

Effects of Hydrogen Peroxide Bleaching and Acetic Anhydride on Photodegradation of Hornbeam CMP Pulp

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In this study, the effects of hydrogen peroxide bleaching and acetic anhydride as acetylation agent on photo degradation of hornbeam CMP pulp investigated. Hornbeam chips pulped under CMP conditions at the yield of 85 %. Then, one portion of pulp was bleached using hydrogen peroxide and DTPA as chelating agent and 60 g/m² handsheets were made from bleached and unbleached pulp. A number of unbleached handsheets were acetylated using acetic anhydride at 80 °C for 30 and 60 min. The handsheet were irradiated for 10, 20, 30 and 40 min for accelerated aging. The optical characteristics of the handsheets were measured before and after optical aging. The results showed that following bleaching and accetylation, absorption coefficient, K/S ratio, opacity, yellowness, greenness and post colour number were decreased and brightness was increased. Acetylated handsheets, especially those acetylated for 60 min, have better brightness stability and less brightness reversion.

Key Words: Photo degradation, Accelerated optical aging, H₂O₂ bleaching, Acetylation, Hornbeam.

INTRODUCTION

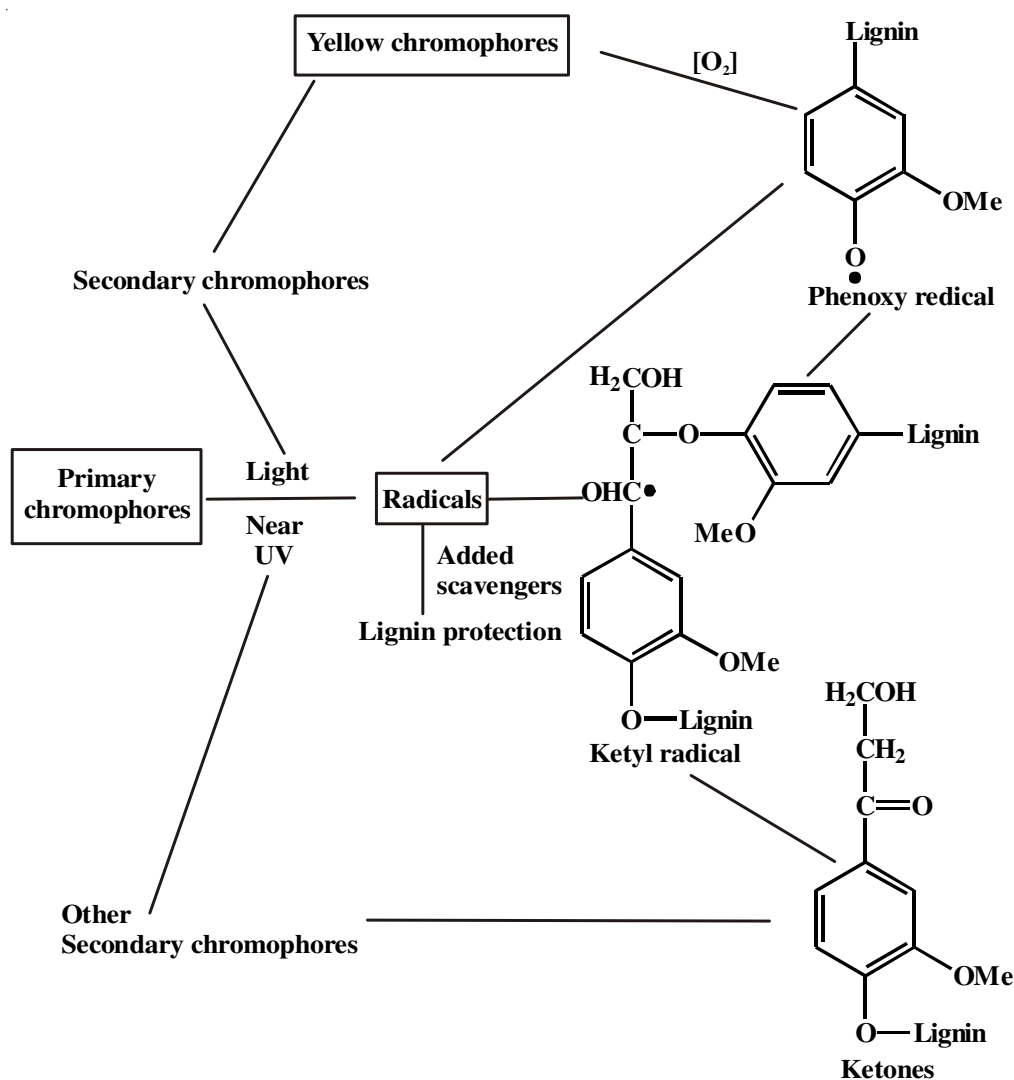
Lignin-rich pulps are susceptible to photo-oxidative reactions which cause the pulps to become discoloured and brightness reversion. The main cause of the yellowness in high-yield and mechanical pulps are oxygen, α -carbonyl structures, lignin double bond structures, singlet oxygen, various radicals, phenolic groups (catechols), *ortho*-quinones, *para*-quinones such as methoxy-*p*-benzoquinone, lignin β -O-4 structures, hydroquinones and stilbenes formed from the phenylcoumaran-type entities. This phenomenon has been attributed to a light-induced oxidation of the lignin present in the pulp. Forsskahl *et al.*¹ reported that 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 photo-stabilizing methods. However, no single approach so far has become technically or economically feasible to meet all the needs of the paper industry. Monica *et al.*² 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. Paulsson *et al.*³ reported that untreated and acetylated aspen CTMP exposed to argon, ambient air and oxygen atmospheres showed that the degree of photo-yellowing of the untreated CTMP decreased when the air in the surrounding atmosphere was replaced with oxygen-free argon, indicating

that atmospheric oxygen is not of sole importance for the light-induced discolouration or that trace amount of oxygen is necessary to cause discolouration. Andrady and Searle⁴ reported newsprint exposed to polychromatic radiation showed the largest amount of yellowing when exposed to irradiation in the wavelength region of 330 to 385 nm (UV-A region); such yellowing has been attributed to the formation of new phenolic and carboxylic groups from quinines radicals during photo-yellowing and long-optical aging.

EXPERIMENTAL

In this research, hornbeam chips were chosen randomly from chips pile at Mazandaran Wood and Paper Mill and prepared by T 289 om-97 TAPPI standard test method. Then chips cooked under CMP conditions (l/w: 7, SO₂: 116 g/L, NO₂: 106 g/L), sodium sulfite: 20 % and for 60 min in 160 °C and pulps were prepared⁵ at the yield of 85 %.

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 %, Na₂SiO₃: 3 %, pulp consistency: 12 %, time: 1 h and temperature: 75 °C. Then pulps were refined with PFI Mill to 300 CSF freeness and 60 g/m² handsheets were made from bleached and unbleached pulp according to TAPPI T 205 om-88 before acetylation^{5,6}.



Scheme-I Photo-yellowing reactions are high-rich lignin pulps

Acetylation: A number unbleached handsheets were acetylated using a technical grade of acetic anhydride (liquid phase, without any catalyst) at 80 °C for 30 and 60 min. The procedure was as follow: conditioned hand sheets were placed in preheated flask with an excess of acetic anhydride. After the reaction time was completed, the handsheets were immersed in water to stop the acetylation reaction. The acetylated paper were then thoroughly washed with water to remove remaining chemicals and thereafter pressed for five minute at 400 kpa. The sheets were dried on the press plates (24 h) and then conditioned at 23 °C and 50 % relative humidity according to TAPPI T 205 om-88^{3,6,7}.

FT-IR Spectroscopy: For investigation on the acetylation reaction in handsheets were using FT-IR spectroscopy. So that, first was provided handsheets flour with laboratorial hammer mill. Then were provided specific KBr taplet from handsheets flour and FT-IR spectrums by using Bomen (model MB100) FT-IR spectrometer^{3,6}.

Irradiation of paper sheets and optical measurements: TAPPI brightness and colour change according to the CIELAB colour scale (L^* , a^* , b^* values) were measured on 60 g/m² paper sheets using a technibrite micro TB-1C spectrophotometer and

TAPPI test method T 224 om-94 respectively. The paper sheets were subjected to accelerated light-induced aging in an apparatus (made by author) providing with 12 UV-fluorescent lamps (black light made by Phillips Co.). Then the handsheet were irradiated for 10, 20, 30 and 40 min for accelerated aging. The optical characteristics of the handsheets were measured before and after optical aging. Brightness, opacity, yellowness, greenness were determined according to ISO methods. The specific light scattering(s), light absorption (k) coefficient, K/S ratio and post colour (PC) number were calculated using the Kubelka-Munk theory. The K/S value and PC number are calculated by the following equations^{2,3}:

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

$$PC \text{ number} = 100[(k/s)_t - (k/s)_{t=0}]$$

where, S = light scattering coefficient; K = light absorption coefficient; T = irradiation time and R = reflectivity of an infinite pile of sheets.

RESULTS AND DISCUSSION

In this research, effect of accelerated irradiation aging investigation on the optical behaviour of paper sheets and those were estimated by using acetylation and bleaching. The results

of this study showed that following accelerated irradiation aging up to 40 h, absorption coefficient, K/S ratio, opacity, yellowness, greenness and post colour number were increased and brightness was decreased. The post colour number is scale for paper aging and that is zero for zero for accelerated aging.

Most of the post colour number and the least brightness stability were observed in H₂O₂ bleaching. In the following bleaching and acetylation, absorption coefficient, yellowness (Fig. 1), brightness (Fig. 2), post colour (PC) number (Fig. 3), opacity (Fig. 4) and K/S ratio (Fig. 5), were decreased and brightness was increased. Following aging up to 40 h, all optical properties (except brightness) were increased. These changes are more tangible up to 20 h irradiation. Among the handsheets, acetylated handsheets, especially those acetylated for 60 min, have better brightness stability and less brightness reversion and therefore better resistance towards optical deterioration. The investigation on the acetylated and non-acetylated FT-IR spectra indicated that acetyl group band (1742 cm⁻¹ peak) was observed in the acetylated paper sheets.

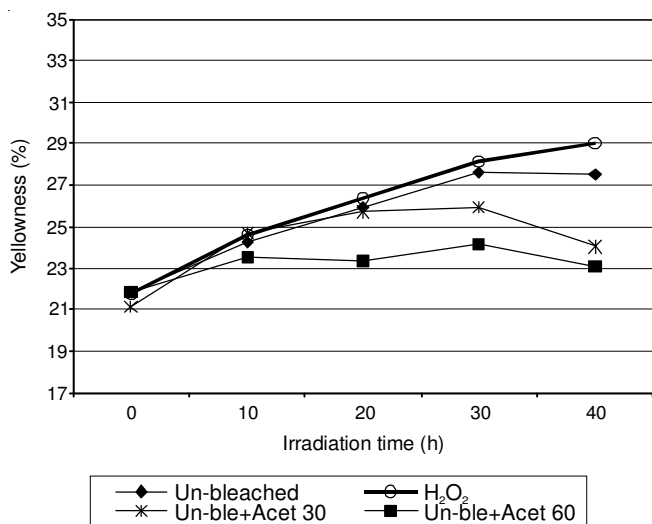


Fig. 1. Changes yellowness of acetylated and non-acetylated hornbeam CMP pulp following accelerated irradiation aging

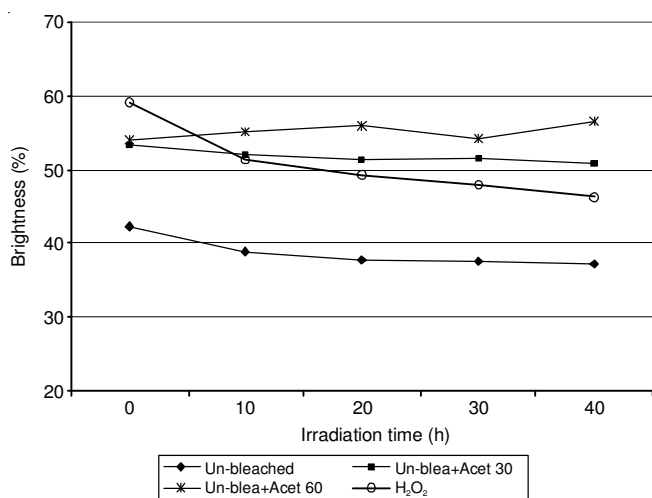


Fig. 2. Changes brightness of acetylated and non-acetylated hornbeam CMP pulp following accelerated irradiation aging

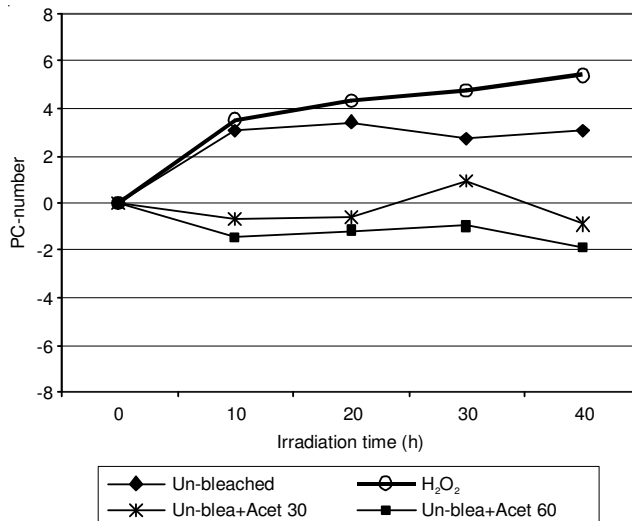


Fig. 3. Changes post-colour number of acetylated and non-acetylated handsheets hornbeam CMP pulp following accelerated irradiation aging

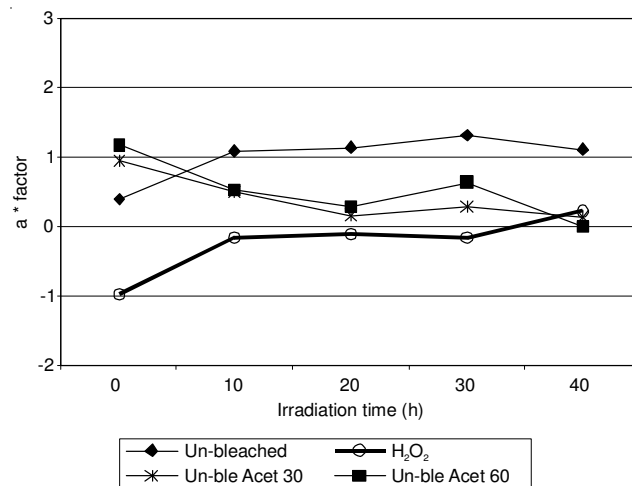


Fig. 4. Changes a* factor of acetylated and non-acetylated handsheets hornbeam CMP pulp following accelerated irradiation aging

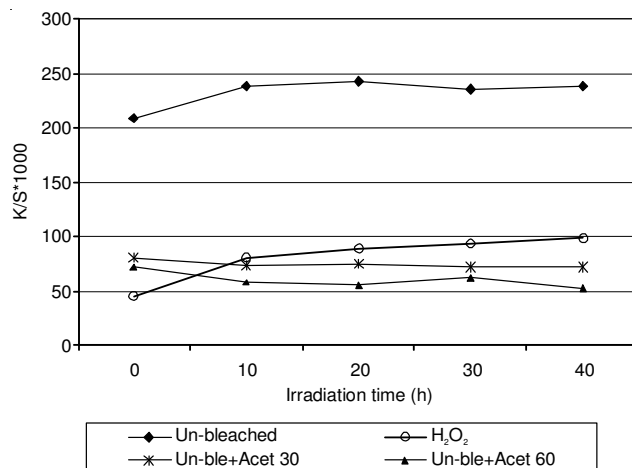


Fig. 5. Changes k/s of acetylated and non-acetylated hornbeam CMP pulp following accelerated irradiation aging

The quinone structures and quinone precursors such as hydroquinones and catechols are important reactions in the photo-yellowing process in acetylated ground wood pulps².

Following long-aging, the least brightness stability and most of optical deterioration were observed in unbleached paper and H₂O₂ bleaching, too. It is because the oxidizer H₂O₂ is reduced chromophores (quinones) to acid functional groups in hydrogen peroxide bleaching. newsprint exposed to polychromatic radiation showed the largest amount of yellowing when to irradiation in the wavelength region of 330-385 nm (UV-A region)⁴.

However, phenolic and carboxylic news groups formation from quinines radicals during photo-yellowing and long-optical aging. This news groups could formation colour groups with metallic ions. those factors are caused less optical properties and brightness reversion.

Conclusion

In this work, effects of H₂O₂ bleached and acetic anhydride acetylated on the optical behaviour of hornbeam CMP pulp following accelerated irradiation aging investigated. The results showed that following bleaching and acetylating, absorption coefficient, K/S ratio, opacity, yellowness, greenness and post colour number were decreased and brightness was increased. Following aging up to 40 h, all optical properties (except bright-

ness) were increased. These changes are more tangible up to 20 h irradiation. Among the handsheets, acetylated handsheets, especially those acetylated for 60 min, have better brightness stability and less brightness reversion and therefore better resistance towards optical deterioration. Among different samples and following optical aging, it was found that in long-term aging, DTPA spray has considerable affect on the stability of brightness and increasing its durability against optical deterioration. DTPA spray has better brightness stability and less brightness reversion and therefore better resistance towards optical deterioration.

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