Research paper

Effects of the BCTMP Content in Furnish on the Performance of Fluorescent Optical Brightening Agents

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【Summary】

The purposes of this study were to use fluorescent optical brightening agents (OBAs) to study the effect of the bleached chemi-thermomechanical pulp (BCTMP) content in papermaking stock on the optical properties of the resulting paper, and find means to improve problems associated with BCTMP use, such as paper yellowing and the tendency for such paper to have lower brightness and apparent whiteness. The OBAs used were commercial di- (2S) and tetra-sulfonic (4S) types which were added to pulps with different BCTMP contents. The optical properties, including brightness, apparent whiteness, CIE L*a*b* values, and light-fastness, of the resulting handsheets were then tested. The results indicated that the 2S-OBA group exhibited greater efficacies with regard to brightness and apparent whiteness than the 4S-OBA group. At an OBA dosage of < 1.0% and a BCTMP content of 10%, the whiteness-enhancing effect was maximized. At OBA dosages of > 1.0%, however, 15% of BCTMP in the furnish yielded the best effect. The 2S-OBA tended to shift the paper color more toward the green-blue axis than did the 4S-OBA. The saturation point occurred when the 2S-OBA dosage reached 1.0~1.5%; and for 4-S OBA it was 1.5%. Yellowing of paper tended to increase with an increasing BCTMP content. In BCTMP-containing paper, adding OBAs decreased the yellowing trend which was proportional to the OBA dosage. Yellowing was more moderate with the 2S-OBA than the 4S-OBA with regard to apparent whiteness; however; for brightness measurements, both OBA groups had similar yellowing trends. Summarizing the above results, the 2S-OBA was more suited to BCTMP-containing furnishes.

Key words: fluorescent optical brightening agent, bleached chemithermomechanical pulp (BCTMP), yellowing, brightness, apparent whiteness.

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研究報告

漂白化學熱磨木漿含量對於螢光增白劑表現的影響

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摘 要

本研究目的為探討漿料中漂白化學熱磨木漿含量對於手抄紙添加螢光增白劑的光學性質影響，期能建立使用漂白化學熱磨木漿時降低白度及視白度與黃化現象的對策。螢光增白劑使用市售的二磺酸及四磺酸螢光增白劑，添加在不同比例漂白化學熱磨木漿的漿料中。手抄紙光學性質量測白度、視白度、CIE L*a*b*及光老化現象等。實驗結果顯示二磺酸螢光增白劑較四磺酸螢光增白劑有較佳的白度及視白度表現。在螢光增白劑添加量低於1.0及10%漂白化學熱磨木漿含量時，有最佳的增白效果。但在螢光增白劑添加量高於1.0%時，15%漂白化學熱磨木漿含量呈現最佳的增白效果。二磺酸螢光增白劑對於紙色趨向綠-藍軸較四磺酸螢光增白劑明顯。二磺酸螢光增白劑在添加量1.0~1.5%達到綠化點，但四磺酸螢光增白劑則在1.5%。手抄紙黃化現象隨著漂白化學熱磨木漿含量而加劇，但添加螢光增白劑會降低黃化現象，隨著添加量成正比例關係。對於視白度而言，二磺酸螢光增白劑減緩黃化現象較四磺酸螢光增白劑明顯。但是對於白度而言，兩種螢光增白劑效應差不多。總而言之，二磺酸螢光增白劑較適合應用在含化學熱磨木漿的漿料。

關鍵詞：螢光增白劑、漂白化學熱磨木漿、黃化、白度、視白度。

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INTRODUCTION

In order to maintain competitiveness in a globalized marketplace, lighter grammage has become a goal for which paper mills are striving. How to meet customers' quality requirements while lowering costs has become a major concern, and one often-taken route by various mills is to increase proportions of bleached chemi-thermomechanical pulp (BCTMP) added to pulp mixes. The measure can increase the bulk and opacity of paper products, but due to the higher lignin content of the pulp, is also liable to cause problems of yellowing and decreased apparent whiteness (Sykes et al. 1998). Hence, fluorescent optical brightening agents (OBAs) are often added to enhance the brightness and apparent whiteness of the paper products.

The most commonly used OBAs in the paper industry are triazinyl diaminostilbene derivatives. The number of sulfonic groups on the derivatives influences the solubility of the OBA and its affinity to fibers. The OBAs that are added at the wet end of paper machine are generally di- (2S) and tetra-sulfonic (4S) OBAs. The basic whitening mechanisms of OBAs are absorbing ultraviolet light and re-emitting it as bluish light. As a consequence, paper with OBA looks brighter and whiter when it is exposed to daylight or UV light. OBA molecules diffuse through the cell wall structure and become fixed through hydrogen bonding. The performance of an OBA depends on the influences of its concentration, drying conditions, and other paper

additives. The whitening effect of OBAs is often quenched by a cationic polymer (Crouse and Snow 1981). Adding OBA to furnishes containing mechanical pulps can lower the intensity of UV reaching the fibers and thus lessen the yellowing of such papers (Roltsch and Lloyd 1987, Ragauskas et al. 1998, Bourgoing et al. 2001).

Effects of the process variables on OBA applications, such as contact time, process water hardness, furnish makeup, anionic trash and fines, PCC filler, etc., on the whitening efficacy and OBA retention rate were examined (Zhang 2007a-c). The results indicated that at a contact time of more than 5 min and water hardness of 25 ppm, the OBA performance was optimized. OBA retention in BCTMP-containing paper was poorer than those of wood-free ones. The large amount of anionic trash and fines arising from BCTMP somewhat affected the OBA retention, while adding PCC filler did not affect OBA retention, but reduced its whitening effect. In practical use, they noted that at a BCTMP proportion of < 30% and an OBA dosage of > 0.5%, the OBA retention was > 90%.

The purposes of this study were to use fluorescent OBAs to study the effect of the BCTMP content in papermaking stock on the optical properties of the resulting paper, and to find means to improve problems associated with BCTMP use, such as paper yellowing and the tendency for such paper to have lower brightness and apparent whiteness. The OBAs used were commercial 2S and 4S types which were added to pulps with different BCTMP contents. The optical properties, including the brightness, apparent whiteness, CIE L*a*b* values, and light-fastness, of the resulting handsheets were then tested.

MATERIALS AND METHODS

Materials

The bleached softwood kraft pulp (BSKP), from Canfor, McKenzie, Canada, had a freeness of 425 mL CSF, a sampling consistency of 37.61%, and a brightness of 87~88% GE. The bleached hardwood kraft pulp (BHKP), on the other hand, was supplied by Chunghwa Pulp and Paper Co., Haulien, Taiwan, and also had a freeness of 425 mL CSF, a sampling consistency of 36.37%, and a brightness of 87~88% GE. The BCTMP used was from Millar Western, Whitecourt, Alberta, Canada, and had a freeness of 250 mL CSF, a sampling consistency of 91%, and a brightness of 85% GE.

The 2 types of OBAs added were 2S and 4S types, both made by former Ciba Specialty Chemicals Inc., Basel, Switzerland, with trade names of Tinopal UP and Tinopal ABP, respectively. Both chemicals were in a form of an anionic liquid. A direct violet dye added in the study was Irgalite violet R-L by Ciba, which was an anionic liquid.

Experimental design and methods

The experimental design entailed using 2 OBAs (2S and 4S types) under different dosages (0.5, 1.0, 1.5, and 2.0%, with respect to the dry pulp) to various BCTMP- content pulps (with a content of BSKP of 20%, and BHKP/BCTMP ratio of 70/10, 65/15, 60/20, and 50/30% of the pulp mixes) and examined the effects on the optical properties of the resulting handsheets. Irgalite violet R-L at a fixed 0.05% dosage was also added. Optical properties investigated included pulp brightness, apparent whiteness, CIE L*a*b* values, and light-fastness. There were 70 sets of specimens and 210 handsheets.

The procedure for stock preparation entailed stirring pre-blended pulps of BSKP-BHKP and BCTMP of 1.2% consistency at 150~180 rpm. Then, a suitable quantity of OBA (0~2.0% to dry pulp) was added. After stirring for 5 min, 0.05% Irgalite violet R-L

was added and further stirred for 5 min. The pulp furnish was then diluted to a 0.3% consistency and used to prepare the handsheets.

Handsheets were prepared according to the TAPPI T205 standard method, but the basis weight of the handsheets was 80 g m^{-2} instead of 60 g m^{-2} for optical measurement purposes. The couched handsheets were placed in an oven maintained at 105±2℃ for 20~30 min. Then the handsheets were placed in a constant temperature and humidity (CTH) room for 24 h before testing. Measurements of the optical properties were conducted in accordance with the TAPPI T452 om-02 standard method using a Technidyne (New Albany, IN, USA) model Micro S-5 unit (D_{65} illuminant) for measuring brightness, apparent whiteness, and CIE L*a*b* values. Light-fastness was tested according to ISO 4892, using an accelerated aging environment provided by a Q-panel (Q-Lab, Cleveland, OH, USA), wherein specimens were irradiated with UV light for 2, 8, and 24 h, and retested for the light-fastness of the specimens. In the optical property tests, 3 handsheets were prepared for each condition, and 5 points on a handsheet were tested for a total of 15 data points. Then, the average and standard deviation were calculated.

RESULTS AND DISCUSSION

Brightness and apparent whiteness

The brightness and apparent whiteness of the handsheets with a nominal basis weight of 80 g m^{-2} are shown in Fig. 1. The pooled standard deviations of brightness and apparent whiteness were 0.12 and 0.15% GE, respectively. Both the brightness and apparent whiteness of the handsheets decreased with an increasing content of BCTMP. To begin with, the brightness and apparent whiteness of the BCTMP were lower than those of the BSKP and BHKP; hence, the greater the amount of BCTMP there was, the lower the brightness and apparent whiteness of the base paper were. Thus, the range of brightness was 83.4~81.5% GE, whereas the apparent whiteness decreased from 75.4 to 73.1% GE.

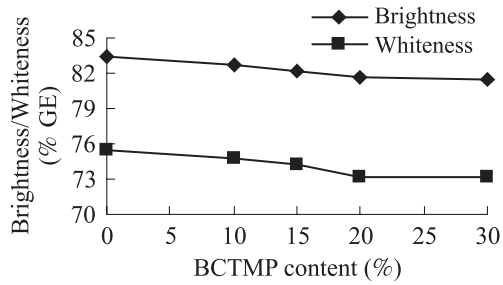

Fig. 1. Effects of bleached chemi-thermomechanical pulp (BCTMP) contents on handsheet brightness and apparent whiteness.

The effects of both the BCTMP content and the 2S- and 4S-OBA dosages on the brightness and whiteness measurements of the handsheets are shown in Figs. 2 and 3. The figures indicate that the blending proportions of BCTMP and OBA dosages affected the handsheet brightness and apparent whiteness with similar trends. When furnish contained no BCTMP, adding the 4S OBA tended to produce paper with a higher brightness than those with the 2S-OBA added. However, for pulp blends containing BCTMP, the performance was reversed; the latter was brighter than the former. As for the apparent whiteness, regardless of whether there was BCTMP in the pulp or not, the 2S-OBA group always had higher values than the corresponding 4S-OBA one. For BCTMP-containing furnishes, both the 2S- and 4S-OBA groups exhibited increasing patterns of brightness and apparent whiteness with increasing dosages, before reaching a maximum, then decreasing with a further increase in the OBA dosage. When the OBA dosages were < 1.0%, the maximum

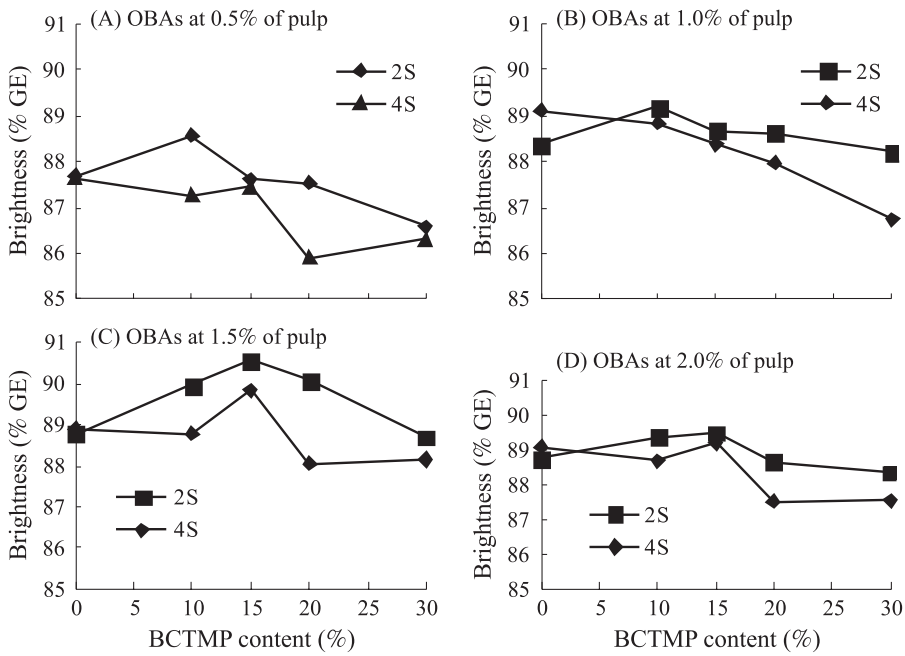

Fig. 2. Effects on handsheet brightness at different dosages of 2 types of optical brightening agents (OBAs) for handsheets from furnishes with different bleached chemi-thermomechanical pulp (BCTMP) content.

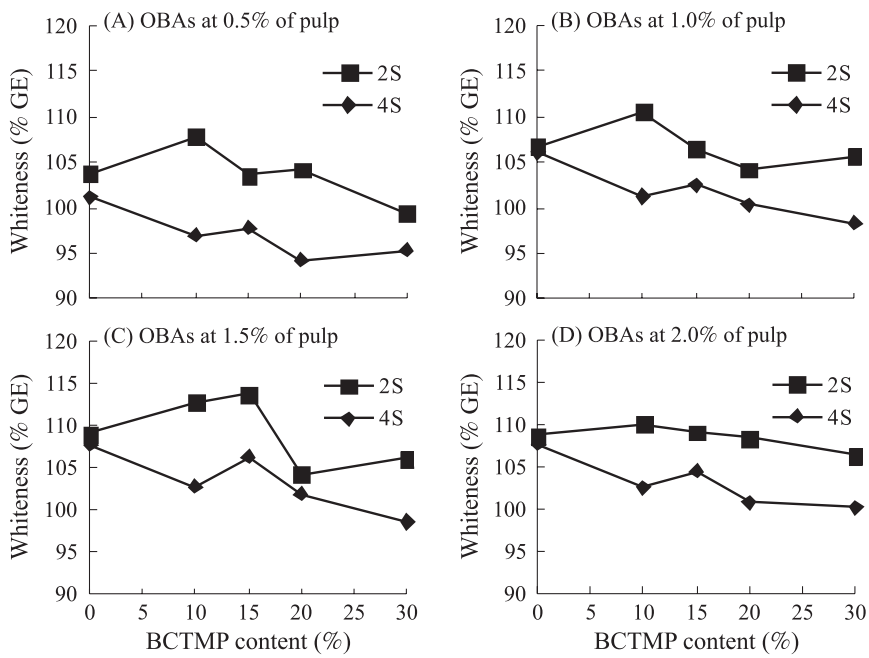

Fig. 3. Effects on handsheet apparent whiteness at different dosages of 2 types of optical brightening agents (OBAs) for handsheets from furnishes with different bleached chemi-thermomechanical pulp (BCTMP) content.

brightness and apparent whiteness occurred in paper from furnishes containing 10% BCTMP. For OBA dosages > 1.0%, however, the maximum brightness and apparent whiteness shifted to the paper containing 15% BCTMP. From graphs (A) to (D) in Fig. 2, apparently both brightness and apparent whiteness increased with OBA dosages to a maximum at a 1.5% dose. When the OBA dosage reached 2.0%, both the brightness and apparent whiteness decreased. Supported by the CIE L*a*b* measurements, at this level, the OBA was already overdosed and past the saturation point.

Ni's research group (Zhang et al. 2007a-c) pointed out that when BCTMP was added to the furnish, the fibers retained most of the original lignin in the wood. Compared to chemical pulp, there were fewer pores onto which the OBA could adsorb. In addition, BCTMP contained greater amounts of fines and anionic trash, which thus also affected retention of the OBA as well. Thus, when the furnish contained BCTMP, retention of the OBA was lower than that with the chemical pulp (Zhang et al. 2007a-c). The 2S-OBA intrinsically contained fewer sulfonic groups than the 4S-OBA. Hence, it had a better affinity with cellulosic fibers and a lower water solubility (Crouse and Snow 1981). Due to OBAs' charge-carrying nature and preferential adsorption onto micropores, the 2S- OBA group exhibited better whitening effects than did the 4S-OBA group. The results of the 2S-OBA group indicated that when a small amount of BCTMP was added to the furnish, the resulting paper showed an even better whitening effect than for paper with chemical pulp only. However, for furnishes containing > 15% BCTMP (with OBA dosages 0.5 and 1.0%) or 20% (with OBA dosages of 1.5 and 2.0%), the whitening effect began to decrease. In the 4S-OBA group, however, any amount of BCTMP reduced the whitening effect compared to paper with chemical pulp only. Yet graphs (C) and (D) of Fig. 2 indicate that at a BCTMP charge of 15% and 4S OBA dosages of 1.5 and 2.0%, the whitening effect suddenly rebounded. The cause for this requires further investigation.

CIE L*a*b* values

Figure 4 shows the effects of various BCTMP contents and the 2 types of OBAs on CIE L*a*b* values of the resulting handsheets. The pooled standard deviations of L*a*b* were 0.13, 0.056, and 0.038, respectively. L* values of 2S-OBA-treated paper are shown in graph (A) of Fig. 4. L* values ranged 90.5~91.0, with no statistical significance. Graph (B) of Fig. 4 shows that a* value of the 2S-OBA group slightly increased at a 10% BCTMP content. A further increase in the BCTMP content caused a* values to decrease, indicating that the paper color shifted from redness to greenness. At a 1.5% dosage of 2S-OBA, the a* value reached a maximum; and at a 2.0% dosage, the a* value began to decrease, suggesting that the dosage had exceeded the OBA saturation point. From graph (C) of Fig. 4, it appears that b* values of the 2S-OBA group decreased with an increasing BCTMP content, and at 15% BCTMP, it reached an inflection point and began to increase. A decrease in b* values indicates that the paper color shifted from yellowness to blueness. At a 2S-OBA dosage of 1.0%, the b* value was at a minimum; while at dosages of > 1.5%, b* values increased, indicating that the saturation point had been reached. From both graphs, at a BCTMP charge of < 15%, the 2S-OBA could shift the paper color to greenness-blueness and achieved a whitening effect as shown in Figs. 2 and 3 above.

L* values of 4S-OBA-treated paper are shown in graph (D) of Fig. 4. L* values ranged 90.7~92.0. For paper containing 10%

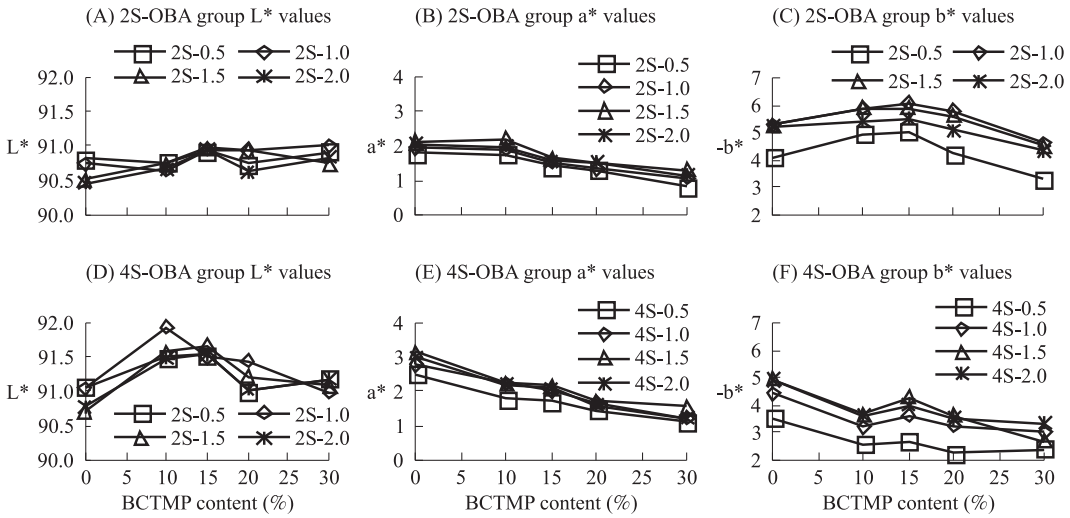

Fig. 4. Effects on handsheet CIE L*a*b* values at different dosages of 2 types of optical brightening agents (OBAs) for handsheets from furnishes with different bleached chemi-thermomechanical pulp (BCTMP) content.

BCTMP, the L* value reached a maximum; whereas as the dosage increase, L* value began to decrease. The a* values of 4S-OBA-treated paper, as shown in graph (E) of Fig. 4, tended to decrease with an increasing BCTMP content. The slope of the decrease was greater than that of the 2S-OBA group. Decreasing a* values suggest that the paper color shifted from redness to greenness. At a 4S-OBA dosage of 1.5%, a* reached a maximum; whereas at a dosage of 2.0%, a* began to decrease, indicating that the greening point had been reached. The b* values of paper treated with 4S-OBA, as shown in graph (F) of Fig. 4, tended to increase with an increasing BCTMP content, except for the 15% one. The b* value was at a minimum for paper containing 15% BCTMP. A decrease in b* indicates that the paper color shifted from yellowness to blueness. At 4S-OBA dosages of > 2.0%, b* further increased, similar to a* values, indicating that the saturation point had been reached. The overall a*b* results suggested that when the 4S-OBA was applied to BCTMP-containing furnishes, the resulting paper tended to have a greenness- yellowness coloration. The OBA produced a better whitening effect only for those with 15% BCTMP as shown in Figs. 2 and 3.

Figure 4 also indicates that the 2S-OBA was more suitable for use in BCTMP-containing furnishes than was the 4S-OBA. It produced a paper color that tended toward greenness-blueness, and provided a better whitening effect. At a BCTMP charge of 15%, the best whitening efficacy was reached. The causes of this require further investigation. The saturation point of the 2S-OBA might be between 1.0 and 1.5%; whereas, the saturation point for the 4S-OBA appeared to be at a 1.5% dosage.

Light-fastness of the whitening effect

All handsheets were irradiated with UV inside an accelerated aging chamber for 2, 8, and 24 h, and then their brightnesses were compared. The results are shown in Figs. 5~7.

Figure 5 indicates that at an OBA dosage

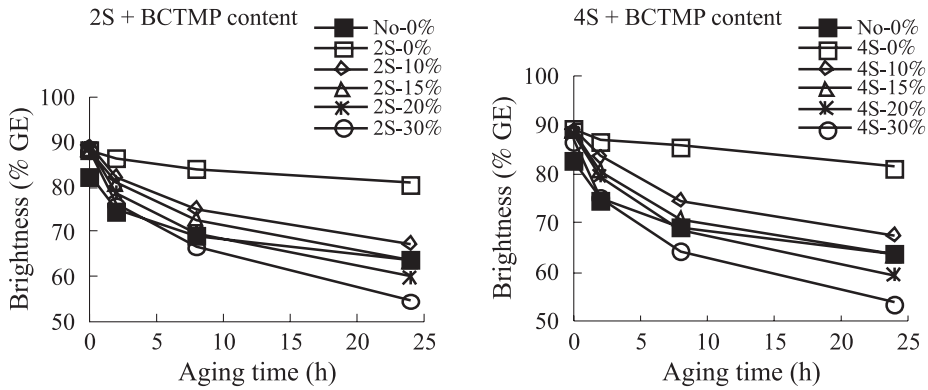

Fig. 5. Effects of ultraviolet irradiation length on the brightness of handsheets made from different bleached chemi-thermomechanical pulp (BCTMP)-containing pulps treated with 2 types of optical brightening agents (OBAs) at a 1.0% dosage.

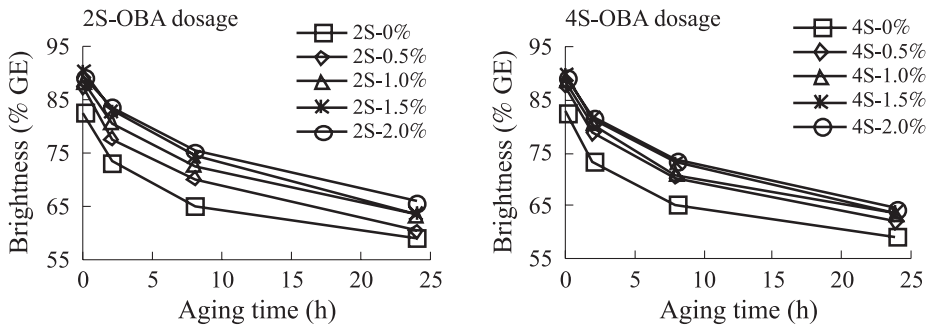

Fig. 6. Effects of ultraviolet irradiation length on the brightness of handsheets made from 15% bleached chemi-thermomechanical pulp (BCTMP)-containing pulps treated with different dosages of 2 types of optical brightening agents (OBAs).

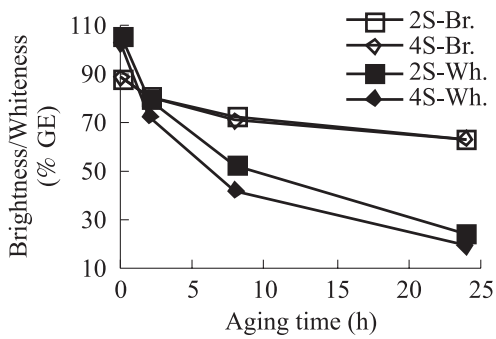

Fig. 7. Effects of ultraviolet irradiation length on the brightness or whiteness of handsheets with 15% bleached chemi-thermomechanical pulp (BCTMP) and 1.0% of either types of optical brightening agents (OBAs).

of 1.0%, yellowing generally became more severe along with an increasing BCTMP content. When there was no BCTMP in the furnish, adding either the 2S- or 4S-OBA moderated the rate of yellowing. Figure 6 indicates that at a furnish BCTMP content of 15%, adding OBAs could reduce the rate of yellowing. The retardation of yellowing tended to increase with increasing OBA dosages. The retarding effect was in agreement with the results of Roltsch and Lloyd (1987), Ragauskas et al. (1998), and Zhang et al. (2007a, c). Figure 7, on the other hand, indicates that for the apparent whiteness, the 2S-OBA group had a more-moderate yellowing

trend with the UV irradiation time than that of the 4S-OBA group. However, the yellowing trends of handsheet brightness for both OBAs appeared to be quite similar.

CONCLUSIONS

When an OBA was applied to a BCTMP-containing furnish, the results indicated that for both paper brightness and apparent whiteness, the whitening effect of the 2S-OBA was superior to that of the 4S-OBA. At an OBA dosage < 1.0% and a BCTMP content of 10%, the whiteness-enhancing effect was maximized. At an OBA dosage of > 1.0%, however, the best whitening performance was exhibited by papers containing 15% BCTMP. Adding the 2S-OBA tended to shift the paper color more toward the greenness-blueness axis than did the 4S-OBA. The saturation point for the 2S-OBA was probably at a dosage between 1.0 and 1.5%; whereas, that for the 4S-OBA was at a 1.5% dosage. The yellowing phenomenon increased with an increasing BCTMP content in the pulp furnish. For BCTMP-containing furnishes, adding OBAs slowed down the yellowing. The moderating effect increased with an increasing OBA dosages. For the apparent whiteness of the resulting paper, yellowing of the 2S-OBA-treated paper was slower than those treated with the 4S-OBA. But for paper brightness, the 2 OBAs performed similarly. In summary, the 2S-OBA appeared more suitable for use with BCTMP-containing furnishes.

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