The Effects of H_2O_2 Bleaching and DTPA Spraying on the Brightness Stability of Hornbeam CMP Pulp following Accelerated Irradiation Aging

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In this research, hornbeam chips were cooked under chemimechanical pulp (CMP) conditions, and the pulps were prepared at a yield level of 85%. The CMP pulps were separately bleached with hydrogen peroxide and sodium dithionite with and without treatment with DTPA. Then 60 gr/m^2 handsheets were made. The goal was to determine whether complementary bleaching with sodium dithionite improves optical behavior of the handsheets. Following DTPA solution spraying on the surface of hand sheets, brightness, opacity, and yellowness were improved, and the *K*/*S* ratio and PC number were decreased. Among different samples and following optical aging, it was found that in long-term aging, DTPA spray has considerable effect on improving the stability of brightness and increasing the paper's durability against optical deterioration.

Keywords: DTPA spray; Brightness stability; H_2O_2 bleaching; Hornbeam; Optical aging

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INTRODUCTION

High-yield mechanical and chemimechanical pulps are susceptible to photo-oxidative reactions that cause the pulps to become discolored and to undergo brightness reversion. Newsprint exposed to polychromatic radiation has shown the largest amount of yellowing when exposed to irradiation in the wavelength region of 330 to 385 nm (UV-A region). The formation of new phenolic and carboxylic groups from quinine radicals takes place during photo-yellowing and long-optical aging (Andrady and Searle 1995). Several factors and structural elements, as follows, have been proposed or considered as initiators of the main cause of the yellowing in high-yield and mechanical pulps: oxygen, α-carbonyl structures, lignin double bond structures, singlet oxygen, various radicals, phenolic groups (catechols), ortho-quinones, para-quinones such as methoxy-p-benzoquinone, lignin ß-O-4 structures, hydroquinones, and stilbenes formed from the phenylcoumaran-type entities (McGarry *et al.* 2000; Saint-Cyr *et al.* 2002; Yuan and McGarry 2002; Yuan *et al.* 2002). This phenomenon has been attributed to a light-induced oxidation of the lignin present in the pulp (Saint-Cyr *et al.* 2002; Tran 2003; Vichnesky *et al.* 2003). Extensive and comprehensive research, performed during the last decade, has given not only new information about the photochemical reactions causing yellowing, but also information on potential photostabilizing methods (Saint-Cyr *et al.* 2002; Yuan *et al.* 2002). However, to date, no single approach has become technically or economically feasible to meet all needs of the paper industry (Forsskahl 2000).

Ek *et al.* (1992) reported that the quinone structures and quinone precursors such as hydroquinone and catechols are important reactions in the photo-yellowing process in acetylated ground wood pulps. Paullsson *et al.* (2001) investigated the effect of photo-yellowing on untreated chemi-thermo-mechanical pulp (CTMP) under argon, ambient, and oxygen atmospheres. They found that the degree of photo-yellowing of untreated CTMP decreased when the air in the surrounding atmosphere which replaced with oxygen-free argon. Also, they concluded that the atmospheric level of oxygen is not requires for light-induced discoloration; rather, a trace amount of oxygen is sufficient to cause discoloration.

In long-term aging, DTPA spray has considerable effect relative to the stability of brightness and in the increase of durability against optical deterioration in hornbeam CMP pulp following accelerated irradiation aging (Vaysi and Mirshokraie 2007). The catalytic activity of Mn^{+2} and Mn^{+3} relative to the decomposition of hydrogen peroxide was evaluated with DTPA as the only stabilizer. It was found that the addition of DTPA to a Mn^{+2}-containing system is more effective than if it is added to a Mn^{+3}-containing system. To decrease the catalytic effect of Mn^{+3}, sodium borohydride and DTPA under acidic conditions were considered to reduce Mn^{+3} to Mn^{+2}. Newsprint exposed to polychromatic radiation showed the largest amount of yellowing when exposed to irradiation in the wavelength region of UV at range of 330 to 385 nm (Fig. 1).

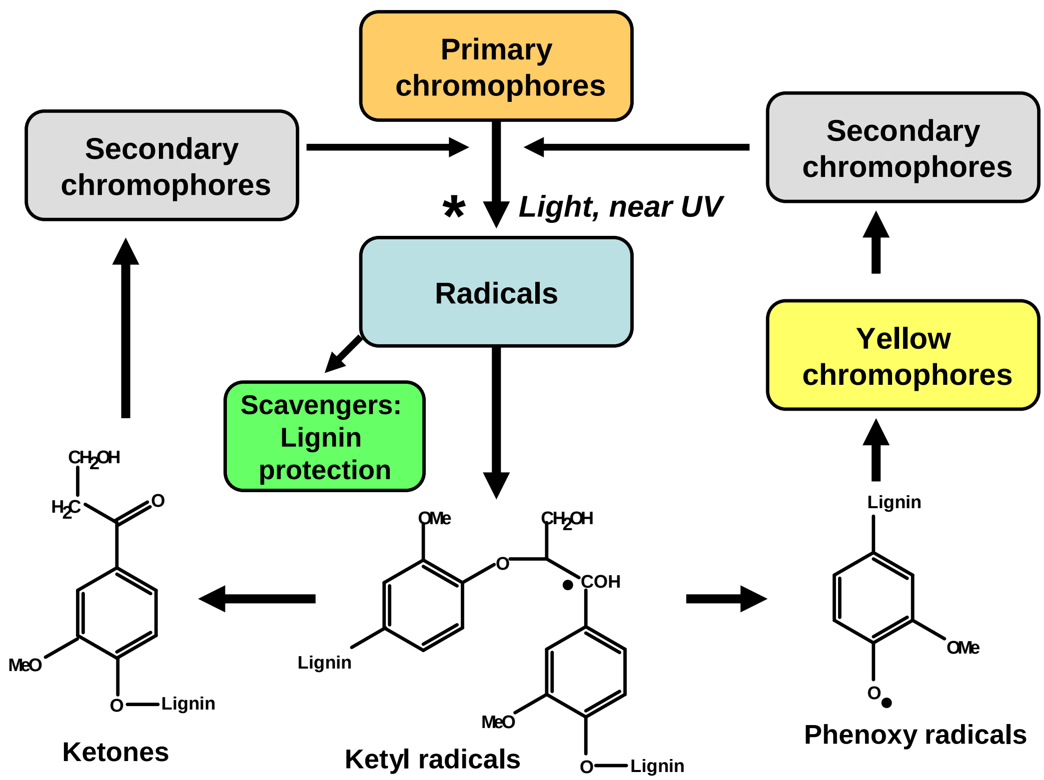

Fig. 1. Photo-yellowing reactions in lignin-rich pulps (Redrawn based on concept of Andrady and Searle 1995).

In this research the effect of H_2O_2 bleaching and DTPA spraying on the brightness stability of chemi-thermo-mechanical pulp (CTMP) following accelerated irradiation aging has been considered.

EXPERIMENTAL

Pulp

Hornbeam chips were chosen randomly from a chip pile at Mazandaran Wood and Paper Mill (MWPM) and cooked under CMP conditions (The ratio of liquor to wood (L/W): 7, SO_2: 116 g/L, NO_2: 106 g/L, sodium sulfite: 20% for 60 min at 160 ^oC), and pulps were prepared at the yield of 85% (Barzan and Soraki 2002).

Pulp Bleaching

One portion of pulp was bleached using hydrogen peroxide and DTPA as chelating agent according to the method proposed under following conditions: Hydrogen peroxide: 3%, sodium hydroxide on hydrogen peroxide ratio: 0.7% , DTPA charge: 0.3%, Na_2SiO_3: 3%, pulp consistency: 12%, time: 1 h; and temperature: 75 ^oC. Then, the pulps were refined to a freeness of 300 mL (CSF) by PFI Mill. Some of the pulps were bleached with sodium dithionite. Then 60 g/m^2 handsheets were made from bleached and unbleached pulp; 0.5% DTPA was sprayed onto the handsheets. Optical properties of the handsheets after drying were measured according to the TAPPI method. In addition, 60 g/m^2 handsheets were made from bleached and unbleached pulp according to TAPPI T 205 om-88 before acetylating (Barzan and Soraki 2002; Vaysi and Mirshokraie 2007).

Irradiation of Paper

TAPPI brightness and color change according to the CIELAB color scale (L^*, a^*, b^* values) were measured on 60 g/m^2 paper sheets using a Technibrite Micro TB-1C spectrophotometer and TAPPI Test Method T 224 om-94. The paper sheets were subjected to accelerated light-induced aging in an apparatus (made by authors) provided with 12 UV-fluorescent lamps ("black light" made by Phillips Co.). The handsheets were irradiated for zero, 10, 20, 30, and 40 min for optical aging. The optical characteristics of the handsheets were measured before and after optical aging. Brightness, opacity, yellowness, and greenness were determined according to ISO methods. The specific light scattering (S), light absorption (K) coefficient, K/S ratio, and post color (PC) number were calculated using the Kubelka-Munk theory. The K/S value and PC number were calculated using the following equations (Ek *et al.* 1992; Paullsson *et al.* 2001; Vaysi and Mirshokraie 2007),

$$K/S = (1-R_\infty)^2 / 2R_\infty \qquad (1)$$

$$\text{PC number} = 100((K/S)_t - (K/S)_{t=o}) \qquad (2)$$

where T is the irradiation time and R_∞ is the reflectivity of an infinite pile of sheets.

RESULTS AND DISCUSSION

Figures 1 to 7 show that an increase of accelerated irradiation aging results in an increase of the absorption coefficient, *K*/*S* ratio, opacity, yellowness, *a** factor, and post color (PC) number, but brightness and greenness decreased.

Another interesting result in Figs. 1 to 7 is that brightness, greenness, and opacity improved following bleaching and DTPA spraying on the handsheets, but *K*/*S* ratio and PC decreased. Also, with accelerated irradiation aging up to 40 h, all optical properties (except brightness) increased. These changes were more tangible up to 20 h irradiation. It can be concluded that the oxidizer H_2O_2 changes chromophores (quinones) to acid functional groups during hydrogen peroxide bleaching.

The quinine structures and quinine precursors such as hydroquinones and catechols are important reactions in the photo-yellowing process of acetylated ground wood pulps. In fact, the new phenolic and carboxylic groups are formed from quinines radicals during photo-yellowing and long-optical aging. These new groups could form chromophoric groups in combination with metallic ions. Such factors may account for the observed unfavorable effects on optical properties, including brightness reversion (Ek *et al.* 1992).

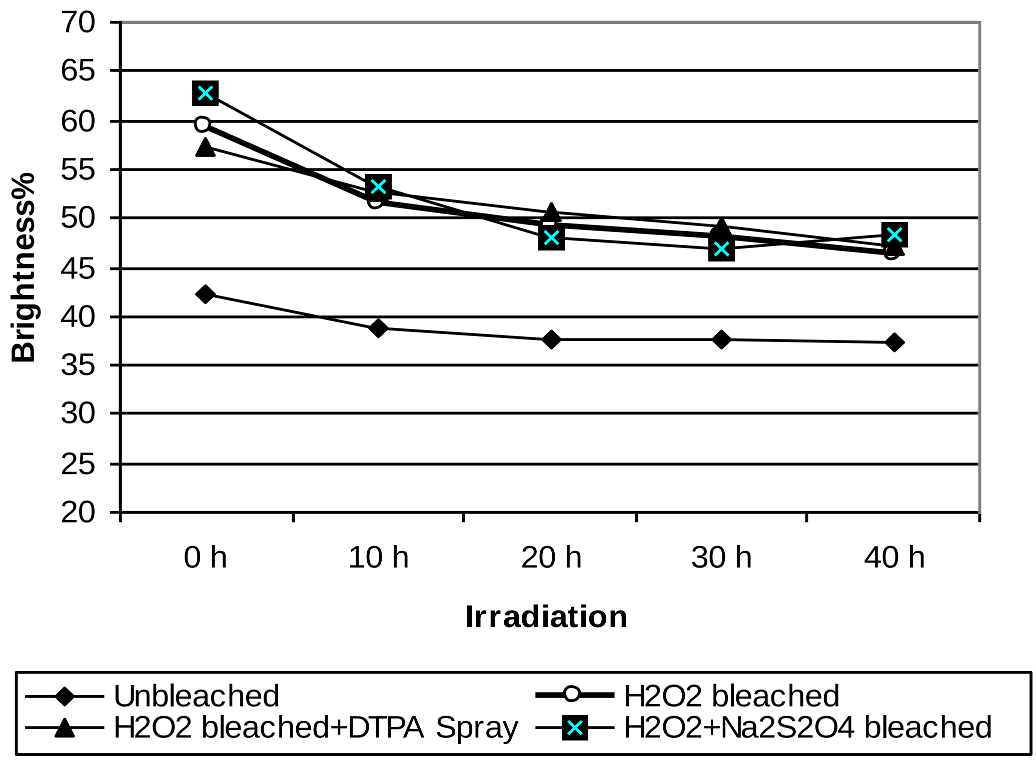

Fig. 2. Changes post color (PC) number in handsheets of DTPA sprayed and H_2O_2 + $Na_2S_2O_4$ bleached hornbeam CMP pulp following accelerated irradiation aging

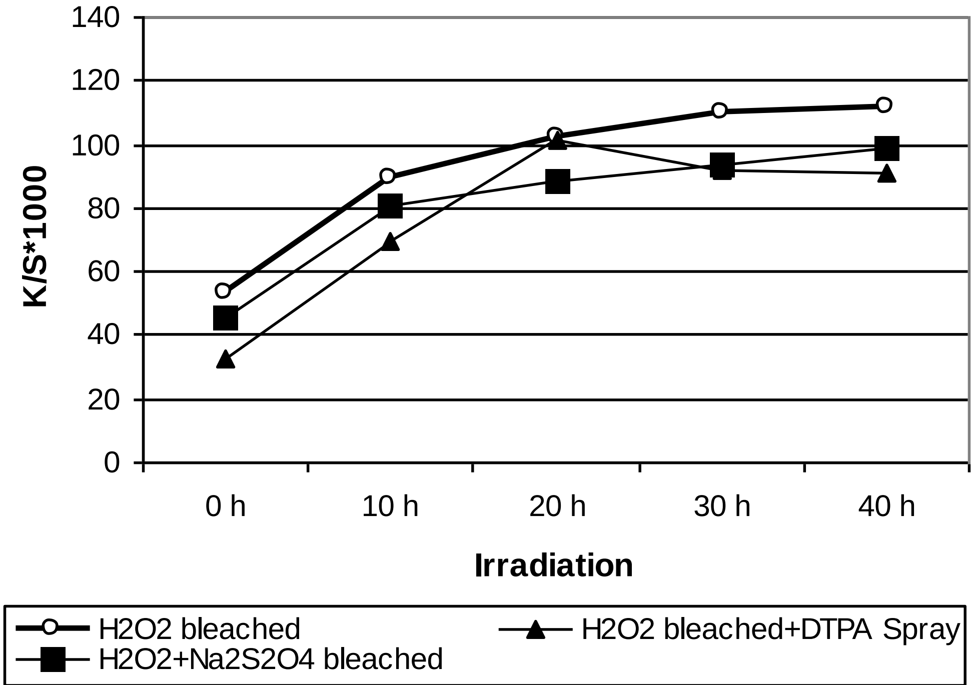

Fig. 3. The changes post color (PC) number in handsheets of DTPA sprayed and H_2O_2 + $Na_2S_2O_4$ bleached hornbeam CMP pulp following accelerated irradiation aging

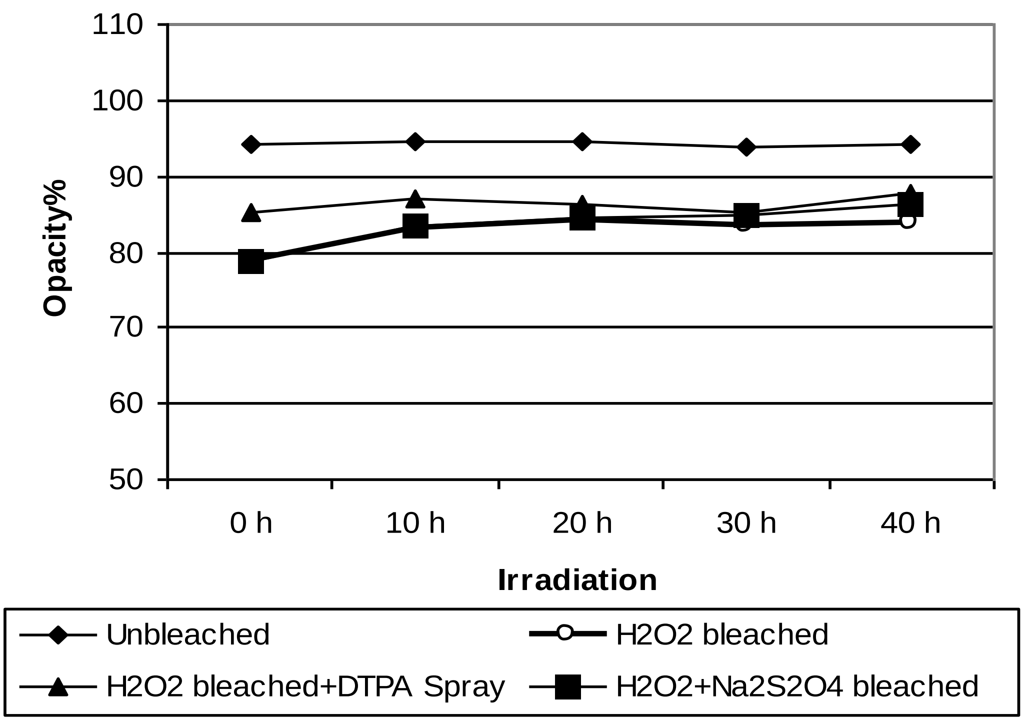

Fig. 4. Changes in post color (PC) number in handsheets of DTPA sprayed and H_2O_2 + $Na_2S_2O_4$ bleached hornbeam CMP pulp following accelerated irradiation aging

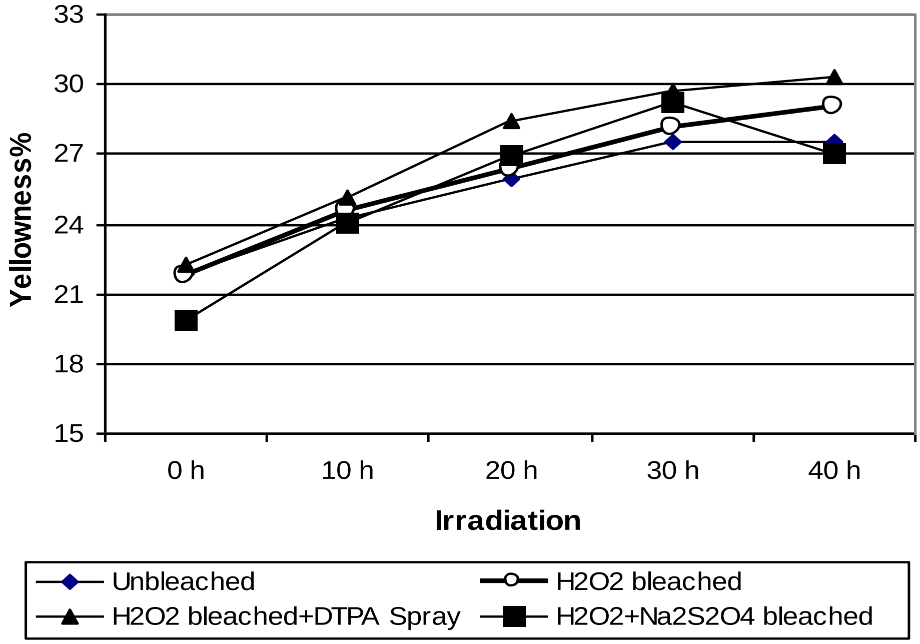

Fig. 5. Changes in post color (PC) number in handsheets of DTPA sprayed and H_2O_2 + $Na_2S_2O_4$ bleached hornbeam CMP pulp following accelerated irradiation aging

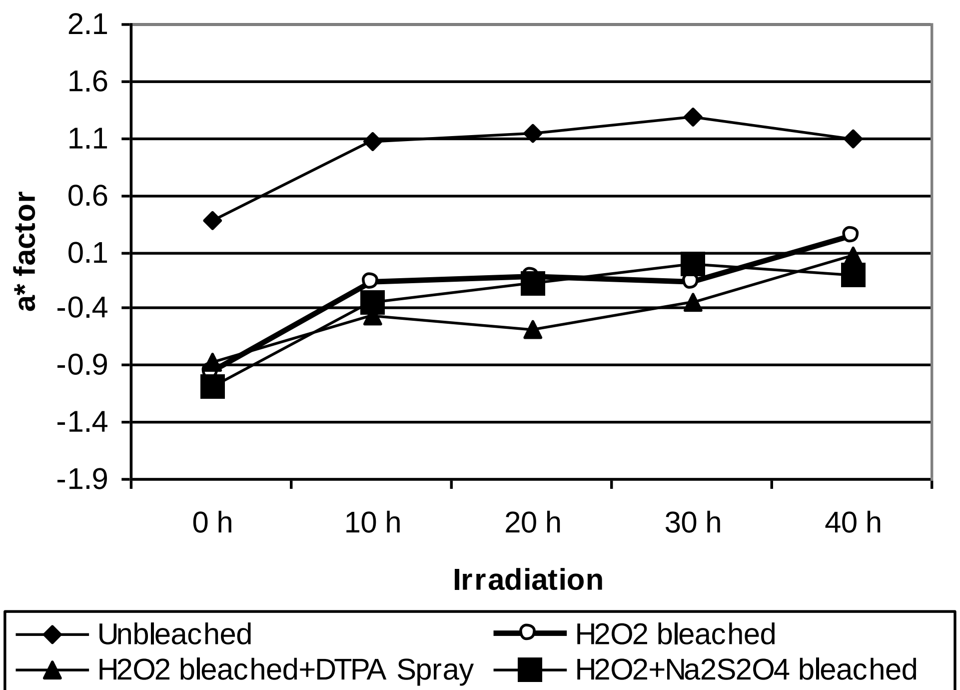

Fig. 6. Changes post color (PC) number in hand sheets of DTPA sprayed and H_2O_2 + $Na_2S_2O_4$ bleached hornbeam CMP pulp following accelerated irradiation aging

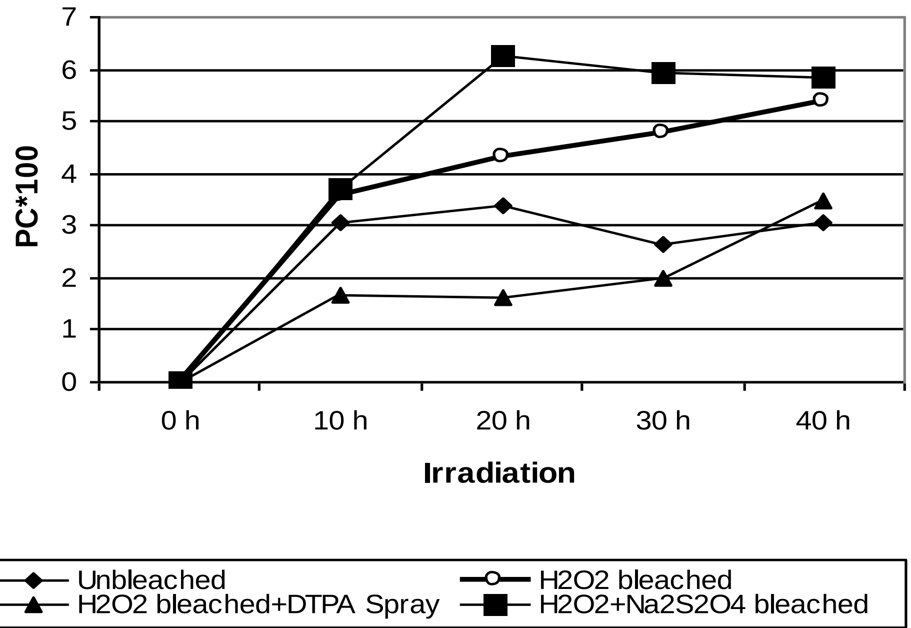

Fig. 7. Changes in post color (PC) number in handsheets of DTPA sprayed and H_2O_2 + $Na_2S_2O_4$ bleached hornbeam CMP pulp following accelerated irradiation aging

According to Table 1, the highest PC value and the least brightness stability were observed in H_2O_2 bleaching and complementary bleaching with sodium dithionite. In addition, complementary bleaching with sodium dithionite improved the optical behavior of the handsheets in short-term aging. However, following long-term aging, the lowest brightness stability and most of the optical deterioration were observed in unbleached paper, H_2O_2 bleaching, and the combination of H_2O_2 bleaching with complementary bleaching using sodium dithionite.

Table 1. Changes in Optical Properties of Acetylated and Bleached Hornbeam CMP Pulp Following Accelerated Irradiation and Thermal Aging

Treatment	Brightness%	K/S *1000	PC*100	Absorption coef.(m^2/kg)	Opacity %	L^*	a^*	b^*
Unbleached	38.73	232.1	2.4	6.95	94.24	71.59	0.99	12.73
H_2O_2 bleached	53.84	69.29	2.2	1.87	82.28	82.97	-0.45	13.96
H_2O_2+ DTPA Spray	54.77	56.06	0.5	1.79	85.02	87.92	-0.58	16.45
H_2O_2+ $Na_2S_2O_4$	55.72	59.73	2.7	1.69	82.46	86.29	-0.55	15.13
Optical Aging	51.15	87.63	1.94	2.56	85.21	84.13	-5.21	15.61

CONCLUSIONS

1. Following irradiation of up to 40 h, yellowness, opacity, absorption coefficient, *K*/*S* ratio, and post color (PC) number increased and brightness decreased.

2. Following optical aging up to 40 h, all optical properties (except brightness) were increased. The PC value is an indicator of paper aging, which is defined as zero for zero hours of accelerated aging. The greater proportions of the observed changes occurred during the first 20 h of irradiation.

3. The DTPA treatment in long-term irradiation and the use sodium dithionite and hydrogen peroxide with lowest aging yielded better brightness stability.

4. Following extended aging, the least brightness stability and the greatest optical deterioration were observed in unbleached paper and also in the case of H_2O_2 bleaching.

5. Complementary bleaching with sodium dithionite improved the optical behavior of the handsheets exposed to short-term aging, but in long-term aging, the least brightness stability and most of optical deterioration were observed in unbleached paper and a combination of H_2O_2 bleaching and complementary bleaching with sodium dithionite.

6. Following DTPA solution spraying on the surface of handsheets, brightness, greenness, and opacity improved, but, *K*/*S* ratio and post color (PC) number decreased. In long-term aging, DTPA spray has considerable effect on the stability of brightness and increasing its durability against optical deterioration. DTPA spray yielded better brightness stability and less brightness reversion and therefore better resistance towards optical deterioration.

REFERENCES CITED

Andrady, A. L., and Searle N. D. (1995). "Photo-yellowing of mechanical pulps; Part 2: activation spectra for light-induced yellowing of newsprint paper by polychromatic radiation," *TAPPI J.* 78(5), 131-138.

Barzan, A., and Soraki S. (2002). "Procedure for experimental," Mazandaran Wood and Paper Industries, Sari, Iran, 111-121.

Ek, M., Lennholm, H., Lindblad, G., and Iversen, T. (1992). "Study on the mechanism of the photo-yellowing of partially acetylated ground wood pulps," *Nord. Pulp and Paper Res. J.* 7(3), 108-112.

Forsskahl, I. (2000). "Participation of carbohydrate-derived chromospheres in the yellowing of high-yield and TCF pulps," *J. Pulp and Paper Sci.* 26(7), 245-249.

McGarry, P., Heitner, C., Schmidt, J., Seltzer, R., Cunkle, G., and Wolf, J. P. (2000). "Hindered nitroxide: A new yellowing inhibitor for mechanical pulps," *J. Pulp and Paper Sci.* 26(2), 59-63.

Paullsson, M., Lucia, L. A., Ragauskas A. J., and Li, C. (2001). "Photo-yellowing of untreated chemi-thermo-mechanical pulp under Argon, ambient and oxygen Atmosphere," *J. Wood. Chem. Technol.* 21(4), 343-360.

Saint-Cyr, K., van de Ven, T. G. M., and Garnier, G. (2002). "Adsorption of yellowing inhibitors on mechanical pulp," *J. Pulp and Paper Sci.* 28(3), 78-83.

Tran, A. V. (2003). "Thermal yellowing of hard wood kraft pulp bleaching with a chlorine

dioxide based sequence," *J. Pulp and Paper Sci.* 28(4), 115-121.
Vaysi, R., and Mirshokraie, S. A. (2007). "Investigation on the optical behavior of acetylated and non-acetylated hornbeam CMP pulp following accelerated irradiation aging," *J. Sci. Techniq. Natur. Resour.* 2(2), 79-88.
Vichnesky, S., Fuhr, B., and Melnichuk, J. (2003). "Characterization of wood and non-wood mechanical pulps by differential thermal analysis," *J. Pulp and Paper Sci.* 29(1), 17-20.
Yuan, Z., and McGarry, P. (2002). "Application of yellowing inhibitors to mechanical papers using a pilot liquid application system," *J. Pulp and Paper Sci.* 28(5), 159-166.
Yuan, Z., Schmidt, J., and Heitner, C. (2002). "Compatibility of yellowing inhibitors with several surface sizing agents," *J. Pulp and Paper Sci.* 28 (10), 354-358.

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