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# Using $H_2O_2$ Bleaching and DTPA Spraying on the Brightness Stability of Beech CMP Pulp Following Accelerated Irradiation Aging

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In this research, beech chips were chosen randomly from the chips pile of Mazandaran pulp and Paper Mill in north of Iran and cooked under CMP conditions and pulps were prepared at the yield 85 %. The CMP pulp was separately bleached with hydrogen peroxide and sodium dithionite with and without treating with DTPA. Then 60 g/m$^2$ handsheet were made. A solution of 0.5 % of DTPA was sprayed over a number of handsheets. Then the handsheets were irradiated for, 10, 20, 30 and 40 h and their optical characteristics were measured and compared before and after irradiation using TAPPI standard test methods. The results of this study explored that following irradiation up to 40 h, yellowness, opacity, absorption coefficient, K/S ratio and post colour number increased and brightness decreased. Also complementary bleaching with sodium dithionite improved the optical behaviour of the handsheets. Following DTPA solution spraying on the surface of handsheets brightness, opacity and yellowness in improved and K/S ratio and post colour number is decreased. 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 it durability against optical deterioration.

**Key Words: $H_2O_2$ bleaching, Optical aging, DTPA spraying, Brightness stability, Beech.**

## INTRODUCTION

The use of high-yield mechanical and chemimecanical pulps are important, today's. These lignin-rich pulps are susceptible to photo-oxidative reactions which cause the pulps to become discoloured and brightness reversion. Several factors and structural elements have been proposed or considered as initiators or 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), *o*-quinones, *p*-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. 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 the potential photostabilizing methods, although no single approach so far has become technically or economically feasible to meet all needs of the paper industry. Monica *et al.*[1] reported that quinone structures and quinone precursors such as hydroquinones and catechols are important reactions in the photo-yellowing process in acetylated groundwood pulps. Forsskal and Tylli[2] reported that the degrees of both photo-yellowing and photo-bleaching were linearly dependent on light intensity. Paulsson *et al.*[3] found that untreated and acetylated aspen CTMP exposed to argon, ambient and oxygen atmospheres showed the degree of photo-yellowing of the untreated CTMP decreased when the air in the surrounding atmosphere was replaced with oxygen-free argon and indicating that atmospheric oxygen is not sole important for the light-induced discolouration or that trace amount of oxygen is necessary to cause discolouration. The acetylation clearly diminished the kinetics of photo-yellowing in all atmospheres resulting in substantially less absorption in the entire visible range (wavelength less of 400 nm). Qiu *et al.*[4] reported that the catalytic activity of $Mn^{2+}$ and $Mn^{3+}$ in decomposing hydrogen peroxide was studied by using DTPA as the only stabilizer. It was found that the addition of DTPA to a $Mn^{2+}$ containing system is more effective that if it is added to a $Mn^{3+}$ containing system. To decrease the catalytic activity of $Mn^{3+}$, sodium borohydride and DTPA under an acidic condition were considered to reduce $Mn^{2+}$ to $Mn^{3+}$. The effect of pH on using DTPA to decrease Mn induced peroxide decomposition is discussed.

## EXPERIMENTAL

**Pulp:** In this research, beech chips were chosen randomly from chips pile at Mazandaran Wood and Paper Mill (MWPM) and cooked under CMP conditions (l/w: 7, $SO_2$: 116 g/L, $NO_2$: 106 g/L, sodium sulfite: 20 % and for 1 h in 160 ºC) and pulps were prepared at the yield of 85 %[4,5].

**Pulp bleaching:** Then, 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. Some of the pulps were complementary bleaching with sodium dithionite under following conditions: Sodium ditionite: 3 %, EDTA or DTPA charge: 0.3 %, pulp consistency:12 %, time: 1 h and temperature: 65 ºC, too. Then pulps were refined with PFI Mill to 300 C.S.F. freeness and 60 g/m$^2$ handsheets were made from bleached and unbleached pulp according to TAPPI T 205 om-88. Next 0.5 % of DTPA were sprayed on the hand sheets[4,5].

**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/m$^2$ 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 providing with 12 UV-fluorescent lamps (black light made by Phillips Co.). Then the handsheet were irradiated for zero, 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 post colour number are calculated by the following equations[1,3,4]:

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

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

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 bleaching and DTPA spraying. The results showed that following accelerated irradiation aging up to 40 h, absorption coefficient, K/S ratio, opacity, yellowness, a* factor and post colour number were increased and brightness and greenness were decreased. The post colour number is scale for paper aging and that is zero for zero hour accelerated aging. In that, the most of post colour number and the least brightness stability were observed in $H_2O_2$ bleaching and complementary bleaching with sodium dithionite. In the following bleaching and DTPA spraying on the handsheets, brightness, greenness, opacity improved and K/S ratio and post colour number were decreased. Following aging up to 40 h, all optical properties (except brightness) were increased. These changes are more tangible up to 20 h irradiation (Table-1 and Fig. 1-3).

Also, the complementary bleaching with sodium dithionite improved the optical behaviour of the hand sheets in short-term aging. But in case of long-aging, the least brightness stability and most of optical deterioration were observed in unbleached paper and $H_2O_2$ bleaching and complementary bleaching with sodium dithionite, too. It is because the oxidizer $H_2O_2$ is reduced chromophores (quinones) to acid functional groups in hydrogen peroxide bleaching. Monica *et al.*[1] reported

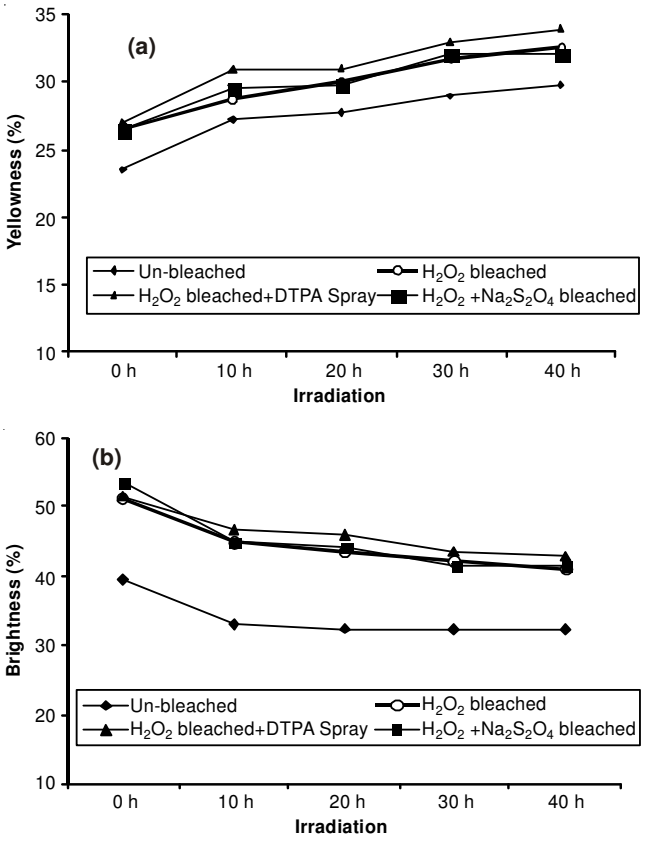


Fig. 1. Changes yellowness (a) and brightness (b) in handsheets of $H_2O_2$ bleached and DTPA sprayed beech CMP pulp following accelerated irradiation aging

TABLE-1
EFFECTS OF $H_2O_2$ BLEACHING AND DTPA SPRAYING ON OPTICAL PROPERTIES OF BEECH CMP PULP FOLLOWING ACCELERATED IRRADIATION AGING

| Treatment | Brightness (%) | Opacity (%) | Absorption coefficient | K/S *1000 | PC*100 | L* | a* | b* |
|---|---|---|---|---|---|---|---|---|
| Unbleached | 39.30 | 94.11 | 10.20 | 333.43 | 3.31 | 84.20 | 0.77 | 17.86 |
| $H_2O_2$ bleached | 46.97 | 84.93 | 2.60 | 96.70 | 2.64 | 83.72 | 0.53 | 18.00 |
| $H_2O_2$bleached + DTPA spraying | 48.47 | 85.19 | 2.26 | 78.13 | 1.12 | 85.83 | 0.24 | 19.36 |
| $H_2O_2$ + $Na_2S_2O_4$ bleached | 48.05 | 84.05 | 2.32 | 89.95 | 3.33 | 86.29 | 0.27 | 18.36 |

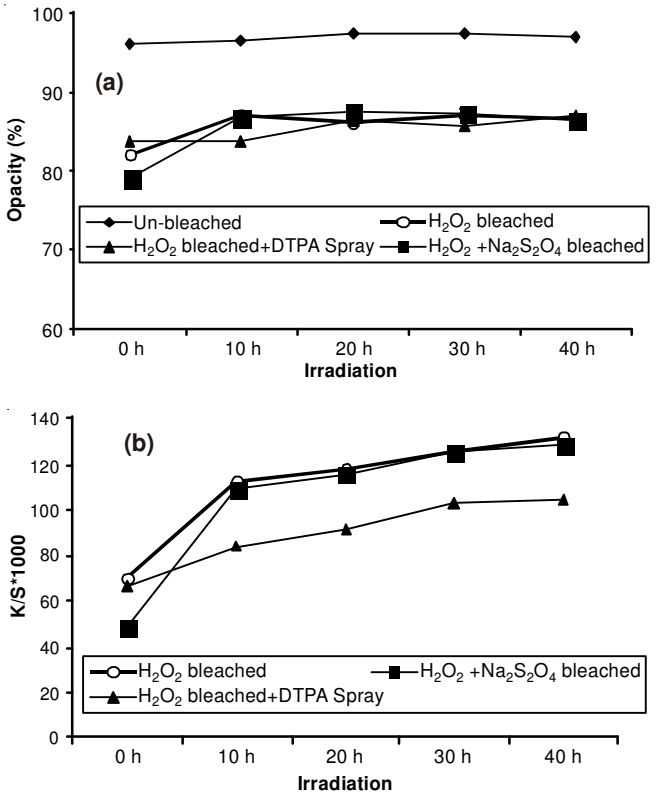


Fig. 2. Changes opacity (a) and K/S*1000 (b) in the handsheets of $H_2O_2$ bleached and DTPA sprayed beech CMP pulp following accelerated irradiation aging

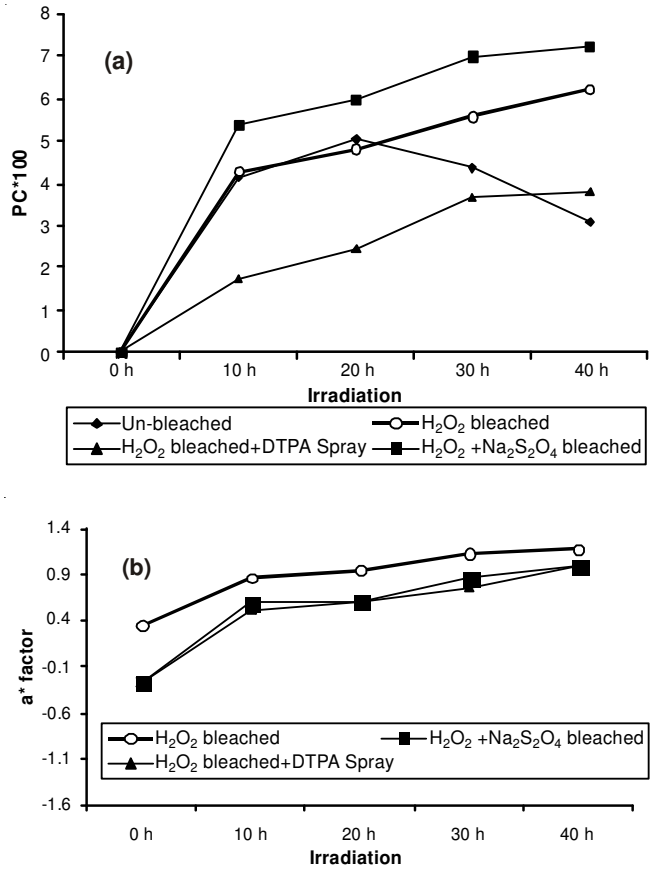


Fig. 3. Changes post colour (PC) number (a) and a* factor (b) in the handsheets of $H_2O_2$ bleached and DTPA sprayed beech CMP pulp following accelerated irradiation aging

that quinone structures and quinine precursors such as hydroquinones and catechols are important reactions in the photo-yellowing process in acetylated ground wood pulps. Qiu *et al.*[4] reported that the catalytic activity of $Mn^{2+}$ and $Mn^{3+}$ in decomposing hydrogen peroxide was studied by using DTPA as the only stabilizer. It was found that the addition of DTPA to a $Mn^{2+}$ containing system is more effective that if it is added to a $Mn^{3+}$ containing system. To decrease the catalytic activity of $Mn^{3+}$, sodium borohydride and DTPA under acidic condition were considered to reduce $Mn^{2+}$ to $Mn^{3+}$. The effect of pH on using DTPA to decrease Mn induced peroxide decomposition is discussed[4]. However, phenolic and carboxylic groups formation take place from quinines radicals during photo-yellowing and long-optical aging. This news groups could from the colour groups with metallic ions. Those factors are caused less optical properties and brightness reversion.

## Conclusion

The results of this study showed that the irradiation up to 40 h, yellowness, opacity, absorption coefficient, K/S ratio and post colour number increased and brightness decreased. Also complementary bleaching with sodium dithionite improves optical behaviour of the hand sheets in short-term aging. But in long-aging, the least brightness stability and most of optical deterioration were observed in unbleached paper and $H_2O_2$ bleaching and complementary bleaching with sodium dithionite. Following DTPA solution spraying on the surface of hand sheets, brightness, greenness, opacity improved and K/S ratio and post colour number were decreased. 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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