

## **Investigation on the Brightness Reversion of Horn Beam CMP Pulp Following Accelerated Irradiation Aging**

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### **Abstract**

In this research, Horn Beam chips were chosen randomly from the chips pile of Mazandaran Pulp and Paper Mill and cooked under CMP conditions and Pulps were prepared at the yield 85%. The CMP pulps were separately bleached with hydrogen peroxide and sodium dithionite with and without treating with DTPA. Then 60 gr/m<sup>2</sup> hand sheet were made. A solution of 0.5 percent of DTPA was sprayed over a number of hand sheets. Then the hand sheets were irradiated for 10, 20, 30 and 40 hours 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 hours, yellowness, opacity, absorption coefficient, K/S ratio and Post color (PC) number increased and brightness decreased. Also Complementary bleaching with sodium dithionite improves optical behavior of the hand sheets. Following DTPA solution spraying on the surface of hand sheets brightness, opacity and yellowness in improved and K/S ratio and PC number is decreased. Among different samples and following optical aging, it was found that in long-term aging, DTPA spray has considerable affect can the stability of brightness and increasing it durability against optical deterioration.

Key-words: Color change, Optical Aging, Irradiation, DTPA Spray, Sodium Dithionite, Brightness Stability and Horn Beam.

## **INTRODUCTION**

The use of High-yield mechanical and chemimechanical pulps are important, today's. These lignin-rich pulps are susceptible to photo-oxidative reactions which cause the pulps to become discolored 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,  $\alpha$ -carbonyl structures, lignin double bond structures, singlet oxygen, various radicals, phenolic groups (catechols), ortho-quinones, Para-quinones such as methoxy-p-benzoquinone, lignin  $\beta$ -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 photo stabilizing methods; although no single approach so far has become technically or economically feasible to meet all needs of the paper industry. Monica et al. (1991) reported that quinone structures and quinone precursors such as hydroquinones and catechols are important reactions in the photo-yellowing process in acetylated ground wood pulps (5). Forsskal and Tylli (1993) reported that the degrees of both photo-yellowing and photo-bleaching were linearly dependent on light intensity (2). Paulsson et al. (2001) 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 of sole importance for the light-induced discoloration or that trace amount of oxygen is necessary to cause discoloration. And acetylation clearly diminished the kinetics of photo-yellowing in all atmospheres resulting in substantially less absorption in the entire visible range (wavelength less than 400 nm) (8). Qiu et al. (2003) reported that the catalytic activity of  $Mn^{+2}$  and  $Mn^{+3}$  in hydrogen peroxide decomposing 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 than 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 (9).

## **EXPERIMENTAL**

### **Pulp**

In this research, horn beam 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 gr/l,  $NO_2$ :106 gr/l, sodium sulfite:20% and for 60 minutes in  $160^\circ C$ ), and pulps were prepared at the yield of 85% (1,9).

### **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 hour and temperature:  $75^\circ C$ . 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: 60 min and temperature: 65 °C, too. Then pulps were refined with PFI Mill to 300 C.S.F. freeness, and 60 gr/m<sup>2</sup> hand sheets were made from bleached and unbleached pulp according to TAPPI T 205 om-88. Next 0.5 percent of DTPA were sprayed on the hand sheets (1,9).

### **Irradiation of paper sheets and optical measurements**

TAPPI brightness and color change according to the CIELAB color scale ( L\*,a\*,b\* values) were measured on 60 g/m<sup>2</sup> 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 hand sheet were irradiated for zero , 10 , 20 , 30 and 40 minutes for accelerated aging . The optical characteristics of the hand sheets 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 color(PC) number were calculated using the Kubelka-Munk theory. The K/S value and PC number are calculated by the following equations (5,8,9):

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

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

Where S= light scattering coefficient

K= light absorption coefficient

T= irradiation time and R<sub>∞</sub> = reflectivity of an infinite pile of sheets

### **RESULTS AND DISCUSSION**

In this research, effect of accelerated irradiation aging investigation on the optical behavior of Paper sheets and those were estimated by using bleaching and DTPA spraying. The results of this study showed that following accelerated irradiation aging up to 40 hours, absorption coefficient, K/S ratio , opacity , yellowness , a\* factor and post color(PC) number were increased, and brightness and greenness were decreased .The post color(PC) number is scale for paper aging, and that is zero for zero hour accelerated aging .In that, the most of post color(PC) number and the least brightness stability were observed in H<sub>2</sub>O<sub>2</sub> bleaching and complementary bleaching with Sodium dithionite In the following bleaching and DTPA spraying on the hand sheets, brightness, greenness, opacity improved and K/S ratio and post color(PC) number were decreased. Following aging up to 40 hours, all optical Properties (except brightness) were increased. These changes are more tangible up to 20 hours irradiation (fig1-3).

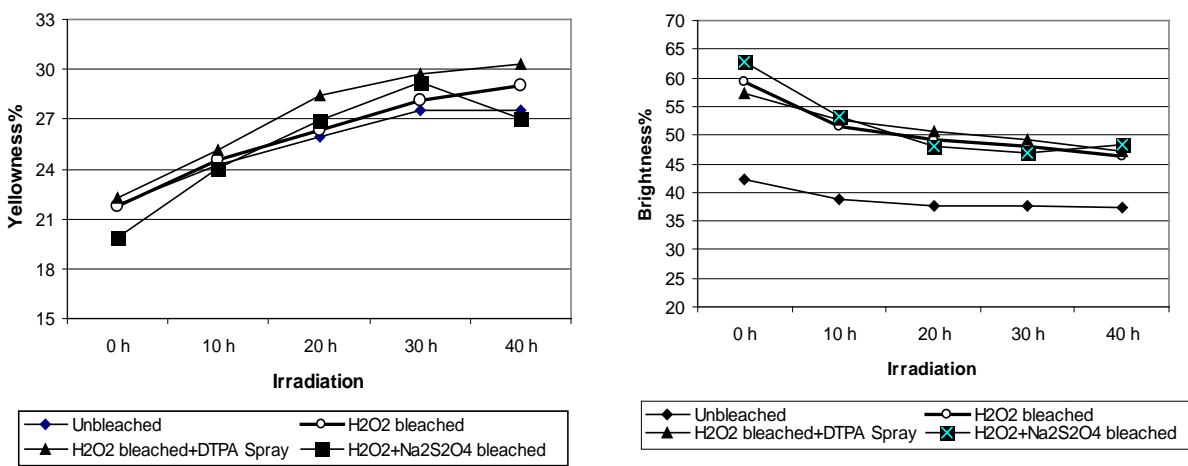


Fig.1. The changes yellowness (left) and brightness (right) in hand sheets of H<sub>2</sub>O<sub>2</sub> bleaching and DTPA spraying on optical properties of horn beam CMP pulp following accelerated irradiation aging

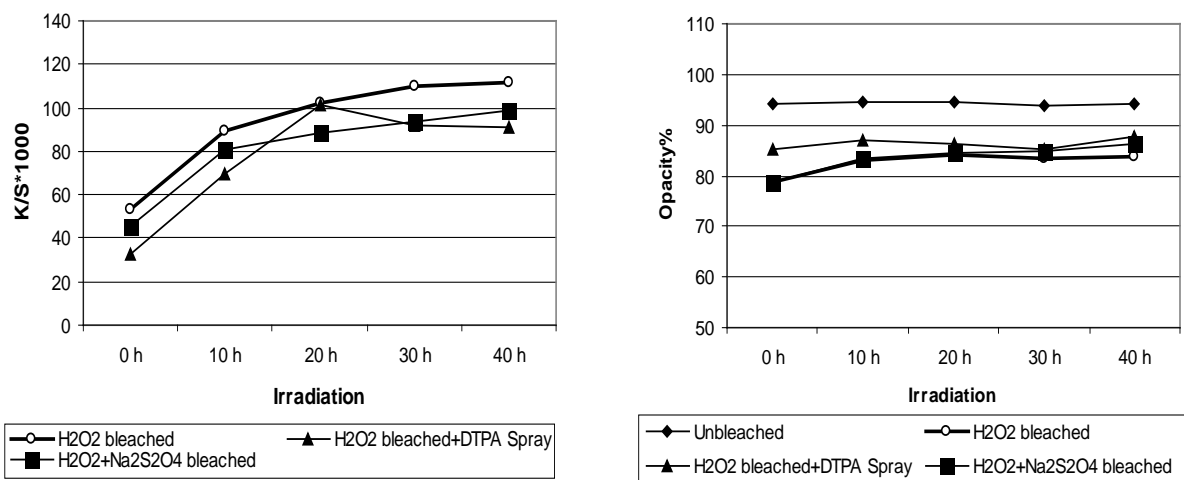


Fig.2. The changes Opacity (right) and K/S\*1000(left) in the hand sheets of H<sub>2</sub>O<sub>2</sub> bleaching and DTPA spraying on optical properties of horn beam CMP pulp following accelerated irradiation aging

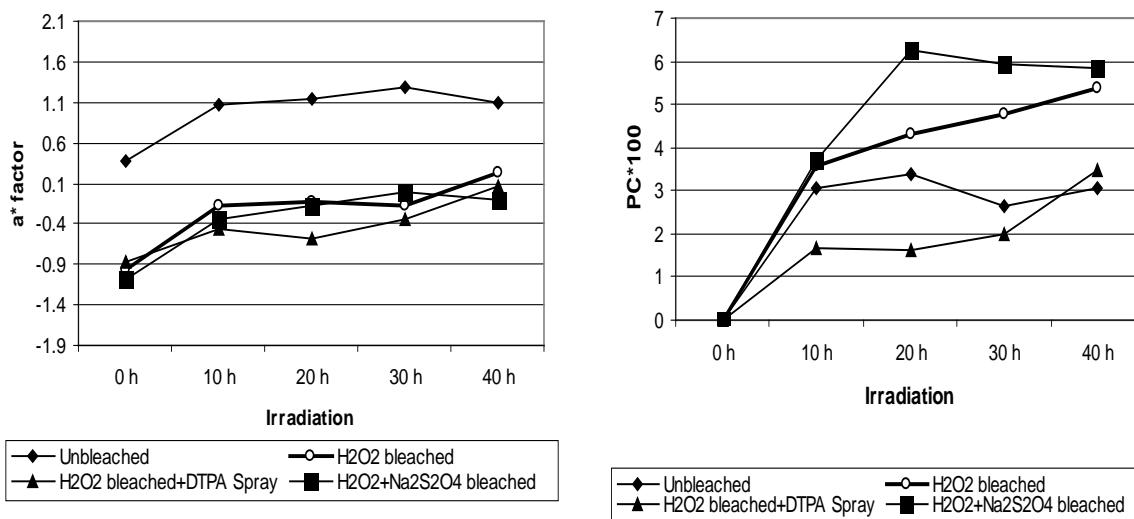


Fig3. The changes post color (PC) number (right) and a\* factor (left) in the hand sheets of H<sub>2</sub>O<sub>2</sub> bleaching and DTPA spraying on optical properties of horn beam CMP pulp following accelerated irradiation aging

Also complementary bleaching with sodium dithionite improved optical behavior of the hand sheets in short-term aging, but in Following long-aging, the least brightness stability and most of optical deterioration were observed in unbleached paper and H<sub>2</sub>O<sub>2</sub> bleaching H<sub>2</sub>O<sub>2</sub> bleaching and complementary bleaching with Sodium dithionite, too. It is because the oxidizer H<sub>2</sub>O<sub>2</sub> is reduced chromophores (quinones) to acid functional groups in hydrogen peroxide bleaching. Qiu et al. (2003) reported that the catalytic activity of Mn<sup>+2</sup> and Mn<sup>+3</sup> in hydrogen peroxide decomposing was studied by using DTPA as the only stabilizer. It was found that the addition of DTPA to a Mn<sup>+2</sup> containing system is more effective that if it is added to a Mn<sup>+3</sup> containing system. To decrease the catalytic of Mn<sup>+3</sup>, sodium borohydride and DTPA under an acidic condition were considered to reduce Mn<sup>+2</sup> to Mn<sup>+3</sup>. The effect of pH on using DTPA to decrease Mn induced peroxide decomposition is discussed (9). However, phenolic and carboxylic news groups formation from quinines radicals during photo-yellowing and long-optical aging. This news groups could formation color groups with metallic ions. Those factors are caused less optical properties and brightness reversion.

## CONCLUSIONS

The results of this study showed that following irradiation up to 40 hours, yellowness, opacity, absorption coefficient, K/S ratio and post color (PC) number increased and brightness decreased. Also complementary bleaching with sodium dithionite improved optical behavior 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<sub>2</sub>O<sub>2</sub> 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 color (PC) 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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