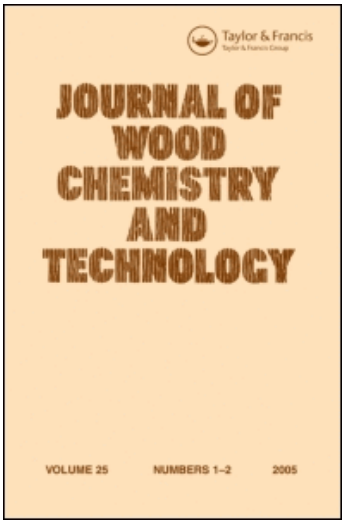


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# Interactions of Optical Brightening Agents With High Yield Pulps

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**Abstract:** The interactions of Optical Brightening Agents (OBA) with High Yield Pulp (HYP) fibers under two methods of OBA addition were evaluated on a softwood TMP and hardwood (aspen) HYP: OBA added to the peroxide bleach liquor (Method A), and OBA added conventionally at the wet end (Method B). The treated pulps were fractionated and OBA retention and efficiency in each fraction were determined. Adding OBA to the bleach liquor gave a higher OBA retention than adding OBA at the wet end; the hardwood HYP had a higher OBA brightening efficiency than the softwood TMP. The results are explained in terms of pulp morphology, lignin content, and process conditions (temperature and contact time). Adding OBA to the mechanical pulp also improved the brightness stability during the light-induced yellowing process.

**Keywords:** Contact time, fluorescent, fractionation, high yield pulp (HYP), HW HYP, Optical Brightening Agents (OBA), SW TMP, temperature

## INTRODUCTION

High yield pulp (HYP), due to its many unique properties such as high bulk and high light scattering coefficient, as well as its lower price, find many applications, including printing and writing paper products.[1–5] However, the market HYP still has a lower brightness in comparison with hardwood kraft pulps. There is a market interest to improve the optical properties of the HYP. An Optical Brightening Agent (OBA) can be used to increase the pulp brightness at a reasonable cost.[6] Much of the earlier research[7–9] has focused on the brightening of chemical pulps, but the results on the OBA interactions with HYP are limited.

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OBA can also effectively improve the optical properties of HYP.[6,10–11] An earlier study showed that the OBA brightening process can be conveniently incorporated into the alkaline peroxide bleaching process.[12] This approach has several advantages over the conventional method, whereby, OBA is added in the wet end of the papermaking process. First, the quenching effect on OBA by the wet end cationic polymers such as poly-ethylene–imine (PEI) can be decreased by fixing OBA on HYP fibers before going into the papermaking process. Moreover, the negative impact of metal ions in the white water system on the OBA performance can be minimized when OBA is pre-adsorbed and fixed on HYP fibers. Furthermore, the photo-yellowing (color reversion) of HYP and HYP-containing paper sheets can be decreased when more OBA is on HYP fibres to protect them from harmful UV radiation.

In this study, we further compared the two OBA addition methods: Method A is defined as OBA added in the peroxide bleaching process, while Method B is referred to as adding OBA in the wet end after peroxide bleaching. The objective is to determine why the two OBA addition methods can produce different results.



## EXPERIMENTAL

### Materials and Procedures

An OBA, Tinopal HW, was obtained from Ciba Specialty Chemicals. Figure 1 shows the chemical structure of the OBA. The dosage of OBA used

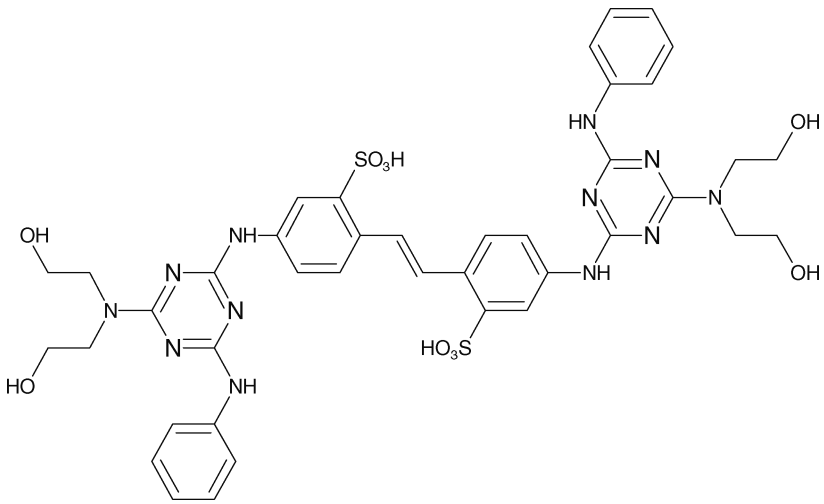


***Figure 1.*** Chemical structure of Tinopal HW OBA.

in this study was based on liquid product as received (containing 13% active OBA content). An unbleached softwood (spruce) TMP (50% ISO brightness) and an unbleached hardwood HYP (aspen CTMP, 45% ISO brightness) were obtained from mill A and mill B. The pulps were stored in a freezer before they were processed. First, the pulp was thawed in a microwave oven for 3 min, and then disintegrated in hot deionized water (65°C) for 40 min. After the DTPA (0.2%) washing process, the pulps were filtered with a 150 mesh screen, and the filtrate was recycled in order to recover the fines; finally the pulps were pressed to 39% consistency and fluffed.

## OBA Addition Methods

Two OBA addition methods were examined in this study:

- **Method A**: OBA added in the bleaching liquor. The typical bleaching liquor consisted of 6% $H_2O_2$, 4.5% NaOH, 0.2% DTPA, and 3% $Na_2SiO_3$ by weight of oven dry (O.D) pulp. The bleaching conditions were 20% pulp consistency, a temperature of 70°C, and reaction time of 3 h.
- **Method B:** OBA added into the wet end. The bleached pulp was disintegrated in deionized water (23°C) at 1% consistency for 10 min. The pH of the pulp suspension was adjusted to about 6 with sodium metabisulfite, and then 2.3% Tinopal HW was added into the pulp suspension and mixed for 3 min.



## Fiber Fractionation

We followed the Dynamic Drainage Jar (DDJ) method: first, 40 g OBA processed wet pulp was disintegrated in DI water of known hardness (2000 ppm for SW TMP, and 100 ppm for HW HYP), which was prepared by adding $CaCl_2$ and $MgSO_4$ at a weight ratio of 1:1 to de-ionized water.Next, the well-dispersed pulp suspension was transferred into a 10-liter Dynamic Drainage Jar (DDJ) with a 200 mesh screen installed. The pulp suspension was washed 3 times with 7 liter water and the filtrate containing the fines that passed the 200 mesh screen (P200) was collected and the fines allowed to stand overnight. The pulp retained on the 200 mesh screen was further fractionated by washing with an additional $3 \times 7$ liter water with a 20 mesh screen installed. Those retained on the 20 mesh screen would be the long fibers, and those that pass the 20 mesh were collected as the medium fibers.

## Analysis

The fiber size distribution was characterized by using a Fiber Quality Analyzer (FQA) of Optest Equipment Inc. The specific surface area of fibers was

determined by measuring the turbidity of the suspension using a Turbidity meter (Lisle-Metrix DRT-290 Turbidimeter). The method was based on the theory that turbidity of the pulp suspension is a function of some intrinsic measure of ability of particles to scatter light and the concentration of the particles in suspension. The ability of particles to scatter light directly relates to the specific surface of the particles. The detailed procedures were as following: The bleached SW TMP and HW CTMP fractions (No OBA) were diluted into a 1 liter 0.15% consistence pulp suspension and well dispersed prior to the turbidity testing. Each fraction was tested in duplicate and averaged. The 0.15% suspension was diluted first by a factor of two and then by a factor of four into consistency of 0.07% and 0.035%. The turbidity of three suspensions were recorded and plotted against the pulp consistency. The specific area of the fiber was calculated from the slope of the plot.

The OBA retention on the pulp fractions was determined based on the Kjeldahl nitrogen analysis. The OBA-treated pulp samples (whole pulp or DDJ fractions) were digested in concentrated sulfuric acid, dissolved as an ammonium sulfate solution. An excess amount of base was then added to the solution, converting $NH_4^+$ to ammonia gas ($NH_3$), and then trapped by cooling it to a boric acid solution. The ammonium–borate complex was titrated by a sulphuric acid standard solution. The quantitative amount of sulphuric acid was used to calculate the total amount of nitrogen ($M_n$) from the following equation

$$M_n = (T - B) \times 14X0.02X1000/W \quad (1)$$

where, $M_n$ = Total amount of nitrogen in mg/kg
$T$ = Volume of 0.02N $H_2SO_4$ used in sample titration in ml
$B$ = Volume of 0.02N $H_2SO_4$ used in blank titration in ml
$14$ = the molular weight of nitrogen in grams
$W$ = the oven-dried weight of OBA-treated pulp sample in grams

The light stability of OBA-processed pulp fractions were tested following a method of McGarry et al.[12] The fluorescent component of the OBA-processed pulp was determined according to the PAPTAC Standard E.1 using a Technidyne TB-1C instrument.

## RESULTS AND DISCUSSION

### Characteristics of DDJ Fractioned Fibers

The morphology, chemical composition, as well as optical properties of pulp fraction vary dramatically depending on type of pulp and pulping process. The

**Table 1.** Characteristics of bleached pulp fractions (no OBA)

| Sample | Fraction | S ($m^2$/kg) | K ($m^2$/kg) | Lignin content (% O.D) | Mass content (% O.D) | Bright. (%ISO) | Specific surface area |
|---|---|---|---|---|---|---|---|
| SW TMP | Whole | | | | | 80.0 | |
| | Long | 41.3 | 1.1 | 25.6 | 55 | 78.0 | 3.4 |
| | Medium | 70.2 | 1.4 | 27.6 | 18 | 80.6 | |
| | Fine | 80.9 | 2.0 | 35.5 | 27 | 79.0 | 9.6 |
| | Whole | | | | | 84.0 | |
| HW HYP | Long | 37.4 | 0.7 | 14.7 | 50 | 83.5 | 2.4 |
| | Medium | 47.8 | 0.9 | 17.3 | 25 | 83.7 | |
| | Fine | 67.9 | 1.9 | 28.3 | 25 | 78.8 | 4.5 |



general characteristics of the peroxide bleached and DDJ fractioned pulps are summarized in Tables 1 and 2. The SW TMP fractions all have higher lignin content than HW HYP fractions. As lignin has a strong absorption in the visible light, higher lignin content will result in stronger absorption of blue light. This is in line with the observed specific light absorption coefficient, k value. The specific light absorption coefficient, k, of the SW TMP fractions for example, is larger than for the HW HYP fractions (see Table 1). As the pulp brightness is measured at 457 nm, the strong absorption of the visible light will induce a lower brightness; as a result, it is easy to understand most of the SW TMP pulps fractions have lower brightness than HW HYP fractions. It is interesting to note that the SW TMP fine fraction has a brightness of 79% ISO, which is higher than the long fraction (78% ISO), but lower than the medium fraction (81% ISO). Similar results have been reported by others.[13] The brightness is affected by both the absorption coefficient (k) and the scattering coefficient (s), as governed by the Kubelka-Munk equation. As expected, the fines fraction of the SW TMP has the highest absorption coefficient, in agreement with its highest lignin content. However, the fines fraction of the SW TMP also has

**Table 2.** FQA results on fiber length distribution of DDJ pulp fractions

| | | Percentage of fines (L = 0.07–0.2) | | Mean length (0.07–10) | |
|---|---|---|---|---|---|
| Sample | Fraction | Arithmetic (%) | Length weighted (%) | Arithmetic (mm) | Length weight (mm) |
| SW TMP | Long | 26.2 | 4.3 | 0.77 | 1.45 |
| | Medium | 50.6 | 21.3 | 0.28 | 0.54 |
| | Fine | 95.8 | 88.9 | 0.13 | 0.15 |
| HW HYP | Long | 17.5 | 3.7 | 0.60 | 0.83 |
| | Medium | 44.9 | 15.6 | 0.34 | 0.58 |
| | Fine | 96.5 | 89.6 | 0.10 | 0.14 |

the highest scattering coefficient compared with other fractions of SW TMP (Table 1). This off-sets the absorption coefficient, so that the brightness of the fines fraction is between the long fraction and the medium fraction. Compared with the SW TMP, the fines fraction of HW HYP has totally different behavior in terms of the brightness. Hardwood, such as aspen, initially contains less lignin than the softwood (e.g., spruce). After the chemical impregnation in the pulping process, lignin has been softened and further removed, allowing the pulp to attain a higher brightness during bleaching. Even though the fines from the HW HYP have a high scattering coefficient which increases the brightness, they also have the highest absorption coefficient, and the absorption is much stronger than other fractions. For example, compared with the long fraction, fines of HW HYP have 2.7 times the absorption ability of the long fiber fraction, while the scattering coefficient is only 1.8 times that of long fiber fraction (see Table 1). As a result, the overall brightness of the fines of HW HYP is much lower than the long fraction of HW HYP.

When OBA is added in the pulp suspension, the brightening efficiency very much depends on how it interacts with fiber because the brightness increase by OBA is additive to the reflectance of the pulp itself. In order to better understand the interaction of the OBA with fiber fractions, the OBA addition method on the brightening efficiency of the OBA has been investigated and will be discussed in the following sections.



## OBA Addition Methods on the Brightening Efficiency

The effects of the OBA addition method have an effect on brightening efficiency of the pulp fraction. Figures 2 and 3 show that Method A has an overall higher brightening efficiency than Method B in terms of brightness gain. For SW TMP, for example, the brightness gain of each fraction with 2.3% OBA charge are 4.3, 3.7, 3.6 and 3.3, 3.4, 3.2 points for Method A and Method B, respectively. For HW HYP the corresponding brightness gains are 4.9, 4.3, 3.5 points versus 4.4, 4.2, 3.3 points at 0.5% OBA dosage. This higher brightness gain obtained from Method A can be explained by the fact that Method A has a higher OBA retention than Method B caused by the higher temperature, longer contact time, and higher pulp consistency from the peroxide bleaching process.

Secondly, the initial brightness has an effect on the OBA brightening efficiency and it is higher if the initial brightness is higher. The aspen HW HYP has a higher brightness than the SW TMP due to its lower lignin content and higher bleach ability. As the final brightness of the OBA treated fiber is a sum of the pulp initial brightness and the fluorescence contribution from the OBA, the HW HYP treated with 0.5% OBA charge achieved a similar brightness gain as SW TMP fiber treated with 2.3% OBA charge.

Also, the lignin fluorescence quenching has been proven as another factor that determines the brightness gain from OBA. The higher the lignin

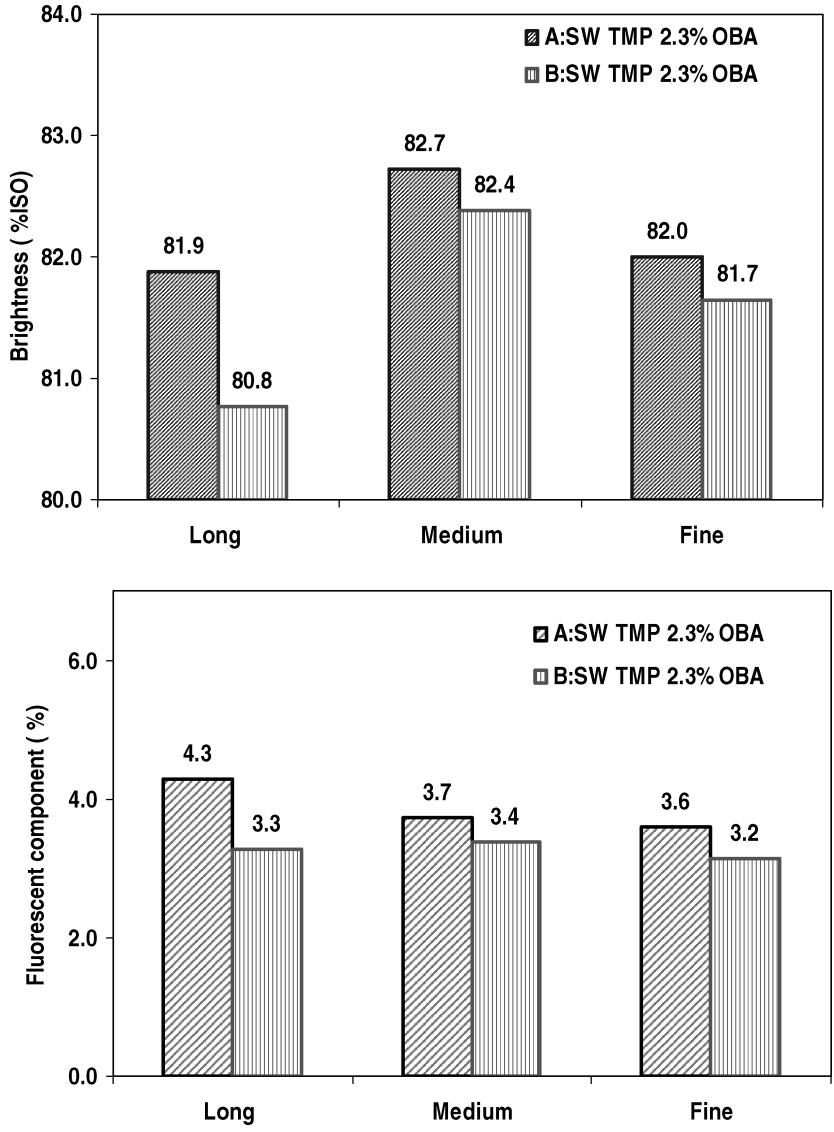


*Figure 2.* SW TMP Brightness and fluorescent component as a function of addition method. (A: OBA added in bleaching liquor, B: OBA added in the wet end. Handsheet made with D.I water hardness made of 2000 ppm hardness).

content, the stronger lignin fluorescence quenching would be. Therefore it is expected that fines, with the highest amount of lignin present, will also have the strongest quenching effect of OBA. When OBA is added to the alkaline peroxide bleaching process, due to the higher temperature, longer contact

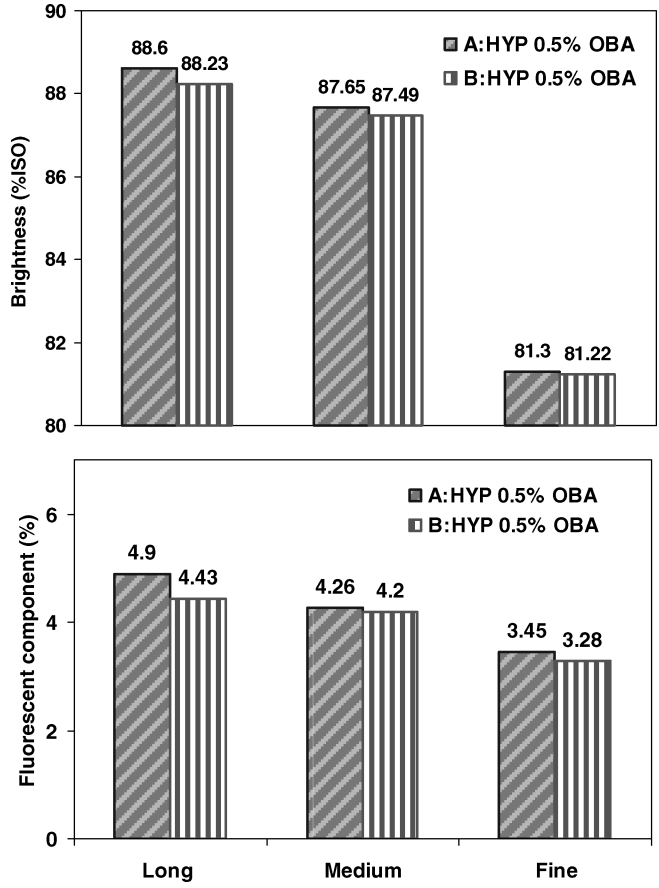


*Figure 3.* Aspen HYP Brightness and fluorescent component as a function of addition method. (**A:** OBA added in bleaching liquor, **B:** OBA added into wet end. Hand sheet made with D.I water hardness made of 100 ppm hardness).

time, higher consistency, and alkaline conditions, all of which favor OBA penetration/diffusion into the fiber wall, it is expected that it may have better OBA retention than the conventional OBA addition method.

## OBA Retention

The absolute amount of the OBA on each of the DDJ separated fractions were measured by nitrogen analysis, which was adapted for determining the OBA retention. It is based on the consideration that there are 12 nitrogen atoms in Tinopal HW OBA. The results are summarized in Table 3.

**Table 3.** OBA retention on SW TMP, HW HYP treated with two OBA addition methods

| Sample | | Nitrogen (mg/kg) | OBA on fiber* (mg/kg) | Retention (%) |
|---|---|---|---|---|
| SW TMP | Method A (2.3% OBA) | | | |
| | Long | 273 | 11449 | 27.4 |
| | Medium | 278 | 11659 | 9.1 |
| | Fine | 452 | 18956 | 22.3 |
| | Method B (2.3% OBA) | | | |
| | Long | 137 | 5746 | 13.7 |
| | Medium | 182 | 7633 | 6.0 |
| | Fine | 349 | 14637 | 17.2 |
| HW CTMP | Method A (0.5% OBA) | | | |
| | Long | 53 | 2223 | 22.2 |
| | Medium | 101 | 4236 | 21.2 |
| | Fine | 215 | 9017 | 45.1 |
| | Method B (0.5% OBA) | | | |
| | Long | 57 | 2390 | 23.9 |
| | Medium | 87 | 3649 | 18.2 |
| | Fine | 104 | 4362 | 21.8 |

SW TMP was fractioned at a water hardness of 2000 ppm, and HW HYP at 100 ppm. OBA formula concentration was 13%.



OBA added in the peroxide bleaching liquor (Method A) has a higher overall OBA retention than the conventional wet end addition (Method B), and this trend was true for both the SW TMP and HW HYP. Fines have a higher retention of OBA than other fractions using both addition methods. The SW TMP fines, for example, retained 60% more OBA than the long or medium fraction for Method A, and twice or more than the long or medium fraction for Method B. The HW HYP fines, however, retained four times the amount of the long fraction, and twice the amount of the medium fraction for Method A; for Method B, the fines retained twice the amount of OBA as the long fraction, and 1.5 times that of the medium fraction.

These differences can be mainly attributed to the two different factors: one is the process parameter (e.g., temperature, contact time, consistency and pH); the other is the nature of the fiber (e.g., fiber morphology, specific surface area and chemical composition). For OBA added in the bleaching liquor, the interaction of OBA with fiber occurs under a higher temperature, longer contact time, higher consistency, and higher pH than Method B (70°C, 3 h, 20% and pH 11 versus 23°C, 3 min, 1% and pH 7, respectively). The higher pH will enhance the swelling of the pulp fiber;[14] a higher temperature and longer contact time and higher consistency favor the penetration and diffusion of OBA in the swelled fiber.[15] Another aspect is the difference of species. SW TMP has about 50% higher lignin content (see Table 1), than the HW HYP for these

particular samples; a higher content of lignin will hinder the penetration and diffusion of OBA into the fiber wall,[16] as a result, a reduced OBA adsorption was observed on the SW TMP.

One interesting point is that the fines have a much higher OBA retention than the other fractions and this mainly due to its higher specific area caused by the small dimension, as seen from the data in Table 2. For SW TMP, the length-weighted length of the fines is one-tenth that of the long fiber; whereas for HW HYP, the length-weighted length of fine is one-eighth that of the long fiber. Usually the smaller the size, the larger the specific surface area will be. The specific area was measured by using the turbidity method. Smaller size particles have a higher turbidity due to their higher scattering. As the consistency of the suspension increases, the scattering and resulting turbidity will also increase. Therefore, by measuring the turbidity at different pulp consistency the specific area can be determined by the slope of the plot of turbidity and consistency (see turbidity test in the Experimental section). The specific area of SW TMP fines is 3 times that of the long fiber, whereas for HW HYP, fines have twice the specific area as that of long fiber. A higher specific area will create more absorption sites, which will enhance the adsorption of OBA, resulting in a higher OBA retention (Table 3).

With a higher OBA retention on fiber, a higher brightness and high fluorescence would be expected; however, this is not always the case. The fines of HW HYP absorbed the greatest amount of OBA but they had the lowest brightness instead, which is caused by the highest lignin content, and its quenching effect, as discussed in the previous section.



## Light Stability of OBA-Treated Fractionated Fibers

OBA improves not only the pulp brightness, but also the light stability due to its UV screening ability.[17] In the present study, the brightness stability of pulp fractions treated with OBA was tested following an accelerated aging procedure. This method has been used by others.[12] Handsheets (200 g/m$^2$) were irradiated in a photoreactor with cool white fluorescent lamps that emitted both UV and visible radiation. The light intensity measured on the surface of the handsheets was 975 footcandles (FC), which was 19 times stronger than the regular office ambient light radiation (50 FC). This accelerated method has been proven[18] to be an effective way to quickly rank the relative light stability of the pulps. The post color number, an indicator of chromophore generation during the accelerated aging process was determined for the pulps with and without OBA treatment, and plotted against accelerated aging time. The results are shown in Figure 4. It can be seen that, compared with the control (0% OBA), handsheets with OBA treatment have less amount of chromophores generated during the light-induced yellowing process, supporting the conclusion that the presence of OBA decreased the light-induced yellowing process for high yield

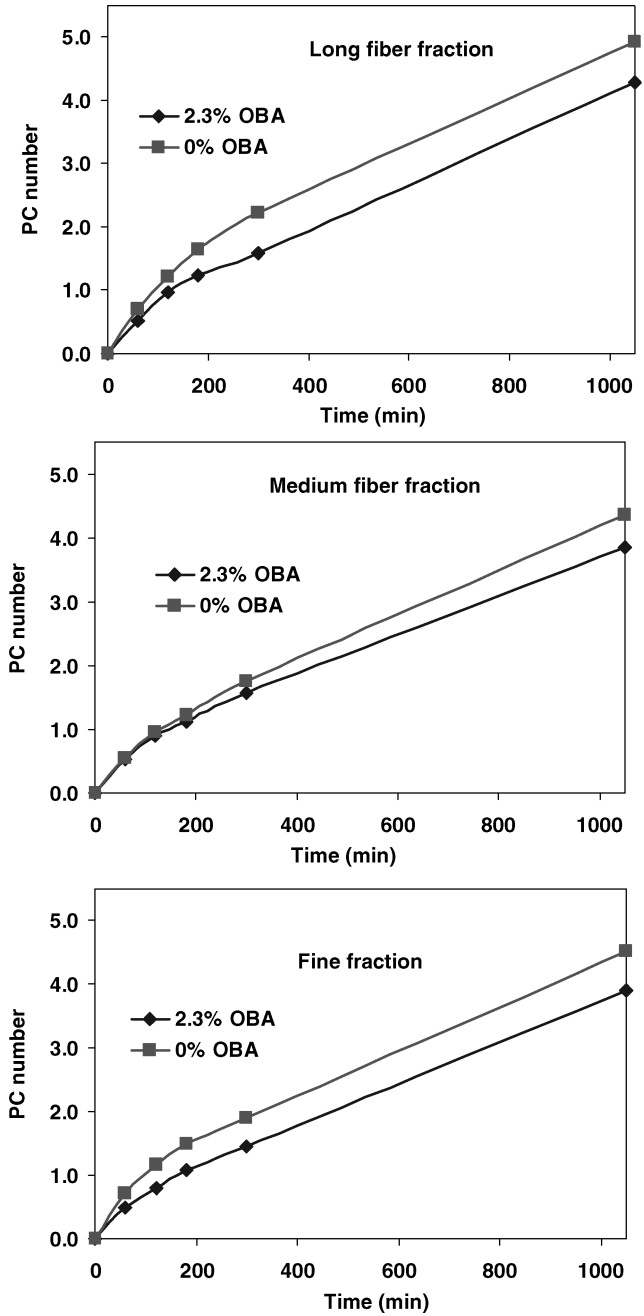


*Figure 4.* Effect of OBA on the light-induced brightness of softwood TMP fractions (OBA charge 2.3%, and added in bleaching liquor).

pulps. Figure 4 shows a two-phase light-induced yellowing process, an initial rapid discoloration followed by a slower, less detrimental secondary phase. This is in line with the results of others.[18–20]

## CONCLUSIONS

- OBA added in bleaching liquor has a higher OBA retention than OBA added in the wet end. This applies to both HW HYP and SW TMP.
- HW HYP fibers have higher affinity for OBA than SW TMP fibers.
- Fines absorb more OBA due to their high specific surface area. However, the fines' brightness is lower than other fractions, and the brightness gain obtained from OBA was quenched by the higher lignin content. The brightness of OBA treated and fractionated fibers will depend on their morphology and chemical composition.
- The presence of OBA in the bleached mechanical pulp decreased the light-induced yellowing.



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