump based on the pulp production rate. The addition rate for Y was automatically controlled by the mill's control system at 8.0 kg/t pulp (i.e. 0.8% Y) prior to, during and after the "THPS + Y" bleaching trial.

Samples of the pulp slurries were manually taken once every four hours or longer at various locations with the key sampling points being at the exit of the spruce SGW storage tank (Sample Point A) and at the exit of the down-flow bleach tower (Sample Point B) (Fig. 4). The temperature and pH of the pulp slurries were measured immediately after sampling, and the ISO brightness values of the pulps were measured on the handsheets made from the pulps.

Fig. 3. Set-up for the "THPS + Y" bleaching mill trial.

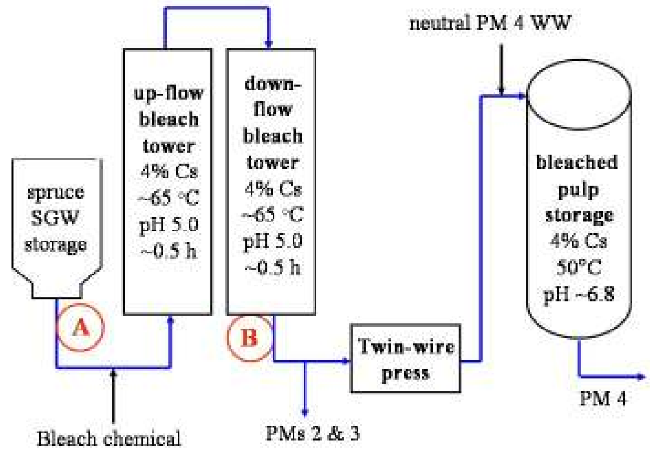


Fig. 4. Simplified bleaching process diagram in the bleach plant and the two key sampling points A and B during mill trial of "THPS + Y" bleaching.

Data collected over the first three days of the mill trial are listed in Table II. Before THPS was added to the system, control Y bleaching samples were taken and analyzed. The ISO brightness gain from the Y bleaching was 4.5 points (from 64.2 to 68.7%). Such a brightness gain was typical of what the mill had been able to achieve with 8.0 kg Y/t pulp.

A few hours after the "THPS + Y" bleaching had been started and the system reached a steady state, samples were taken again and analyzed. The ISO brightness gain from the "1.0 kg THPS/t pulp + 8.0 kg Y/t pulp" bleaching was 6.7 points (from 65.0 to 71.7%), 2.2 points more than the control Y bleaching. The next six sets of samples taken from the "THPS + Y" bleaching all gave superior results with the ISO brightness gains ranging from 5.2 to 8.2 points (Table II). It was noticed that the highest brightness gain of 8.2 points was achieved on the unbleached pulp with the highest temperature (77°C) while the lowest brightness gains (5.2 and 6.0 points) were obtained on the unbleached pulps with the lowest temperatures (≤63°C) (Table II).

TABLE II. DATA[a] FOR MILL TRIAL OF "THPS + Y" BLEACHING, SODIUM HYDROSULFITE CHARGE WAS 8.0 KG/T

THPS (kg/t)	ISO Brightness (%) at sample point A[b] (unbleached)	ISO Brightness (%) at sample point B[b] (bleached pulp)	ΔBrightness (ISO point)	Unbleached pulp temp. (°C)
-	64.2	68.7	4.5	68
1.0	65.0	71.7	6.7	67
1.0	63.9	69.9	6.0	62
1.0	64.9	70.1	5.2	63
1.0	61.9	70.1	8.2	77
1.0	63.4	71.1	7.7	72
1.0	62.9	70.5	7.6	71
1.0	62.5	68.9	6.4	70

[a]From samples collected over 3 days; [b](*See* Fig. 4 for location of sample point).

Encouraged by these results, the "THPS + Y" bleaching was allowed to run for 5 more days and twelve additional sets of pulp samples were taken and analyzed. Eight additional sets of pulp samples for the control Y bleaching were also taken and analyzed several hours after THPS addition stopped and the system reached a steady state. These control Y bleaching samples were taken over a period of 42 days.

Figure 5 shows the brightness gains of the Y bleaching and of the "THPS + Y" bleaching vs. the bleached and the unbleached pulp slurry temperatures, respectively, from the analyses of these additional samples and those shown in Table II. The brightness gain from the Y bleaching correlated linearly (with $R^2 = 0.8706$) to the bleached pulp temperature. The brightness gain from the "THPS + Y" bleaching correlated linearly with the unbleached pulp temperature, but the data were more scattered ($R^2 = 0.4861$) than those from the Y bleaching. Nonetheless, an average, additional brightness gain of 2.0 – 2.3 ISO points was clearly demonstrated for the "THPS + Y" bleaching over the Y bleaching. When the brightness gain of Y bleaching was plotted vs. the unbleached pulp slurry temperature, or the brightness gain of THPS bleaching was plotted vs. the bleached pulp slurry temperature, a lower R^2 was obtained ($R^2 = 0.5226$ and 0.2296, respectively), but an average, additional brightness gain of ~2.0 ISO points could again be clearly seen for the "THPS + Y" bleaching over the Y bleaching.

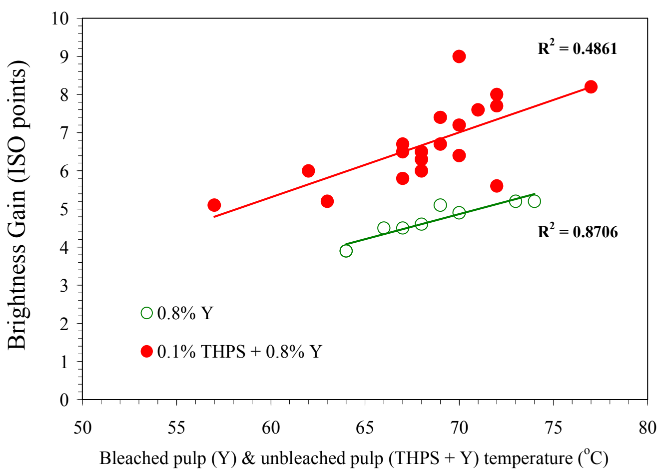


Fig. 5. ISO Brightness gain of 0.8% Y and "0.1% THPS + 0.8% Y" bleaching vs. bleached and unbleached pulp slurry temperatures, respectively, from the analysis of samples collected over 50 days.

During the 8-day mill trial of the "THPS + Y" bleaching, there were no process upsets in the bleach plant or on the paper machine. Compared with bleaching with hydrosulfite only, on average, the amount of Y used for the trim bleaching of the pulp going to PM 4 was reduced by 2.6 kg/t, while the ISO brightness of the pulp after trim bleaching was 1.2 points higher.

Mill Implementation of "THPS + Y" Bleaching and Estimated Cost Saving

Following the successful mill trial discussed above, the mill has implemented "THPS + Y" bleaching on a semi-permanent basis. The mill has consistently obtained an additional ISO brightness gain of ~2.0 points on the SGW pulp with 1.0 kg THPS/t pulp added to the Y bleaching. Such an additional brightness gain has allowed the mill to reach the brightness target when the ISO brightness of the unbleached SGW pulp is lower than 62.0% in the summer months, and to reduce the dosage of brightness-enhancing additives in the coating color when producing hi-brite, ≥75% ISO LWC papers. The cost saving from "THPS + Y" bleaching has been estimated at Cdn$250,000/year by the mill personnel.

CONCLUSIONS

An 8-day mill trial of using the phosphonium compound, THPS, as a complementary bleaching agent to sodium hydrosulfite (Y) in the bleaching of spruce stone-ground wood (SGW) pulp, has been successfully conducted. Addition of 1.0 kg THPS/t pulp to the hydrosulfite bleaching provided an average, additional brightness gain of 2.0-2.3 ISO points to the pulp without any process upsets in the bleach plant or on the paper machine. The brightness gain from such a "THPS + Y" bleaching correlated linearly with the unbleached pulp slurry temperature.

The additional brightness gain from "THPS + Y" bleaching over the Y bleaching has been sustained during the subsequent commercial implementation. It has allowed the mill to reach the brightness target when the ISO brightness of the unbleached SGW pulp is lower than 62.0% in the summer months, and to reduce the dosage of brightness-enhancing additives in the coating color when producing hi-brite, ≥75% ISO LWC papers. The cost saving to the mill has been estimated at Cdn$250,000/year.

Use of "THPS + Y" bleaching with a weight ratio of Y/THPS ≥6.0 removes the formaldehyde formed from the dissociation of THPS to THP through the reaction of formaldehyde with Y and/or bisulfite.

ACKNOWLEDGEMENTS

We would like to thank: people at the Paprican member mill who participated in the mill trial for their participation and support; Drs. Tom Browne and Paul Watson of Paprican for supporting our work; Dr. Gilles Dorris of Paprican for an internal review of the manuscript; and NSERC for financial support via an I2I grant.

REFERENCES

1. PRESLEY, J.R. and HILL, R.T., "The Technology of Mechanical Pulp Bleaching, Chapter 1: Peroxide Bleaching of (Chemi)mechanical Pulps", *in:* Pulp Bleaching - Principles and Practice, Eds. DENCE, C.W. and REEVE, D.W., Tappi Press, Atlanta, p.457-489 (1996).
2. ELLIS, M.E., "The Technology of Mechanical Pulp Bleaching, Chapter 2: Hydrosulfite (Dithionite) Bleaching", *in:* Pulp Bleaching - Principles and Practice,

Eds. DENCE, C.W. and REEVE, D.W., Tappi Press, Atlanta, p.491-512 (1996).
3. BRAUER, P., KAPPEL, J. and HOLLER, M., “Anionic Trash in Mechanical Pulping Systems – The Bleaching Reaction is a Major Source of Anionic Trash”, *Pulp Paper Can.*, 102(4): 44-48 (2001).
4. MAYER, W.C. and DONOFRIO, C.P., “Reductive Bleaching of Mechanical Pulp with Sodium Borohydride”, *Pulp Paper Mag. Can.* 157-166 (1958).
5. KUTNEY, G.W., “The Bleaching Action of Thiols on Mechanical Pulps”, *J. Pulp Paper Sci.* 12(4): J129-131 (1986).
6. KUTNEY, G.W. and EVANS, T.D., “Sulphur Dioxide and its Derivatives: The Forgotten Bleaching Chemicals”, *J. Pulp Paper Sci.* 12(2): J44-49 (1986).
7. BLECHSCHMIDT, J., WURDINGER, S. and ZIESENIS, G., “Single- and Multistage Bleaching of High-yield Pulps with Hydrogen Peroxide and Formamidine Sulfinic Acid”, *Papier* 45(5): 221-225 (1991).
8. KUYS, K. and ABBOT, J., “Bleaching of Mechanical Pulps with Sodium Bisulfite”, *Appita* 49(4): 269-273 (1996).
9. VARENNES, S., DANEAULT, C. and PARENTEAU, M., “Bleaching of Thermomechanical Pulp with Sodium Perborate”, *Tappi J.* 79(3): 245-250 (1996).
10. PEDNEAULT, C., ROBERT, S. and PELLERIN, C., “Bleaching with New Reductive Chemicals: Replacement of Hydrosulfite”, *Pulp Paper Can.* 98(3): 51-54 (1997).
11. DJERDOURI, N.E. and ROBERT, S., “Reductive Bleaching of High Yield Pulps Using Phosphorus Chemicals”, *Proc. 9th Intern. Symp. Wood Pulping Chem.* 23-1-23-3 (1997).
12. LEDUC, C., GARCEAU, M., DANEAULT, C. and ROBERT, S., “Bleaching of a Mechanical Pulp with Sodium Percarbonate and Amineborane – Bleaching Response and Brightness Stability”, *J. Pulp Paper Sci.* 28(5): 171-175 (2002).
13. KRONIS J.D., “Optimum Conditions Play Major Role in Recycled Fiber Bleaching with FAS”, *Pulp & Paper* 9: 113-117 (1996).
14. FILLION, M., AGER, P. and GAUDREAULT, “Comparison of Bleaching Sequence (PF, PH and PY) for Deinked Mixed Office Waste (MOW) Containing Various Percentages of Mechanical Pulp”, *Proc. 92nd PAPTAC Annual Meeting*, B179-186 (2006).
15. HU, T.Q. and JAMES, B.R., “New Bleaching Agents for Mechanical Pulps - A Discovery Made Possible by the Pursuit of Green Chemistry”, *Can. Chem. News* 56(4): 27-28 (2004).
16. HU, T.Q., JAMES, B.R., YAWALATA, D. and EZHOVA, M.B., “Bleaching and Brightness Stabilization of Lignocellulosic Materials with Water-soluble Phosphines and Phosphonium Compounds”, *PCT/WO 2004/070110 A1* (August 19, 2004).
17. HU, T.Q., JAMES, B.R., YAWALATA, D. and EZHOVA, M.B., “A New Class of Bleaching and Brightness Stabilizing Agents. Part I: Bleaching of Mechanical Pulps”, *J. Pulp Paper Sci*. 30(8): 233-240 (2004).
18. HU, T.Q., JAMES, B.R., YAWALATA, D., EZHOVA, M.B. and CHANDRA, R., “A New Class of Bleaching and Brightness Stabilizing Agents. Part II. Bleaching Power of a Bisphosphine”, *J. Pulp Paper Sci.* 31(2): 69-75 (2005).
19. HU, T.Q. and JAMES, B.R., “A New Class of Bleaching Agents for Mechanical Pulps”, *Proc. 91st PAPTAC Annual Meeting* C97-101 (2005).
20. HU, T.Q., JAMES, B.R., YAWALATA, D. and EZHOVA, M.B., “A New Class of Bleaching and Brightness Stabilizing Agents. Part III: Brightness Stabilization of Mechanical Pulps”, *J. Pulp Paper Sci*. 32(3): 131-136 (2006).
21. RICKELTON, W.A., “Phosphine and Its Derivatives”, *in* Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed. Vol. 18, 656-668 (2000).
22. CALAMARI, T.A. and HARPER, R.J., “Flame Retardants for Textiles”, *in* Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed. Vol. 10, 998-1022 (2000).
23. JEFFERY, J.C., ODELL, B., STEVENS, N. and TALBOT, B., “Self Assembly of a Novel Water Soluble Iron(II) Macrocyclic Phosphine Complex from Tetrakis(hydroxymethyl)phosphonium Sulfate and Iron(II) Ammonium Sulfate: Single Crystal X-ray Structure of the Complex $[Fe(H_2O)_2\{RP(CH_2N(CH_2PR_2)CH_2)_2PR\}]SO_4{\bullet}4H_2O$ ($R = CH_2OH$)”, *Chem. Commun.* 101-102 (2000).
24. HAACK, T.K., DOWNWARD, B. and TALBOT, B., “Tetrakishydroxymethyl Phosphonium Sulfate (THPS): A New Biocide with Environmental Benefits for Paper Mills”, *1997 Tappi Engineering & Papermakers Conference Proceedings*, Tappi Press: Atlanta, 1115-1119 (1997).
25. ELLZEY, S.E., JR., “Preparation of Pure THP Sulfate”, *Textile Chem. Color.* 10(5): 12 (1978).
26. FRANK, A.W., DAIGLE, D.J. and VAIL, S.L., “Chemistry of Hydroxymethyl Phosphorus Compounds, Part II. Phosphonium Salts”, *Textile Res. J.* 52(11): 678-693 (1982).
27. CHANDRA, R., HU, T.Q., JAMES, B.R., EZHOVA, M.B. and MOISEEV, D.V., “A New Class of Bleaching and Brightness Stabilizing Agents. Part IV: Probing the Bleaching Chemistry of THP and BBHPE”, *J. Pulp Paper Sci.* in press (2007).
28. HAN, J.C. and HAN, G.Y., “A Procedure for Quantitative Determination of Tris(2-carboxyethyl)phosphine, an Odorless Reducing Agent More Stable and Effective than Dithiothreitol”, *Anal. Chem.* 220: 5-10 (1994).
29. “Analysis of Sodium Hydrosulfite”, TAPPI Standard Testing Method T 622 cm-01 (2001).
30. “Forming Handsheets for Optical Tests of Pulp (British Sheet Machine Method)”, PAPTAC Standard Testing Method C.5 (1993).
31. “Brightness of Pulp, Paper and Paperboard”, PAPTAC Standard Testing Method E.1 (1990).