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**IPST Technical Paper Series Number 718**

Chemical Modification of Lignin-Rich Paper  
Part 7: Photostabilizing High-Brightness Aspen CTMP  
by Combining Various Classes of Additives and Acetylation

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April 1998

Submitted to  
Nordic Pulp and Paper Research Journal

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# Chemical modification of lignin-rich paper

## Part 7. Photostabilizing high-brightness aspen CTMP by combining various classes of additives and acetylation

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*Keywords:* Acetylation, CTMP, Yellowing, Inhibition, Fluorescent whitening agents, Radical scavengers, Ultraviolet absorbers, Polymers

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**SUMMARY:** Different classes of additives (fluorescent whitening agents, polyethers, ultraviolet absorbers, and a radical scavenger) have been examined as photostabilizing agents for high-brightness, hydrogen-peroxide-bleached aspen chemithermomechanical pulp (CTMP) alone or in combination with chemical modification of the pulp (e.g., acetylation). The high-brightness CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Both the acetylation treatment and the impregnation procedure were carried out on paper sheets.

Efficient inhibition of photoyellowing was obtained when moderate amounts of UV-screens, such as 2-hydroxy-4-methoxybenzophenone or Tinuvin 384 (a benzotriazole derivative), were applied onto acetylated handsheets; more than 90% of the yellowing was hindered by this treatment. Impregnation with fluorescent whitening agents had an effect in reducing the overall rate of discoloration, especially when applied onto unacetylated paper sheets at relatively high application levels. Prolonged irradiation and application onto acetylated paper sheets reduced the effectiveness of the fluorescent whitening agents. Among the other tested additives, polytetrahydrofuran (on a wt% basis) showed the best result in preserving the brightness during irradiation both alone and in combination with acetylation.

With regard to the overall effect of acetylation, i.e., the brightness loss during reaction and the slightly lower efficiency in retarding yellowing compared with other acetylated bleached high-yield pulps, the results (under the conditions examined) indicate that the pretreatment step with hydrogen-peroxide introduced leucochromophoric structures that were detrimental to the aging properties of the acetylated pulp.

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High-yield pulps such as groundwood pulp (GWP), thermomechanical pulp (TMP), and chemithermomechanical pulp (CTMP) use the world's wood resource in an efficient and environmentally friendly way. This is because mechanical pulps contain all three major components of wood (e.g., cellulose, hemicelluloses, and lignin) unlike most chemical pulps that largely utilize the cellulose wood component. Today, it is possible to produce high-yield pulps at less than half the cost of chemical pulps and with brightness and strength properties that permit their use as substitutes for chemical pulps in many high-quality printing and writing papers (Levlin 1990; Stanley, Priest 1994; Mackie, Styan 1995; Ford, Sharman 1996). One of the major remaining obstacles to the wider utilization of these pulps in high-value furnishes is their tendency to undergo light-induced discoloration. If the brightness stability could be improved, the market for bleached mechanical pulps, particularly high-brightness chemithermomechanical pulps, would increase significantly (Cockram 1989).

The light-induced yellowing mechanism includes several complex reactions that are today not completely understood, although much progress has been made in the last decade in understanding some of the key steps in the discoloration process (cf. Gratzl 1985; Heitner, Schmidt 1991; Leary 1994). It is generally accepted that the main photochemical reactivity is associated with the high lignin content of mechanical pulps. Insufficient knowledge of the reactions leading to discoloration has, however, made it difficult to develop methods that are technically and economically feasible in preserving the brightness of the bleached high-yield pulps.

Several approaches have been undertaken to photostabilize lignin-containing pulps. The proposed treatments can be divided into two categories, i.e., addition of inhibitors and chemical modification. The first category is characterized by the addition of compounds such as ultraviolet absorbers (which reduce UV-light absorption by pulp), antioxidants (which trap intermediate radicals), and quenchers (which inactivate excited molecules). The treatments in the second category function by suppressing the formation of chromophores by chemical modification of functional groups in the lignin moiety.

Among the ultraviolet absorbers (UV-screens) tested, 5-phenylpenta-2,4-dienoic acid, 2-hydroxy-benzophenone, and benzotriazole derivatives have shown the best effect in retarding yellowing (Nolan 1945; Kringstad 1969; Gellerstedt et al. 1983; Fournier de Violet et al. 1990; Castellan et al. 1994; Davidson et al. 1995; Pan et al. 1996). Sulfur-containing compounds, the sodium salt of thiodipropionic acid, 1-thioglycerol, glycol dimercaptoacetate, thioglycolic acid, methylthioacetic acid, sodium formaldehyde sulfoxylate (Rongalite), polyethylene glycol dithiol, and 1-dodecanethiol have all shown some effect in preventing discoloration of lignin-containing pulps (Kringstad 1969; Cole, Sarkanen 1987; Janson, Forsskåhl 1989; Fournier de Violet et al. 1990; Daneault et al. 1991; Cook et al. 1996; Pan, Ragauskas 1997). Recent research has shown that 2,2'-oxydiethanethiol, ethylene glycol bis-thioglycolate, 3-mercapto-1,2-propanediol, and 2,2'-dithio-2-oxodiethanol were effective in preventing light-induced brightness reversion of bleached CTMP (Pan, Ragauskas 1995a, b; Ragauskas, Cook 1997). The stabilizing activity of thiols is, however, reduced on long-term storage. Furthermore, the unpleasant odor that most of the sulfurous compounds possess could be a serious problem restricting the field of application. Polyethylene glycol (PEG) with different molecular weights and different end groups can be used to prevent yellowing if relatively large amounts are added (Minemura 1978; Janson, Forsskåhl 1989; Forsskåhl, Janson 1992; Cole et al. 1993; Maiocchi et al. 1994; Davidson et al. 1995; Janson et al. 1995). Polytetrahydrofurans (PTHF) were found to both brighten and photostabilize different mechanical pulps, whereas polypropylene glycol (PPG) showed only a weak effect, and polyvinyl alcohol (PVA) showed no effect in retarding the brightness reversion (Janson et al. 1995; Janson, Forsskåhl 1996). The protective mechanism of polyglycols (or other polyethers) is still not well-

known, although complexing ability, antioxidative effects, and changes in migratability may be considered (Janson et al. 1995, Janson, Forsskåhl 1996). Fluorescent whitening agents (flavonic acid-based) have also been shown to have some effect in retarding yellowing (Bourgoing, Robert 1997).

The chemical modification approach of potential chromophoric or leucochromophoric groups in lignin involves reduction of  $\alpha$ -carbonyl groups (Manchester et al. 1960; Andrews, Des Rosiers 1966; Leary 1968; Lin, Kringstad 1970; Tschirner, Dence 1988; Fournier de Violet et al. 1989; Ek et al. 1990; Francis et al. 1991; Schmidt, Heitner 1991; Castellan et al. 1992a; Paulsson et al. 1995), hydrogenation of ring-conjugated ethylenic groups (Lin, Kringstad 1970; Tschirner, Dence 1988; Castellan et al. 1992b; Hu et al. 1997a, b), and acylation or alkylation of hydroxyl groups (Manchester et al. 1960; Andrews, Des Rosiers 1966; Singh 1966; Leary 1968; Wallis, Wearne 1982; Tschirner, Dence 1988; Ek et al. 1992; Castellan et al. 1992a; Paulsson et al. 1995; Paulsson et al. 1996). Among these treatments, acetylation has shown the best effect in improving the long-term photostability of both unbleached and hydrogen-peroxide-bleached pulps at a low extent of derivatization. This can be achieved with retained or even considerably improved strength properties (e.g., in the wet state) provided that the paper product instead of the pulp is acetylated (Paulsson et al. 1994).

The present paper describes the photostabilizing effect of acetylation alone or in combination with various classes of additives (UV-screens, polymers, and a radical scavenger) for high-brightness hardwood (aspen) CTMP. The possibility of using optical brightening agents (fluorescent whitening agents) that have the ability to absorb ultraviolet light as inhibitors for yellowing is also discussed.

## Experimental

*Pulps and paper samples.* Commercially produced hydrogen-peroxide-bleached aspen (*Populus tremuloides*) CTMP was used as received for the studies described in this paper. The pulp was obtained as dried sample (~93% solids). The high-brightness CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets (60 g·m<sup>-2</sup>) were prepared according to TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% r.h. according to TAPPI Test Method T 402 om-88 before further treatment.

*Solvents and photostabilizing additives.* All solvents and additives; polyethylene glycol (average molecular weight 600 and 3400), polytetrahydrofuran (average molecular weight 250), 2-hydroxy-4-methoxybenzophenone, Tinuvin 384 (a benzotriazole derivative supplied by Ciba-Geigy Corporation), 2-mercaptoethanesulfonic acid monosodium salt and the fluorescent whitening agents Phorwite UW Liquid (Bayer Corporation), and Tinopal SFP (Ciba-Geigy Corporation) were commercial products and were used as received. Footnotes in Table 1 give the chemical composition of the fluorescent whitening agents and the UV-screen Tinuvin 384. Formulas for the examined additives are shown in Appendix 1.

*Acetylation procedure.* The bleached CTMP handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100°C or 110°C) according to the procedure described by Paulsson et al. (1994).

*Impregnation procedure.* Weighted amounts of additives were dissolved in water, methanol, or acetone and sprayed onto handsheets to obtain various levels of addition. At least duplicate tests were performed.

*Analyses.* The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide as previously described in Paulsson et al. (1996). The acetyl content is given as a percentage of the dry weight of the paper. The phenolic hydroxyl content was determined according to the procedure described by Lai et al. (1990). The amount of photostabilizing additive applied onto the handsheets was determined by weighing the handsheets prior to addition and after reequilibrating of the treated handsheets (at 23°C and 50% r.h.). The addition level is given as a percentage of the dry weight of the paper.

*Accelerated light-induced yellowing.* The paper samples were subjected to an accelerated photoyellowing in a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company, Branford, CT, USA) equipped with eight RPR 3500Å UV-lamps ("blacklight," The Southern New England Ultraviolet Company) and a merry-go-round apparatus for uniform irradiation. The temperature was kept close to room temperature by a cooling fan (to minimize heating of the sample). Untreated paper sheets were used in all radiation experiments as controls.

*Optical measurements.* TAPPI brightness, fluorescence, and color changes [according to the CIELAB color scale ( $L^*$ -,  $a^*$ -,  $b^*$ -values)] were measured using a Technidyne Brightimeter (Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94. The post color (PC) number (at 457 nm, according to Giertz 1945) was calculated for the treatment with inhibitor and/or acetylation ( $PC_1$ ) and for the light-induced reversion ( $PC_2$ ) (cf. Janson, Forsskåhl 1989). The sum of  $PC_1$  and  $PC_2$  represents the total effect of the treatment:  $PC = PC_1 + PC_2$ .

## Results and discussion

### The effect of irradiation on the yellowing of additive-impregnated, high-brightness aspen CTMP

To assess the brightness reversion properties of additive-treated, high-brightness hardwood CTMP, a series of test sheets were impregnated with various classes of inhibitors, as summarized in Table 1. The additives studied were two polymers: polyethylene glycol (PEG, molecular weights 600 and 3400) and polytetrahydrofuran (PTHF, molecular weight 250); two optical brightening agents (fluorescent whitening agents, diaminostilbenedisulfonic acid derivatives): Phorwite UW Liquid and Tinopal SFP; two UV absorbers: Tinuvin 384 (a benzotriazol derivative) and 2-hydroxy-4-methoxybenzophenone (HMB); and a radical scavenger: 2-mercaptoethanesulfonic acid, monosodium salt (MESNA).

As can be seen in Table 1, the addition of PEG 600 did not change the brightness value to any great extent, whereas a slight brightening effect (negative  $PC_1$ ) was observed for the PEG 3400- and/or PTHF 250-treated sheets. The effect of increasing application level was small as was the effect of combining the two polymers PEG 3400 and PTHF 250. These results differ from those of Forsskåhl and Janson (1992). They found that aspen pulps (GW and CMP, both unbleached and dithionite or hydrogen-peroxide-bleached) were discolored (up to 3.5 brightness units at a charge level of 10-15%) on impregnation with PEG 600, whereas the corresponding spruce pulps were brightened. The difference in mechanical pulp type could possibly explain the difference in results obtained. The increase in brightness due to treatment with polytetrahydrofuran has been attributed to an increase in the light scattering ability of the treated paper (Janson, Forsskåhl 1996). Both the fluorescent whitening agents, Phorwite UW Liquid and Tinopal SFP, increased the TAPPI brightness values to above 90. The application level to reach 90+ brightness values was higher for

Phorwite UW Liquid (3.0%) than for Tinopal SFP (1.1%). This is because Phorwite UW Liquid contains less of the active fluorescent substance, a diaminostilbenedisulfonic acid derivative (ca. 15% by weight) than Tinopal SFP (ca. 75% by weight). It is also evident that the graying limit for Tinopal SFP is reached when the charge level is about 1%. An increase in the amount applied above this level will therefore not increase the brightness further. The action of optical brightening agents is based on fluorescence; they have the ability to absorb ultraviolet radiation and re-emit visible blue light. The yellow cast of the paper is shifted toward blue, which can be seen as a decrease in the value of the CIELAB color coordinate  $b^*$  and an increase in the value of the coordinate  $a^*$  (Table 1). The addition of the UV absorber Tinuvin 384 resulted in a slight brightness loss of less than one brightness unit, whereas the benzophenone-treated handsheets lost up to four units depending on the charge level used. The brightness loss for the HMB-treated sheets is due to its UV-visible absorption ( $\lambda_{\max} = 323 \text{ nm}$ ) that tails into the visible range. Impregnation with the radical scavenger MESNA increased the brightness value with up to two brightness units. This is probably an effect of its hydrogen-donating ability to certain unsaturated colored structures in the lignin moiety, i.e., to coniferaldehyde and quinonoid units.

The effect of accelerated light-induced aging of untreated and impregnated hydrogen-peroxide-bleached CTMP sheets is summarized in Table 2. Generally, irradiation decreased brightness, increased  $b^*$ , and decreased  $L^*$  for all handsheets. This is equivalent to a more yellow color of the paper. The photostabilizing effect of the two polyglycols was moderate, at least at low charge levels. The different molecular sizes did not generally alter the performance of the polymer even if the high molecular weight PEG was more efficient on a molar basis. The other tested polyether, polytetrahydrofuran, was somewhat more efficient in retarding yellowing (on a wt% basis). The degree of reversion, measured as post color number ( $PC_2$ ), after 4 hours of irradiation was 10.2 for the PTHF-impregnated sheets with the highest charge level (6.9%, see Table 2) compared with 17.2 for the control. The combined polymer treatment (PEG 3400 + PTHF 250) did not significantly improve the stability toward UV-light.

Table 2 shows the rate of yellowing of the FWA-treated sheets. It is evident that the addition of FWA had an photostabilizing effect. Tinopal SFP did retard yellowing somewhat more efficiently than Phorwite UW Liquid due to its higher concentration of active fluorescent substance; a  $PC_2$  value as low as 5.3 (calculated with the fluorescent component of the treated paper after 4 hours of irradiation) was obtained with the high application level (2.0%) (Table 2). It is, however, important to bear in mind that the visual appearance of an optical brightening agent treated paper is dependent on the closeness of match between the light source (UV/blue ratio of the light) employed for visual assessment and the light source (UV/blue ratio) and parameters [cut of filter(s), integrating sphere, and detector] of the fluorescent measurement instrument used. Care should therefore always be taken when optical properties of FWA-treated papers are discussed so that no misjudgments of the total appearance of the paper occur. The Technidyne Brightimeter (Model S-5) used in this investigation for optical measurements is equipped with a quartz tungsten halogen lamp and uses a cutoff filter that is absorbent up to 420 nm that completely excludes the brightening effect of the FWA (cf. Muller et al. 1993). The brightness value without the fluorescent component is given in Table 2, both before aging and after 4 hours of irradiation. It is evident that the addition of optical brightening agents has a real photostabilizing effect (cf. the  $PC_2$ -values in Table 2). This is most likely a result of their ability to absorb ultraviolet radiation and thereby protect the light-sensitive structures in lignin. On prolonged exposure, the fluorescent whitening agents lose their efficiency, an effect that can be seen as a reduction in the fluorescent component ( $\Delta F$  in Table 2).

The influence of addition of Tinuvin 384 and HMB on the photoaging properties is shown in Table 2. Both of the UV absorbers retarded yellowing significantly. The brightness after 4 hours of irradiation was 65.0% (Tinuvin 384) and 67.6% (HMB) for the high charge level, which is more than 10 brightness units higher than for the control (54.6%). The observed photostabilization is probably an effect of a reduction in the ultraviolet light transmitted onto the pulp, although other possibilities such as radical scavenging and triplet quenching, in part, can explain the effectiveness of the examined UV-screens (Castellan et al. 1994; Noutary et al. 1994; Castellan et al. 1996; Cook, Ragauskas 1997). The radical scavenger tested (MESNA) did not stabilize the high-brightness aspen CTMP, at least not for the tested application levels.

The total effect of addition of inhibitors on photoyellowing is best illustrated by the PC-number (cf. Table 2). The most effective additives in preserving a high final brightness of the treated paper, at moderate charge levels, are the FWAs and the UV-screens. However, the most important factor for the paper manufacturer (and the consumer) is that the paper has a stable brightness level, i.e., has a low PC<sub>2</sub>-value. In this sense, benzophenone and Tinopal SFP (charge level ca. 1%) show the most promising results.

### **The effect of irradiation on the yellowing of acetylated high-brightness aspen CTMP**

Table 3 shows the change in optical properties during acetylation. As can be seen, acetylation lowered the brightness considerably even at a low degree of derivatization. The large loss in brightness indicates that new chromophoric structures have been generated. This is contradictory to earlier reported results for hydrogen-peroxide-bleached high-yield pulps where acetylation for 10 minutes (100°C) lowered the brightness of a bleached spruce TMP (initial brightness 77%) with one brightness unit and a bleached aspen CTMP (brightness 80%) with 2 units (Paulsson et al. 1994). The corresponding value for the high-brightness CTMP used in this work was 5.8 brightness units. The decrease in brightness was manifested as a decrease in lightness ( $L^*$ ) and an increase in yellowness ( $b^*$ ), which increased the yellowish cast of the treated paper. The difference in the manufacturing process, i.e., the pretreatment step with hydrogen peroxide for the high-brightness CTMP, is one likely explanation for the altered response toward acetylation. Further experiments are, however, needed to fully elucidate this discrepancy.

The brightness change during irradiation of acetylated test sheets is shown in Table 4. It is evident that acetylation retards photoyellowing, although to a lesser extent than previously reported (Paulsson et al. 1995; Paulsson et al. 1996). The hydrogen peroxide pretreatment step generates not only structures that are detrimental during acetylation, but also light-sensitive structures that form colored chromophores during the accelerated irradiation conditions used (see below). However, most of the photostabilization achieved appears already after a short period of acetylation; only a moderate reduction in the PC<sub>2</sub>-value is obtained at higher derivatization degrees (cf. Table 4). A reaction time of 5 minutes derivatized about 80% of the phenolic hydroxyl groups, which is in accordance with previously reported results (Paulsson et al. 1994).

The accelerated aging system used in this work uses UV-lamps as a light source. These lamps emit light in a band between 300 and 420 nm ( $\lambda_{\text{max}} = 350$  nm), i.e., the visible component of diffuse sunlight or office light is missing. This could be one explanation for the divergence in aging stability obtained for the two hardwood CTMPs. A forthcoming paper will discuss the effect of different light sources on the yellowing properties of unbleached and hydrogen-peroxide-bleached untreated and acetylated high-yield pulps.

## **The effect of irradiation on the yellowing of additive-impregnated, acetylated high-brightness aspen CTMP**

Acetylated test sheets were impregnated with different classes of inhibitors, and the photoaging properties were determined. The results are summarized in Table 5. The two lowest acetylation levels (acetyl content of 4.1 and 6.0%) were chosen together with a low addition of inhibitor (between 0.7 and 4.3% depending on the additive used). This was done to see if an acceptable photostability could be obtained with a moderate use of chemicals. Most of the results presented are from the experiments with the higher acetylated test sheets. The photoaging properties for the low acetylated sheets were, in general, the same, although shifted to a somewhat lower stability level (as indicated by the lower acetyl content), and will therefore not be discussed further.

A comparison of the PC<sub>2</sub>-numbers for PEG 600- and PEG 3400-impregnated acetylated sheets indicated that both of the polyglycols were nearly equally effective in their ability to retard yellowing of acetylated handsheets (Table 5). Polytetrahydrofuran was more effective in preserving the brightness during irradiation as was the case when applied to unacetylated handsheets, whereas a combination of the two polyethers did not significantly improve the performance. This is based on comparison at the same charge level (wt%). The final brightness (after 4 hours of irradiation) was 1 to 3 brightness units higher for the PEG-impregnated acetylated handsheets than for the acetylated sheets alone. The corresponding value for the PTHF-treated acetylated sheets was 3 to 6 units (cf. Table 4 and Table 5).

The photostabilizing effect of the two fluorescent whitening agents was small; the PC<sub>2</sub>-values (4h irradiation, calculated with the fluorescent component) were in the same range as for acetylation alone, i.e., about 7.7 to 9.0 (Table 5). Furthermore, acetylation affected the performance of the FWAs negatively, which can be seen as a lower  $\Delta F$ , i.e., a lower brightness on application. It is well-known that the brighter the pulp is (and the lower the yellow cast is), the better is the effect obtained with FWAs. Because acetylation both increased the yellowness ( $b^*$ ) and decreased the brightness, optical brightening agents are not a good alternative to use in combination with the acetylated high-brightness CTMP used in this work.

The combined treatment, acetylation and 2-hydroxybenzophenone (HMB) or benzotriazole (Tinuvin 384) derivatives, efficiently inhibited the light-induced yellowing even after long periods of irradiation. The final brightness after 4 hours of irradiation of the high charge level (2.9%) 2-hydroxy-4-methoxybenzophenone-treated sheets was 74.5%, which is about 19 brightness units higher than for the control (Table 5). This corresponds to a total photostability as high as 90% (calculated from the PC-number). The radical scavenger, 2-mercaptoethanesulfonic acid (MESNA), did not improve the photoaging properties of acetylated test sheets.

In summary, the use of ultraviolet absorbing compounds in combination with chemical modification (e.g., acetylation) is a possible way to strongly retard the photoyellowing characteristics of high-brightness aspen CTMP.

## **Conclusions**

This work demonstrates that the light-induced brightness reversion of high-brightness, hydrogen-peroxide-bleached aspen CTMP strongly can be retarded if a combination of chemical modification (e.g., acetylation) and ultraviolet-absorbing compounds is employed. This was achieved at a low degree of acetylation (acetyl content less than 5%) and with a low addition of UV-screen.

Fluorescent whitening agents provided a photostabilizing effect, especially when applied onto unacetylated paper sheets at relatively high application levels. The effectiveness of the fluorescent whitening agents was, however, strongly reduced on prolonged irradiation and when applied onto acetylated handsheets. Polytetrahydrofuran was more effective than the polyethylene glycols in hindering the light-induced discoloration both alone and in combination with acetylation, when compared at the same level of addition (wt%).

The high-brightness aspen CTMP responded differently toward acetylation than previously examined unbleached and hydrogen-peroxide-bleached high-yield pulps. The brightness loss during reaction was higher (up to 10.6 brightness units depending on the degree of derivatization) and the inhibiting effect slightly lower than previously noted. The chemical pretreatment step with hydrogen-peroxide employed for the high-brightness pulp and the accelerated aging procedure used could possibly explain the divergence in obtained results. Experiments designed to clarify these differences in response toward acetylation are currently being conducted.

## Acknowledgments

Financial support for this work was provided by the Member Companies of the Institute of Paper Science and Technology and The Gunnar and Lillian Nicholson Graduate Fellowship and Faculty Exchange Fund. The authors would like to thank Ms. Lena Fogelquist, Department of Forest Products and Chemical Engineering, Chalmers University of Technology, for skilful assistance in the experimental work.

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*Table 1. Change in optical properties on impregnation of hydrogen-peroxide-bleached aspen CTMP with various classes of additives.*

Additive	Charge level on o.d. paper		TAPPI brightness, %		L*	a*	b*	PC <sub>1</sub> - number <sup>a</sup>
	wt%	μmol/g paper	before addition	after addition				
(None)	-----	-----	83.2	83.2	95.2	-1.3	4.3	0.00
Polyethylene glycol 600 (PEG 600)	2.0	33	83.1	83.2	95.3	-1.1	4.5	-0.02
	4.2	70	83.2	83.2	95.2	-1.0	4.3	0.00
	10.9	180	83.1	83.4	95.3	-1.2	4.4	-0.07
Polyethylene glycol 3400 (PEG 3400)	1.8	5.3	82.9	83.3	95.3	-1.1	4.4	-0.08
	4.0	12	83.0	83.8	95.4	-1.2	4.3	-0.18
	9.2	27	82.8	83.5	95.3	-1.1	4.2	-0.16
Polytetrahydrofuran 250 (PTHF 250)	2.1	84	82.8	83.2	95.1	-1.4	4.2	-0.08
	3.6	145	83.0	84.0	95.5	-1.3	4.2	-0.21
	6.9	276	82.7	83.6	95.3	-1.1	4.2	-0.19
Polyethylene glycol 3400/ polytetrahydrofuran 250	1.7/1.7	4.9/66	83.3	83.5	95.2	-1.5	4.2	-0.05
	2.3/2.3	6.8/92	82.8	83.6	95.2	-1.5	4.1	-0.18
	5.0/5.0	15/198	82.8	83.7	95.3	-1.6	4.1	-0.19
Phorwrite UW Liquid <sup>b,c</sup>	1.4	n.a.	82.9	84.6 (82.6)	95.0	-1.1	2.9	-0.37
	2.2	n.a.	83.2	87.5 (82.7)	95.2	-0.6	0.8	-0.81
	3.0	n.a.	82.6	90.2 (82.0)	95.2	0.7	-1.4	-1.31
Tinopal SFP <sup>c,d</sup>	0.7	n.a.	82.6	89.0 (82.6)	95.2	0.6	-0.5	-1.15
	1.1	n.a.	83.1	91.2 (82.5)	95.4	0.9	-1.5	-1.29
	2.0	n.a.	83.3	91.9 (82.4)	95.6	0.9	-1.3	-1.31
Tinuvin 384 <sup>e</sup>	0.9	n.a.	83.6	83.3	95.4	-1.1	4.6	0.05
	1.3	n.a.	83.7	83.1	95.4	-1.2	4.8	0.14
	2.5	n.a.	83.5	82.5	95.3	-1.4	5.0	0.22
2-Hydroxy-4-methoxy- benzophenone (HMB)	0.7	31	83.5	82.6	95.4	-1.9	5.3	0.20
	1.6	68	84.0	80.7	95.2	-3.1	6.8	0.80
	3.6	157	82.6	78.4	94.9	-3.3	8.1	1.15
2-Mercaptoethanesulfonic acid, monosodium salt (MESNA)	0.4	26	82.8	84.1	96.1	-0.9	5.2	-0.29
	0.8	51	82.7	84.2	96.0	-0.9	5.0	-0.32
	2.4	148	82.2	84.2	96.1	-0.9	5.0	-0.49

<sup>a</sup>The post color (PC<sub>1</sub>) number at 457 nm (due to treatment with various additives) was calculated according to Gietz (1945).

<sup>b</sup>The active fluorescent component is 2,2-[1,2-Ethenediylbis(3-sulfo-4,1-phenylene)]imino-[6-bis(2-hydroxyethyl)amino]-1,3,5-triazine-4,2-diyli]imino]]bis-1,4-benzenedisulfonic acid, hexasodium salt (ca. 15% by weight).

<sup>c</sup>Brightness values without the fluorescent component are given within parentheses (measured according to TAPPI Test Method T 452 om-92).

<sup>d</sup>The active fluorescent component is 2,2-[1,2-Ethenediylbis(3-sulfo-4,1-phenylene)]imino-[6-(diethylamino)-1,3,5-triazine-4,2-diyli]imino]]bis-1,4-benzenedisulfonic acid, hexasodium salt; sodium chloride (ca. 75% by weight).

<sup>e</sup>Benzotriazole derivative [3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, C7-9-branched alkyl esters], ca. 95% by weight.

Table 2. Change in optical properties during irradiation of hydrogen-peroxide-bleached aspen CTMP treated with various additives.

Additive <sup>a</sup>	Charge level, wt%	Initial TAPPI brightness, %	PC <sub>2</sub> -number <sup>c</sup>		PC-number <sup>d</sup> 4 h	Final TAPPI <sup>e</sup> brightness, %	ΔF <sup>b</sup>	L*	a*	b*
			0.5 h	4 h						
(None)	---	83.2	4.5	17.2	4.5	54.6	89.1	-2.0	18.8	
PEG 600	2.0	83.2	3.9	14.6	3.9	57.0	89.8	-2.1	17.7	
	4.2	83.2	3.9	13.0	3.9	58.5	90.4	-2.2	17.3	
	10.9	83.4	3.2	9.7	3.1	62.4	91.6	-2.3	15.7	
PEG 3400	1.8	83.3	4.3	15.2	4.2	56.4	89.7	-2.0	18.1	
	4.0	83.8	4.1	13.2	3.9	58.4	90.3	-2.1	17.2	
	9.2	83.5	3.5	12.1	3.3	59.5	90.7	-2.2	16.8	
PTHF 250	2.1	83.2	3.7	11.9	3.6	59.7	90.6	-2.4	16.6	
	3.6	84.0	3.9	11.9	3.7	59.9	90.6	-2.3	16.3	
	6.9	83.6	3.1	10.2	2.9	61.8	91.2	-2.1	15.5	
PEG 3400/PTHF 250	1.7/1.7	83.5	3.1	10.8	3.0	61.1	91.1	-2.7	16.1	
	2.3/2.3	83.6	3.1	10.9	2.9	60.9	90.9	-2.9	15.9	
	5.0/5.0	83.7	2.7	8.9	2.5	63.5	91.7	-2.9	14.8	
Phorwite UW Liquid <sup>f</sup>	1.4	84.6 (82.6)	3.6	14.1 (13.8)	3.2	57.9 (57.5)	90.0	-2.5	17.4	
	2.2	87.5 (82.7)	2.7	12.0 (12.1)	1.9	60.6 (59.3)	90.8	-2.6	16.0	
	3.0	90.2 (82.0)	1.7	9.0 (9.8)	0.4	64.9 (61.8)	91.2	-1.7	12.6	
Tinopal SFP <sup>g</sup>	0.7	89.0 (82.6)	2.0	11.4 (12.0)	0.8	61.4 (59.4)	90.3	-1.5	14.5	
	1.1	91.2 (82.5)	1.2	7.1 (8.4)	-0.1	68.1 (63.9)	91.8	-1.4	10.5	
	2.0	91.9 (82.4)	0.9	5.3 (6.6)	-0.4	71.6 (66.4)	92.3	-1.0	9.0	
Tinuvin 384	0.9	83.3	2.4	10.7	2.5	61.2	90.9	-2.0	15.5	
	1.3	83.1	2.1	9.0	2.3	63.2	91.5	-2.1	14.7	
	2.5	82.5	1.7	7.6	1.9	65.0	91.9	-2.3	13.7	
HMB	0.7	82.6	2.1	8.5	2.3	63.7	91.6	-2.7	14.7	
	1.6	80.7	1.4	6.2	2.2	66.3	92.6	-3.7	14.1	
	3.6	78.4	1.0	4.8	2.2	67.6	92.7	-3.8	13.4	
MESNA	0.4	84.1	4.9	17.9	4.6	54.2	89.7	-1.1	20.3	
	0.8	84.2	4.2	17.7	3.8	54.4	89.7	-1.3	20.1	
	2.4	84.2	3.7	16.4	3.3	55.5	90.2	-1.5	19.9	

<sup>a</sup>Abbreviations as in Table 1.

<sup>b</sup>The fluorescent component, ΔF = brightness measured without UV cutoff filter - brightness measured with UV cutoff filter.

<sup>c</sup>The post color (PC<sub>2</sub>) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

<sup>d</sup>The post color (PC) number (at 457 nm) [due to treatment with various additives (PC<sub>1</sub>) + irradiation (PC<sub>2</sub>)] was calculated according to Giertz (1945).

<sup>e</sup>TAPPI brightness after 4 h irradiation.

<sup>f</sup>Brightness and PC<sub>2</sub>-values measured/calculated without the fluorescent component are given within parentheses.

*Table 3. Change in optical properties on acetylation of hydrogen-peroxide-bleached aspen CTMP. Acetylation times (min) are given within parentheses.*

Pulp	Acetyl content, % by mass	TAPPI brightness, %	L*	a*	b*	PC <sub>1</sub> -number <sup>a</sup>
Control	0.6	84.3	95.8	-1.0	4.3	0.00
Acetylated (5) <sup>b</sup>	4.1	80.9	95.3	-1.4	6.4	0.87
(10) <sup>b</sup>	6.0	78.5	94.9	-1.3	7.6	1.56
(10) <sup>c</sup>	9.7	74.3	93.7	-1.1	8.8	3.06
(25) <sup>b</sup>	10.3	73.7	93.7	-1.1	9.3	3.31

<sup>a</sup>The post color (PC<sub>1</sub>) number at 457 nm (due to acetylation) was calculated according to Gertz (1945).

<sup>b</sup>Acetylation temperature, 100 °C.

<sup>c</sup>Acetylation temperature, 110 °C.

Table 4. Change in optical properties during irradiation of hydrogen-peroxide-bleached aspen CTMP acetylated to various degrees. Acetylation times (min) are given within parentheses.

Pulp	Acetyl content % by mass	Initial TAPPI brightness, %	PC <sub>2</sub> -number <sup>a</sup>		PC-number <sup>b</sup>		Final TAPPI <sup>c</sup> brightness, %	L*	a*	b*
			0.5 h	4 h	0.5 h	4 h				
Control	0.6	84.3	4.1	16.2	4.1	16.2	55.6	89.6	-2.1	18.7
Acetylated (5) <sup>d</sup>	4.1	81.0	3.8	12.0	4.7	12.9	59.0	91.5	-1.8	18.8
(10) <sup>d</sup>	6.0	78.6	3.0	9.3	4.5	10.8	61.2	91.9	-1.8	17.5
(10) <sup>e</sup>	9.7	74.6	2.3	6.1	5.4	9.2	63.8	92.6	-1.9	16.2
(25) <sup>d</sup>	10.3	73.7	2.0	5.0	5.3	8.3	64.5	92.8	-1.9	15.8

<sup>a</sup>The post color (PC<sub>2</sub>) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

<sup>b</sup>The post color (PC) number at 457 nm [due to acetylation (PC<sub>2</sub>) and irradiation (PC<sub>2</sub>)] was calculated according to Giertz (1945).

<sup>c</sup>TAPPI brightness after 4 h irradiation.

<sup>d</sup>Acetylation temperature, 100 °C.

<sup>e</sup>Acetylation temperature, 110 °C.

Table 5. Change in optical properties during irradiation of additive-treated, acetylated hydrogen-peroxide-bleached aspen CTMP. The acetyl content (% by mass) was 6.0% unless stated otherwise.

Additive <sup>a</sup>	Charge level <sup>b</sup> wt%	Initial TAPPI brightness, %	ΔF <sup>c</sup>	PC <sub>2</sub> -number <sup>d</sup>		PC-number <sup>e</sup>		Final TAPPI <sup>f</sup> brightness, %	ΔF <sup>c</sup>	L* <sup>g</sup>			
				0.5 h	4 h	0.5 h	4 h			a*	b*		
(None)	----	84.3		4.1	16.2	4.1	16.2	55.6		89.6	-2.1	18.7	
PEG 600	2.1	35	79.2	3.0	8.1	2.7	7.8	63.0		92.3	-1.8	16.5	
	4.3	71	78.7	2.8	7.1	2.5	6.8	64.2		92.6	-2.0	15.8	
PEG 3400	1.7	5.1	78.1	3.3	8.3	3.1	8.1	62.3		92.0	-1.7	16.5	
	3.4	10	78.2	2.8	7.0	2.6	6.8	64.2		92.6	-1.9	15.9	
PTHF 250	1.6	63	78.3	2.4	6.8	2.2	6.5	64.4		92.8	-1.8	16.1	
	3.7	150	78.2	2.1	5.1	1.8	4.8	67.0		93.5	-2.0	15.0	
PEG 3400/PTHF 250	1.1/1.1	3.3/4.5	77.5	2.4	6.7	2.2	6.5	64.2		92.8	-1.8	16.2	
	1.9/1.9	5.6/7.6	78.7	2.2	5.6	1.9	5.2	66.4		93.5	-2.0	15.5	
Phorwite UW Liquid <sup>h</sup>	0.8	n.a.	78.9 (78.0)	0.9	2.9	8.6	2.5	8.2	62.2 (62.1)	0.1	92.4	-1.6	17.6
	1.6	n.a.	83.4 (78.9)	4.5	2.6	9.0	1.6	8.0	63.2 (62.1)	0.1	92.3	-1.2	16.2
Tinopal SFP <sup>h</sup>	0.7	n.a.	79.4 (77.6)	1.8	3.0	8.8	2.3	8.1	62.3 (62.0)	0.3	92.4	-1.6	17.3
	1.1	n.a.	82.3 (77.6)	4.7	2.1	7.7	0.6	6.2	64.8 (63.0)	1.8	92.7	-1.3	15.3
Tinuvin 384	0.8	n.a.	78.1	2.1	6.5	1.8	6.3	64.8		92.8	-1.7	15.6	
	1.4	n.a.	78.6	1.7	5.4	1.0	4.7	66.6		93.2	-1.6	14.6	
HMB	1.7 <sup>h</sup>	75	80.8	1.9	7.1	1.8	7.0	65.0		92.7	-1.7	15.4	
	2.8 <sup>h</sup>	122	80.8	0.7	2.2	0.6	2.0	74.3		94.5	-1.3	10.2	
	1.6	70	78.1	1.9	5.7	1.7	5.4	66.0		93.1	-1.6	15.0	
	2.9	127	79.2	0.5	1.6	0.5	1.5	74.5		94.7	-1.3	10.4	
MESNA	1.5	94	77.5	2.9	9.8	2.7	9.5	60.3		92.0	-1.7	18.4	
	2.3	140	80.3	3.0	10.7	2.6	10.3	60.2		92.0	-2.0	18.5	

<sup>a</sup> Abbreviations as in Table 1.

<sup>b</sup> On o.d. paper.

<sup>c</sup> The fluorescent component, ΔF = brightness measured without UV cutoff filter - brightness measured with UV cutoff filter.

<sup>d</sup> The post color (PC<sub>2</sub>) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

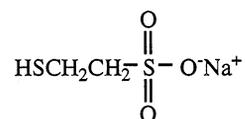
<sup>e</sup> The post color (PC) number (at 457 nm) [due to treatment with various additives and acetylation (PC<sub>2</sub>) + irradiation (PC<sub>2</sub>)] was calculated according to Giertz (1945).

<sup>f</sup> TAPPI brightness after 4 h irradiation.

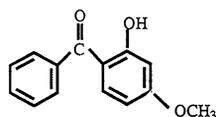
<sup>g</sup> Brightness values without the fluorescent component are given within parentheses (measured according to TAPPI Test Method T 452 om-92).

<sup>h</sup> Acetyl content, 4.1%.

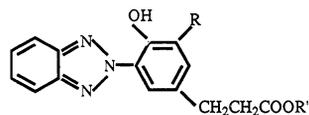
## Appendix 1: Structures of the additives used



**MESNA**

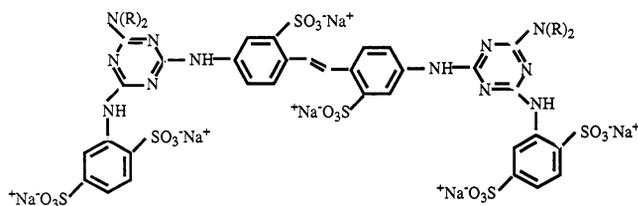


**HMB**



**Tinuvin 384**

$\text{R} = \text{C}(\text{CH}_3)_3$   
 $\text{R}' = \text{C}7\text{-}9\text{-branched alkyl esters}$



$\text{R} = \text{CH}_2\text{CH}_3$   
 $\text{R} = \text{CH}_2\text{CH}_2\text{OH}$

**Tinopal SFP**  
**Phorwite UW Liquid**





