Further Understanding the Combined Bleaching Process of Peroxide and Optical Brightening Agent in a Spruce Thermomechanical Pulp

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Optical brightening agent (OBA) has been successfully applied to a high-yield pulp (HYP) bleaching process (peroxide/OBA, or P/OBA technology) because of its effectiveness for improving the optical properties of treated pulp. In this study, P/OBA technology was optimized for the peroxide bleaching of spruce thermomechanical pulp (TMP). The results obtained were further analyzed using data processing software, and the bleaching chemical cost was estimated. The results showed that the brightness ceiling (the highest "technical brightness") of Koyama spruce TMP from conventional peroxide bleaching was 75.5% ISO. In contrast, the brightness ceiling of the same mechanical pulp could be raised to 85.9% ISO using P/OBA technology. At a low-brightness target, OBA is not effective when added to the peroxide bleach liquor, and thus is not economical for this purpose; however, at a high-brightness target, the P/OBA technology is effective due to the remarkable brightening effect of OBA. When the brightness target was 80% ISO, an optimized economic cost of 280.2 RMB/ton can be obtained under the "relay point" conditions of 2.57% peroxide and 0.6% OBA (on o.d. pulp).

Keywords: Koyama spruce; Peroxide bleaching; OBA; Brightness ceiling; Bleaching chemicals cost

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INTRODUCTION

In the manufacturing of high value-added paper products, the substitution of high-yield pulp (HYP) for bleached kraft pulp is a critical factor for improving profit margins. Most producers in China wish to use HYP as much as possible, while maintaining appropriate paper properties, such as optical and strength properties (Lei *et al.* 2013; Zhang *et al.* 2013). Thus, producing high-quality HYP has become critical for many pulp producers. One important demand for high-quality HYP is its high brightness and brightness stability (Liu *et al.* 2012).

Currently, hydrogen peroxide bleaching technology is usually applied to mechanical pulp bleaching for increasing the pulp brightness. Much work has been conducted to improve the peroxide bleaching processes, and some has been successfully commercialized in pulp mills (He *et al.* 2009). Based on the conventional peroxide bleaching process, HYPs, such as thermomechanical pulp (TMP) and chemithermo-mechanical pulp (CTMP), can technically be bleached to higher brightness levels (*e.g.*, 80% ISO for softwood, and 85% ISO for hardwood) (Ni and He 2011). However, the so-called "brightness ceiling" (*i.e.*, the increase in brightness is halted after a certain brightness level) exists for peroxide beaching; in such cases, a very high chemical cost would be incurred for reaching a high brightness target (Pan 2001; 2004).

OBA can be incorporated into an alkaline peroxide bleaching process (Chen *et al.* 2010; He *et al.* 2010). It seems that there is a higher OBA retention and better OBA diffusion into fibers when it is applied during the peroxide bleaching stage (He *et al.* 2009, 2010; Zhang *et al.* 2013). Therefore, the combined P/OBA brightening process is advantageous compared with conventional peroxide bleaching because part of the brightness gain can be achieved by OBA brightening to avoid harsh peroxide bleaching conditions, so that the unique properties of high-yield pulp can be largely preserved (He *et al.* 2010). For a given brightness target, the bulk and light scattering coefficient of the bleached pulp from the combined P/OBA brightening process were markedly higher than those from the conventional peroxide bleaching process, while less dissolved organic matter (measured as chemical oxygen demand (COD)) and anionic trash (Zhang *et al.* 2009) were generated. OBA can also inhibit the photoyellowing (photoreversion) of HYPs by acting as an ultraviolet screener (Ragauskas *et al.* 2001; Zhang *et al.* 2009).

For pulp producers, OBA is an expensive chemical; its use must be justified with respect to profit margins. Hence, it is particularly important to further optimize the P/OBA bleaching for HYP. In this study, the P/OBA bleaching process was optimized for the spruce TMP bleaching process *via* varying dosages of OBA and hydrogen peroxide. The experimental data was analyzed using data processing software, and the cost of bleaching chemicals was assessed.

EXPERIMENTAL

Materials

An unbleached spruce TMP (Canadian Standard Freeness (CSF) 250 mL, brightness of 58.4% ISO, pretty low metal ions content), was made in the laboratory. A disulphonic OBA sample (about 25% solid content) was obtained from a paper mill in the Henan province of China, and its dosage was based on the liquid products as received.

Methods

Bleaching processes

The single-stage peroxide bleaching and combined peroxide/OBA brightening experiments were conducted in polyethylene bags using the following conditions: 20% pulp consistency, 1% to 8% hydrogen peroxide (H_2O_2), 0.5% Epsom salt(magnesium sulphateheptahydrate, $MgSO_4{\bullet}7H_2O$), 0.5% diethylenetriaminepentaacetic acid (DTPA), 2.4% sodium silicate (41° Baumé), 0.6% to 5% sodium hydroxide (NaOH), at 80°C for 150 min. All required bleaching chemicals were added into a beaker to prepare bleach liquors in the following order: water, DTPA, Epsom salt, silicate, NaOH, H_2O_2, and OBA (if required). The bleach liquor was then added to pulp that was pre-heated to the desired reaction temperature, and mixing was done *via* kneading for 1 min in a plastic bag.

Handsheet making and measurement

In this process, a laboratory sheet former (RK-3A, PTI, Vorchdorf, Austria) was used. The handsheets (basis weight of 60 g/m²) were prepared according to the TAPPI method T205 sp-95 (1995). The brightness of the handsheets was tested on an Elrepho spectrophotometer (SE070, L&W) in accordance with the ISO method 2470 (1999).

Determination of bleaching chemical cost

The chemical cost was calculated only for the bleaching stage based on the chemicals' dosages for the o.d. pulps and the unit prices for OBA (8800 RMB/ton, the liquid products as received), H_2O_2 (3148 RMB/ton, 100% actives), NaOH (2812 RMB/ton, 100% actives), DTPA (6700 RMB/ton, 100% actives), Epsom salt (1180RMB/ton, 100% actives), and silicate (2450 RMB/ton, the liquid products as received), which were provided by a pulp mill in the Henan province in China.

RESULTS AND DISCUSSION

Effect of Hydrogen Peroxide and OBA Dosages on Pulp Brightness in the Combined P/OBA Brightening Process

The effect of peroxide dosage on bleached pulp brightness at various OBA charges was compared in Fig. 1. The pulp brightness increased with the increase in the peroxide dosage for the bleaching process without OBA addition (conventional peroxide bleaching), but the brightness gain decreased as the peroxide dosage increased, indicating that the brightening efficiency deteriorated at a high brightness range. Compared with the unbleached pulp brightness (the original brightness was 58.38% ISO), the brightness of bleached pulp (69.11% ISO) increased by 10.73% ISO when the peroxide dosage was fixed at 2%; when the dosage was increased to 4% and 8%, the brightness of bleached pulp (73.72% ISO and 75.45% ISO) increased by 15.34% ISO and 17.07% ISO, respectively.

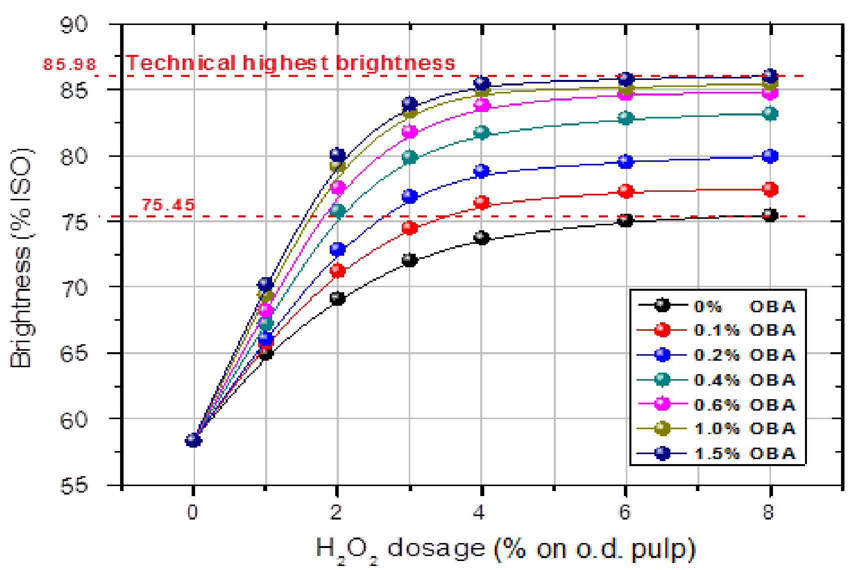

Fig. 1. Effect of peroxide and OBA dosages on bleached pulp brightness during the combined P/OBA bleaching process of a spruce TMP

The brightness increment due to the peroxide dosage was gradually reduced with increasing peroxide dosage (see Fig. 2). For example, when the peroxide dosage was increased from 0% to 4%, the brightness increment increased by 15.3% ISO. When the dosage was increased from 4% to 8%, the increment increased only by 1.73% ISO. Consequently, it can be concluded that with an increase of peroxide dosage, the brightness of single-stage bleached pulp has a brightness ceiling, which is the highest brightness that can be obtained *via* this bleaching configuration.

In this study, the bleached brightness ceiling of spruce TMP was 75.5% ISO, which exists for a single-stage, high consistency peroxide bleaching system. Nowadays, a multi-stage bleaching process is commonly used, and this requires more investment for the related equipment and a greater amount of bleaching chemicals. Adding OBA to the bleaching liquors, the so-called combined P/OBA brightening process, can significantly improve the asymptotic brightness limit of the bleached TMP. As shown in Fig. 1, six levels of OBA dosages were used in the combined P/OBA brightening process, and the highest brightness limit for the bleached pulp was 85.9% ISO. For a fixed OBA charge, the changing trend of bleached pulp brightness was like that of conventional peroxide bleaching (0% OBA). At a low peroxide dosage, the brightness increased significantly (a high brightening efficiency); at a high peroxide dosage, the brightness increased slowly, and gradually approached the brightness ceiling. Also, the pulp brightness approached the asymptotic brightness limit more readily with increase of OBA dosage; the more OBA that was used, the less peroxide that was needed. For instance, with a 1.0% OBA dosage, only 4% peroxide was needed to reach the highest brightness; with a 0.4% OBA dosage, at least a 6% peroxide dosage was needed; without OBA (the conventional peroxide bleaching), more than an 8% peroxide was needed. For comparison, more than 8% peroxide dosage was needed to reach the brightness limit when OBA was not added (*i.e.*, the conventional peroxide bleaching process).

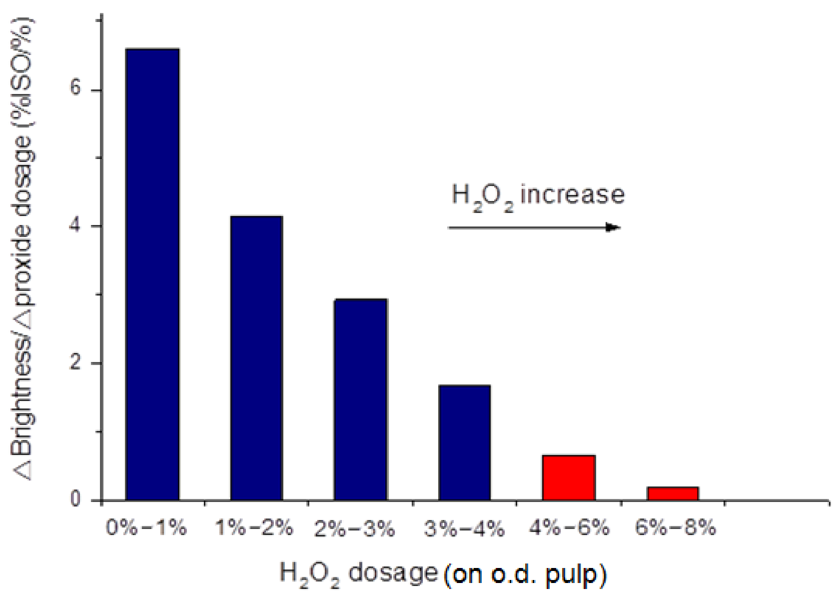

Fig. 2. Calculated incremental brightness increase per incremental peroxide charge at given total peroxide dosages for the conventional peroxide bleaching of a spruce TMP

Figure 1 also shows that both the peroxide bleaching efficiency and the OBA brightening efficiency decreased as their dosages increased. As shown in Fig. 3, at a fixed 4% peroxide dosage, the brightening efficiency of the OBA gradually decreased with the increasing OBA dosage. When the OBA dosage was more than 0.6%, the incremental brightness improvement decreased that was attributable to fluorescence. When the OBA dosage was higher than 1.0%, the brightening efficiency of the additive almost ceased; thus it would have made no sense to add more OBA beyond that dosage level.

In summary, when the OBA dosage was fixed, the pulp brightness increased as the peroxide dosage increased, while the incremental brightening efficiency decreased; when the peroxide dosage was fixed, the pulp brightness increased with an increasing OBA dosage, while the incremental brightening efficiency from the OBA decreased. Figures 2 and 3 show that for a single-stage bleaching process, the peroxide dosage should not exceed 4% and the OBA dosage should not exceed 0.6%, in order to maximize TMP brightness improvement without excessive waste of chemicals. Therefore, optimizing the dosages of peroxide and OBA can have a significant effect on the overall cost of the process.

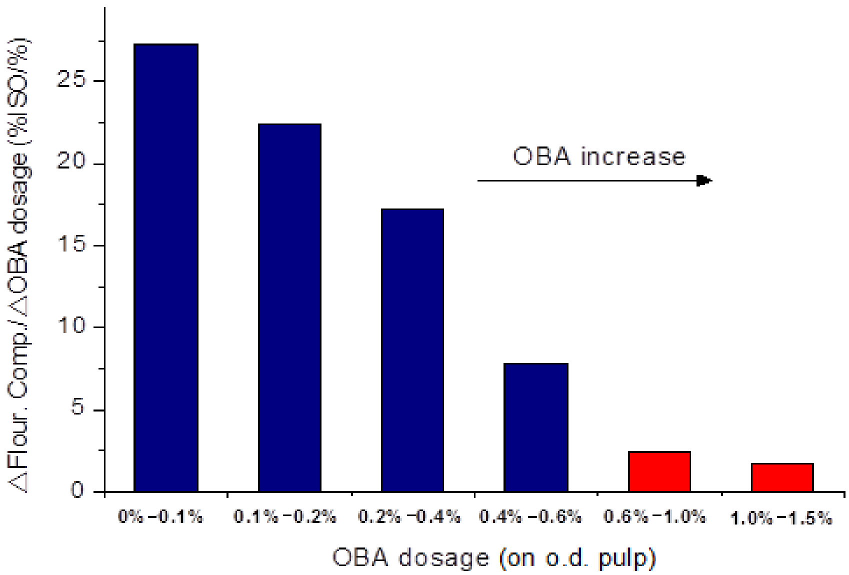

Fig. 3. Calculated incremental TMP brightness increase attributable to fluorescence per incremental OBA charge at given total OBA dosages for the combined P/OBA brightening process (at fixed 4% peroxide dosage)

Effect of OBA and Peroxide

The effects of both OBA and peroxide on the TMP brightness gains caused by fluorescence phenomena are shown in Fig. 4. In the combined P/OBA bleaching process, the overall brightness gains of bleached pulp achieved by the "chemical bleaching" of peroxide, and the "physical brightening" of OBA, known as the fluorescent component (the brightness gain due to OBA "physical brightening"). As shown in Fig. 4(a), the fluorescent component increased with increasing OBA dosages at a fixed peroxide dosage of 4%. Figure 4(b) shows fluorescence brightness gains at a fixed 0.4% OBA dosage and at variable peroxide dosages. When the OBA charge was fixed, the fluorescent component of bleached pulp increased at first with increasing peroxide charge, and then later reached a plateau value. Figure 4(c) also shows a similar story; *i.e.*, when the peroxide dosage was fixed, increasing the OBA dosage caused the fluorescent component to first increase, and then level-off at a plateau value. Figures 4(b) and 4(c) support the conclusions that the peroxide and OBA could improve their effectiveness for each other, and OBA was more useful at a high peroxide dosage condition.

Based on the data above, the hydrogen peroxide and OBA could help each other with respect to the bleaching effectiveness of spruce TMP. The combined P/OBA process is like a "relay race", where the "first runner" runs at high speed and the "second runner" receives a baton hand off. When the "first runner" (peroxide bleaching) slows down, the "second runner" (OBA brightening) should then pick up the baton and finish the race. For a given brightness target, the optimal bleaching/brightening result was achieved through optimizing the dosages of peroxide and OBA. For different brightness targets, the optimal dosages of peroxide and OBA, the so-called "relay point", were quite different, and the "relay point" was affected by many factors, such as bleached pulp brightness, bulk, light scattering coefficient, and bleaching cost. In this study, the pulp brightness and the bleaching cost, both of which are of great importance to pulp manufacturers, were the constraining factors that were of interest.

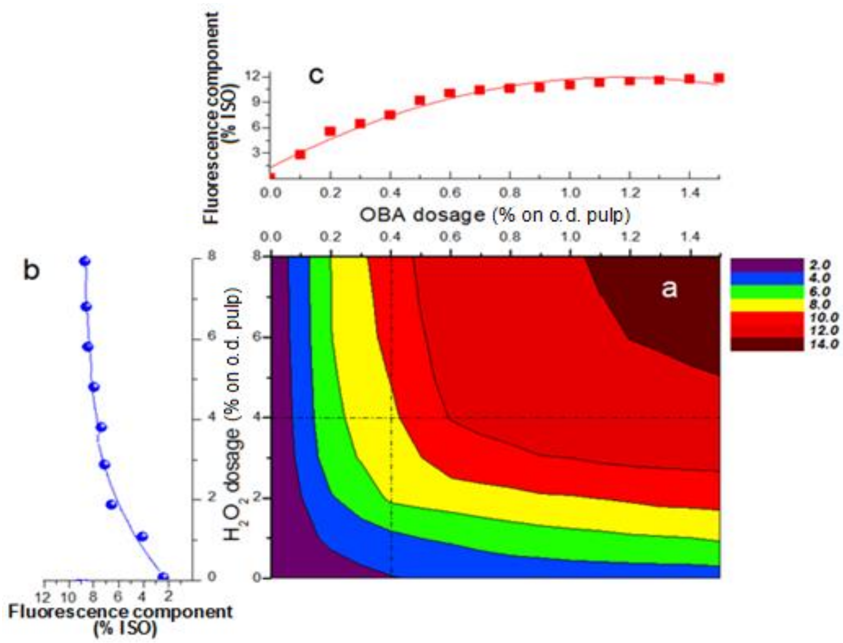

Fig. 4. Contour plot of fluorescence component (a) with different peroxide and OBA dosages in the combined "P/OBA" brightening process (the curves of fluorescence component with peroxide dosage and OBA dosage marked (b) and (c), respectively).

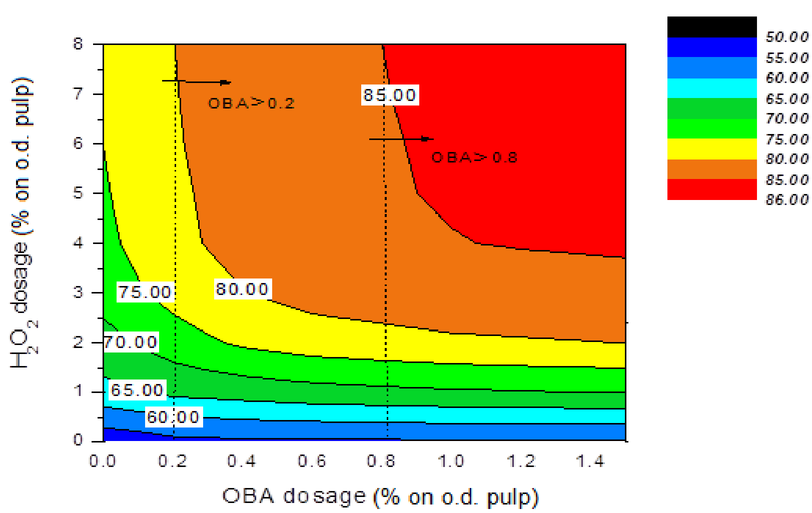

Fig. 5. Bleached pulp brightness contour plot of a spruce TMP treated with the combined "P/OBA" bleaching process

Dosages of Peroxide/OBA at Different Brightness Targets

In the combined P/OBA brightening process, a given brightness target can be attained by adjusting the dosages of peroxide and OBA. The bleached pulp brightness contour, which was plotted by fitting the brightness data of spruce TMP, is shown in Fig. 5. The figure shows the various combinations of peroxide and OBA dosages needed to obtain different brightness targets. Also indicated in this figure is that the bleached pulp could not meet a high brightness target (*i.e.*, >75% ISO), if the OBA dosage was not sufficient (*i.e.*, >0.2% OBA). For example, when the brightness target was 80% ISO, the minimum OBA addition was 0.2%; when the brightness target was 85% ISO, the minimum OBA addition was 0.8%.

Table 1. Optimum Dosages of Peroxide and OBA at Different Brightness Targets of Bleached Pulp (%)

60% ISO		65% ISO		70% ISO		75% ISO		80% ISO		85% ISO	
OBA	H_2O_2	OBA	H_2O_2	OBA	H_2O_2	OBA	H_2O_2	OBA	H_2O_2	OBA	H_2O_2
0.00	***0.70***	0.00	1.31	0.00	2.48	0.00	5.89	0.20	8.00	0.80	8.00
0.10	0.61	***0.10***	***1.04***	0.10	1.90	0.10	3.27	0.30	3.86	0.86	6.00
0.20	0.51	0.12	1.00	***0.20***	***1.60***	0.20	2.57	0.40	3.07	0.90	5.00
0.40	0.45	0.20	0.91	0.30	1.44	0.30	2.17	0.50	2.80	1.00	4.30
0.60	0.41	0.40	0.84	0.40	1.33	***0.35***	***2.00***	***0.60***	***2.57***	***1.07***	***4.00***
1.00	0.37	0.60	0.77	0.50	1.25	0.40	1.91	0.70	2.48	1.10	3.98
1.40	0.35	1.00	0.71	0.60	1.19	0.50	1.81	0.80	2.39	1.20	3.88
1.50	0.35	1.40	0.68	0.80	1.12	0.60	1.72	0.90	2.29	1.30	3.83
—	—	1.50	0.67	1.00	1.06	0.80	1.65	1.00	2.19	1.40	3.77
—	—	—	—	1.40	1.00	1.00	1.57	1.40	2.03	1.50	3.71
—	—	—	—	1.50	0.99	1.40	1.50	1.50	2.00	—	—
—	—	—	—	—	—	1.50	1.49	—	—	—	—

Notes: (1) The optimized total alkali-to-peroxide ratio is (0.60-0.67):1; (2) the italicized bold values represent the optimum low cost conditions.

For a given brightness target, as shown in Table 1, the more OBA that was used resulted in less peroxide that was required. The OBA additive is more expensive than hydrogen peroxide on a mass basis, and thus using excessive amounts of OBA is not cost-effective. Peroxide has a lower price than OBA, but its brightening effect was affected by the alkali dosage to activate the peroxide; the strong alkaline bleaching conditions can lead to the significant losses of bulk, light scattering coefficient, and pulp yield values, as well as other drawbacks. Therefore, the recommended technique is to optimize the OBA and peroxide dosages for producing bleached mechanical pulps with good optical properties, while largely maintaining other desirable properties, such as good bulk and light scattering attributes.

Usually the application concept for hydrogen peroxide is “low cost, large dosage,” which is suitable for low unbleached TMP brightness; in contrast, OBA application is “high cost, low consumption,” which is suitable for the relatively high unbleached TMP brightness. It is possible to reduce the total bleaching cost by optimizing the dosages of peroxide and OBA to meet the required brightness target and economic constraint.

Chemical Cost of P/OBA Bleaching Process at Different Brightness Targets

Figure 6 shows the chemical costs at different brightness targets for the combined P/OBA bleaching of a spruce TMP. As shown in Fig. 6, the chemical costs increased with increasing OBA dosage for brightness targets in the low range (*e.g.*, 60% ISO). The chemical cost was lowest (134.7 RMB/t o.d. pulp) when the dosages of OBA and peroxide were 0% and 0.7%, respectively (Table 1). Gradually, the optimal OBA dosage level increased as the brightness target increased. For example, for a 75% ISO brightness target, the optimal OBA dosage was 0.35% with 2.0%peroxide dosage at a P/OBA chemical cost of 229.5 RMB/t o.d. pulp. At higher brightness targets, it would be necessary to use OBA. In order to reach a brightness of 80% ISO or higher, as an example, it is not possible to brighten the TMP by using only peroxide in a single stage since this higher than the upper asymptotic brightness limit, as shown in Fig. 1; these higher brightness targets can be obtained by using an OBA added to the single peroxide stage (Fig. 6). Furthermore, when the brightness target was 85% ISO, the optimal OBA dosage was 1.07% with 4.0% peroxide dosage, which resulted in P/OBA chemical cost of 392.2 RMB/t o.d. pulp. The observations indicated that the use of OBA in the P/OBA bleaching process makes economic sense for a high brightness target, whereas the P/OBA process is not suitable for a low brightness target that are below the asymptotic brightness limit obtainable with a single peroxide stage (*i.e.*, <75% ISO as shown in Figs. 1 and 6).

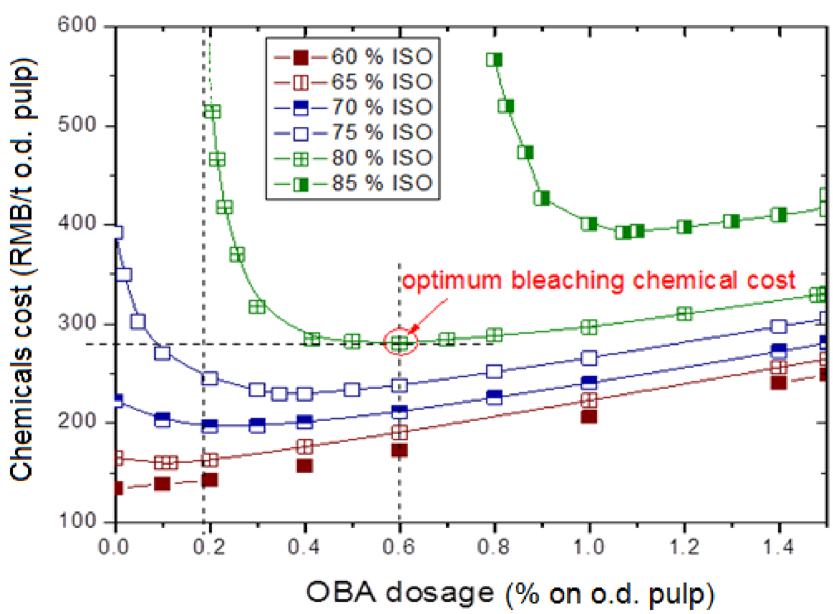

Fig. 6. The cost of bleaching chemicals with OBA at different brightness targets of a spruce TMP (1 RMB (Chinese Yuan) is roughly equal to 0.15 USD (US Dollars) in 2017)

As shown in Fig. 6 and Table 1, different brightness targets correspond to the appropriate optimum dosages of hydrogen peroxide and OBA. For a given brightness target, there was only one optimum peroxide/OBA ratio, corresponding with the optimum cost of bleaching chemicals. Figure 6 shows that as the brightness target increased, the optimum OBA dosage also increased; certainly the "optimum chemical costs" for P/OBA also increased. This is shown in Table 1 with optimum conditions denoted in italicized font for brightness targets ranging from 60 to 85% ISO.

The calculated chemical costs for the optimized conditions denoted in Table 1 are illustrated in Fig. 7. The optimized cost increased with an increasing brightness target. When the bleaching purpose was for high brightness, such as 85% ISO brightness, the mechanical pulp producers usually care about the brightness target and the bleaching cost at the same time. When the brightness was less than 80% ISO, the economic cost was reasonable enough to meet the papermaker's requirements. When the brightness target increased to 80% ISO, the optimum bleaching cost was 280.2 RMB/t o.d. pulp; when the brightness target was raised to 85% ISO, the P/OBA costs escalated to 392.3 RMB/t o.d. pulp.

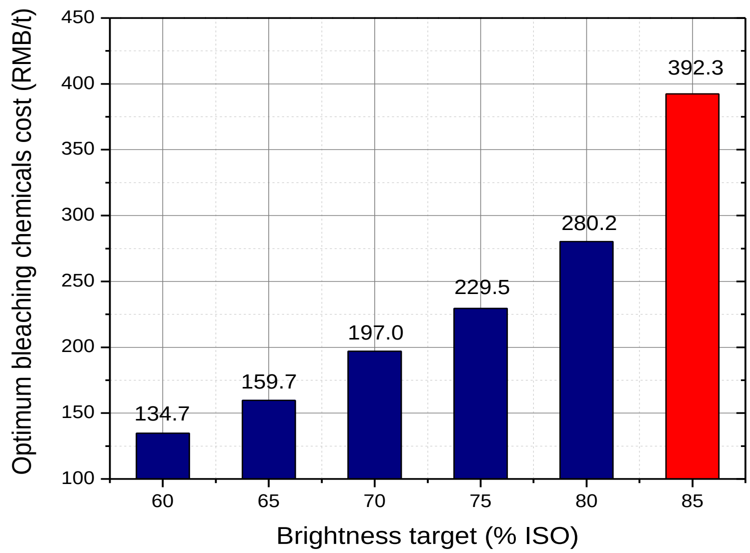

Fig. 7. Relationship between different brightness targets and optimized bleaching cost in the combined P/OBA brightening process of a spruce TMP (based on the optimum conditions of Table 1, 1 RMB (Chinese Yuan) is roughly equal to 0.15 USD (US Dollars) in 2017)

CONCLUSIONS

1. The bleached brightness ceiling of Koyama spruce TMP with a single peroxide stage is 75.5% ISO. This asymptotic limit can be raised to 85.9% ISO if OBA is added to the peroxide stage (*i.e.*, the P/OBA bleaching process). At a low-brightness target, the OBA application was not justified due to its high cost; however, at a higher brightness target, the P/OBA process is economically favorable, due to the effective fluorescent brightening caused by the OBA.
2. For the combined P/OBA brightening process, a "relay effect" between hydrogen peroxide and OBA is achieved. Considering the pulp brightness and the chemical costs, the authors found that the "relay point" (the point of the optimum dosages of peroxide and OBA) indeed exists at different brightness targets. When the brightness target was 80% ISO, the optimized economic cost of 280.2 RMB/t o.d. pulp was obtained under the "relay point" conditions of 2.57% peroxide and 0.6% OBA.

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