REVIEW: USE OF OPTICAL BRIGHTENING AGENTS (OBAs) IN THE PRODUCTION OF PAPER CONTAINING HIGH-YIELD PULPS

He Shi,[a] Hongbin Liu,[a,b,]* Yonghao Ni,[a,c] Zhirun Yuan,[d] Xuejun Zou,[d] and Yajun Zhou [e]

The efficiency of optical brightening agents (OBAs), also known as fluorescent whitening agents (FWAs), has long been of interest in the production of uncoated fine paper, particularly in uncoated fine paper grades containing high-yield pulp (HYP). The increasing levels of whiteness and also the increasing HYP substitution in fine papers has made OBA efficiency an important issue. This paper summarizes recent research findings in understanding and enhancing OBA efficiency in fine papers containing HYP, with focus on the main factors affecting OBA efficiency in both wet end and size press application. These factors include the base sheet brightness and whiteness of the pulp, UV competitors, OBA retention, quenching effects, and OBA migration at the size press. Some new technologies to improve OBA efficiency are discussed.

Keywords: OBA efficiency; Brightness; Whiteness; High-Yield Pulp; Fine paper; UV competitors; OBA retention; Quenching; OBA migration

*Contact information: Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin, 300457, China; b: Jiangsu Provincial Key Laboratory of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing, Jiangsu Province, 210037, China; c: Department of Chemical Engineering & Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, NB, E3B 5A3, Canada; d: FPInnovations, Pointe Claire, Quebec, H9R 3J9, Canada; e: Tembec, Temiscaming, Quebec, J0Z 3R0, Canada; *Corresponding author: hongbin@tust.edu.cn*

INTRODUCTION

Generally, the term "fine papers" refers to white, uncoated printing and writing grades, which are mainly produced from a mixture of fully bleached hardwood and softwood chemical pulps with the addition of suitable amounts of fillers (Levlin 1990). Some new developments have emerged in recent years for fine paper production. One of them is the market demand for increasing levels of brightness and whiteness of uncoated printing and writing paper grades. Figure 1 shows the global whiteness requirements in recent years (Gauto 2007). High brightness and whiteness can impart the sensation of cleanliness and help increase the legibility of the text due to the contrast of the paper with the ink (Blum *et al*. 2004). Another trend affecting uncoated fine paper production is the use hardwood high-yield pulp (HYP) as a substitution for hardwood kraft pulp, particularly in Asia; such substitution has been motivated by the functional attributes that HYP provides, such as higher bulk, higher opacity, and better printability of the paper products (Zhou 2004).

Optical properties are of great importance for printing and writing paper grades (Bobu *et al*. 2004), especially the brightness and whiteness, which are the key parameters to determine the value of the final products (Ionides 2004). There are several approaches to improve the brightness and whiteness of uncoated printing and writing grades: 1) to use high-brightness pulp, 2) to use high brightness and high light-scattering coefficient fillers, such as precipitated calcium carbonate (PCC), ground calcium carbonate (GCC), and titanium dioxide, and 3) to use optical brightening agents (OBAs), also known as fluorescent whitening agents (FWAs) (Gauto 2004; Wild *et al*. 2008). The use of high brightness pulp leads to the increased cost, while increased addition of fillers creates challenges in papermaking (*e.g.* retention, runnability) and product performance (*e.g.* dusting). Addition of OBA is now a main focus to increase brightness, as it can be done cost-effectively in papermaking if its efficiency can be maximized.

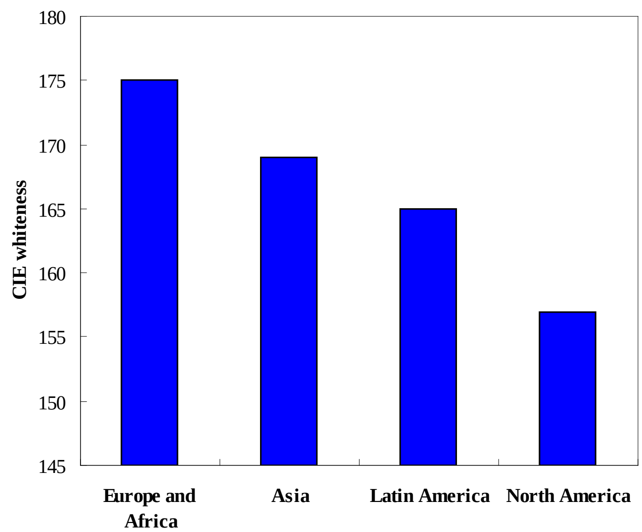

Fig. 1. High whiteness papers by region (Gauto 2007, figure redrawn from the published data)

Usually, the use of OBA is more effective in increasing the brightness gain for the bleached kraft pulps than for HYP. There are a number of reasons for this difference: 1) HYP usually has lower brightness than bleached kraft pulp, for example, an aspen HYP may have 84 to 85% ISO brightness, while the bleached hardwood kraft pulp has a typical brightness of 88 to 90 % ISO; HYP has more lignin (typically 15 to 20%, because of the lignin-preserving nature of peroxide bleaching chemistry) than bleached kraft pulp (with a negligible amount of lignin remaining after the typical chlorine dioxide-based ECF bleaching stages and their subsequent alkaline extraction stages); HYP usually has a higher light scattering coefficient due to the presence of fines. OBAs can play a major role in meeting the demand for higher brightness and whiteness in printing and writing grades. There is a concern on OBA efficiency (the unit of brightness gain/kg of OBA per ton of pulp) in paper mills that use HYP as part of the furnish as HYP containing a large amount of lignin (Gauto 2004; Zhou 2004; Zhang *et al*. 2007, 2009). To address this, many efforts have been made in the fundamental and practical aspects related to using OBA, and or dye/OBA in improving HYP or HYP-containing systems (Zhang *et al*. 2010; He *et al*. 2010; Chen *et al*. 2010; Liu *et al*. 2007, 2008, 2010a,b).

This paper summarizes new insights and understanding related to OBA efficiency in HYP-containing printing and writing paper grades, and presents some new research results regarding OBA efficiency in HYP-containing paper products.

OPTICAL BRIGHTENING AGENTS (OBA)

Optical brightening agents based on diaminostilbenedisulfonic acid (DAST) were introduced as long ago as 1940, yet they remain the most cost-effective means of raising the whiteness level of paper (Jackson 2009). OBAs absorb ultraviolet light within the range of 350 to 360 nm, and re-emit the absorbed energy as blue light at 400 to 500 nm with a maximum wavelength at 430 nm (Branston 2007).

Because sulfonic acid groups present in the OBA structure contribute to water solubility, OBA's affinity for cellulose can be manipulated by changing the number of these groups on a molecule. The higher the number of sulfonic acid groups, the higher the solubility.

Disulfonated OBAs have high affinity for cellulose and are an ideal product type for wet-end addition. The high affinity also contributes to their quick response for the process control of brightness and whiteness. However, this type of OBA cannot be used effectively at the size press due to potential migration from the surface into the base sheet and low compatibility with starch (Rocik *et al*. 2003). Urea-free disulpho OBAs are also available (Tindal 2001). 2-sulpho OBAs are more resistant to quenching by cationic materials in the wet end, for example retention agents and anionic trash quenchers, *etc*.

Tetrasulfonated OBAs are the most commonly used and universal type. They have relatively low cost and medium affinity to the fibers as well as good solubility. They can be used at the wet end, size press, or in a coating formulation. Tetrasulfonated OBAs have adequate affinity and are compatible with starch, making them suitable for a wide range of applications (Rocik 2003).

The hexasulfonated types are relatively expensive specialties with extremely good solubility but very low affinity for fiber surfaces. These characteristics are advantageous for certain surface applications where high whiteness values cannot be achieved using the tetrasulfonated products. Hexasulfonated OBAs are used together with tetrasulfonated OBAs in size press or coating formulations to maximize whiteness and reduce the cost in producing very high whiteness grades of paper.

Some new OBAs have chemical structures that are not identical to the traditional ones, for example, Leusophor NS liquid, Leucophor SCA liquid (both from Clariant), and DSBP OBA (BASF). Some new OBAs are self-carrying, whereas some other OBAs rely on the use of co-additives referred to as carriers. Even cationic OBAs can be found on the market (Tindal 2001).

MAIN FACTORS AFFECTING OBA EFFICIENCY

Critical factors affecting OBA efficiency include competition with other UV absorbers, retention, quenching, the effect of fillers, and migration at the size press.

Competition with Other UV Absorbers

Both lignin and titanium dioxide are potent absorbers of ultraviolet light, which make less ultraviolet light available to the OBAs (Wild *et al*. 2008). Hardwood HYP contains most of the lignin that was originally present in the raw materials. It has been reported that increasing HYP substitution level results in a decrease in the brightness gain under otherwise the same conditions, as shown in Fig. 2 (Zhang *et al*. 2009). However, the HYP-containing sheets with a higher HYP brightness give a higher brightness gain with OBA under otherwise the same conditions, than those with a lower HYP brightness. We further investigated the effect of HYP from different wood species (with different initial brightness, namely, a maple HYP with 79.2% ISO, a spruce HYP with 80.0% ISO, and an aspen HYP with 81.6% ISO) on OBA efficiency, as shown in Fig. 3 and the results confirm that higher HYP brightness give a higher brightness gain with OBA.

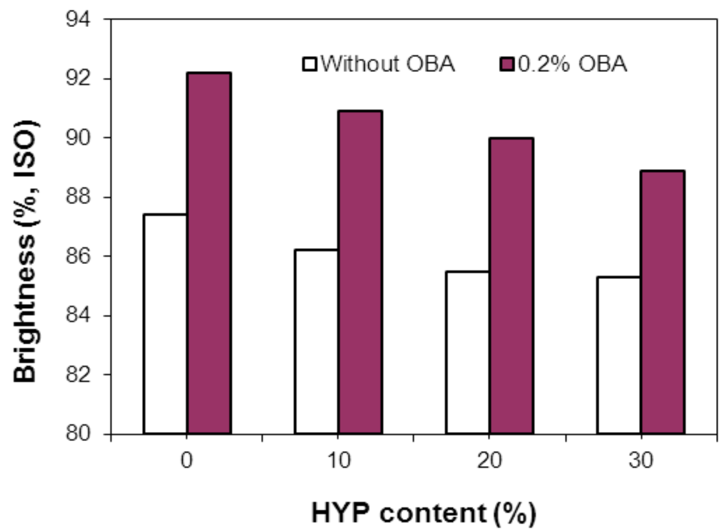

Fig. 2. Effect of HYP content on OBA efficiency (SWBKP: 30%, HWBKP: 40-70%, Aspen HYP: 0-30%, OBA: Tinopal ABP-A, Ca^{2+}: 100mg/L) (Zhang *et al*. 2009, figure redrawn from the data)

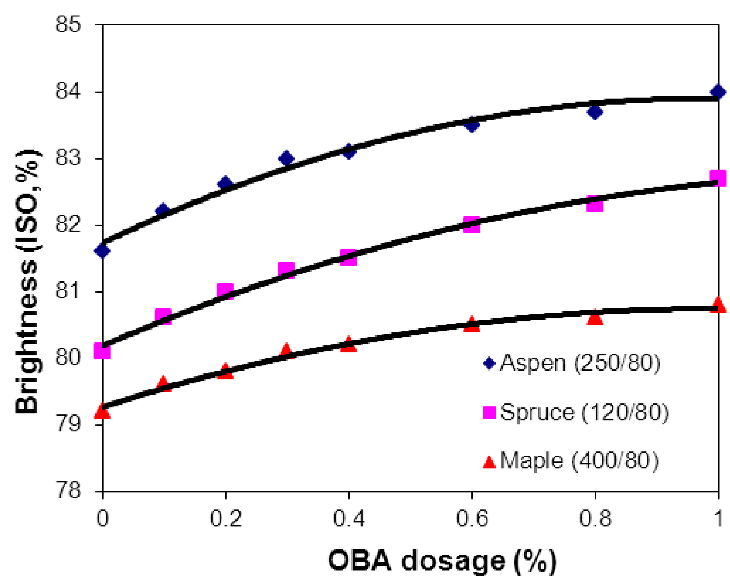

Fig. 3. Effect of HYP made from different wood species on OBA effectiveness (OBA: Tinopal UP, Ca^{2+}: 100mg/L, pH: 7.0, Contact time: 30 min; figure previously unpublished)

The lignin content of aspen, maple, and spruce is 18%, 21%, and 28%, respectively (Zhou 2004). The spruce HYP has higher lignin content than aspen and maple HYP, yet its OBA effectiveness is close to that of the aspen HYP, and even higher than that of the maple HYP. The difference in the lignin structure may be partially responsible. In summary, the higher the original pulp brightness, the higher the OBA efficiency. Therefore, a high original pulp brightness is critical to achieve a very high end brightness and whiteness of OBA-added paper.

TiO_2 has a higher refractive index than calcium carbonate or clay, so it has a much higher light scattering power. It absorbs most of the incident UV radiation, thus lowering OBA efficiency and adversely influencing the whitening performance of OBAs (Covarrubias *et al*. 2007). Thus, OBAs are likely to be ineffective when added at the wet end of a paper machine to furnish that contains TiO_2. This is especially the case for the rutile type of TiO_2, which has a greater negative effect than the anatase type.

OBA Retention

OBA efficiency is affected significantly by its retention when added at the papermaking wet-end. Zhang *et al*. (2007) found that the OBA retention decreased slightly with the increase of HYP substitution at HYP substitution levels of less than 20%; however retention decreased drastically as the HYP substitution further increased above 20%. There are a number of reasons responsible for the decreased OBA retention when using HYP: 1) HYP is known to contain some dissolved and colloidal substances (DCS) (Li *et al*. 2002), and DCS can decrease the OBA retention (Zhang *et al*. 2007); and 2) fines can absorb more OBA than fibers due to their high specific surface and charge characteristics. Thus, if the fines retention is low, OBA may also be not well retained.

The results of fluorescent imaging by Zhang *et al*. (2007) showed different OBA absorption behavior and OBA distribution in the fiber wall when comparing kraft and HYP fibers. As shown in Fig. 4, the fluorescence intensity was less in the middle and inner layers of the cell wall of the HYP fibers than for the hardwood BKP fibers. These results are explained by the hypothesis that HYP fibers have less porosity than kraft pulp fibers (Zhang *et al*. 2007). Hui *et al*. (2009) confirmed that BKP fibers are more porous than HYP fibers by using the solute exclusion technique.

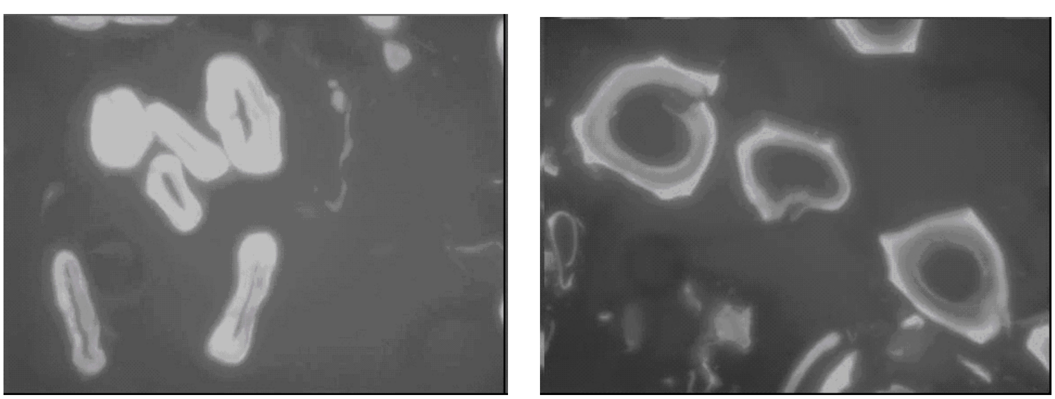

Fig. 4. Fluorescent images of the cross-section of the bleached kraft pulp fibers (left) and HYP fibers (right) dyed with OBA under UV illumination (×160) (Zhang *et al*. 2007, by permission)

Quenching

Quenching refers to any process that decreases the fluorescence intensity of a given substance. Highly charged cationic polyelectrolytes, such as retention agents and sizing promoters, can easily reduce the fluorescence effect of an OBA molecule when they interact with each other.

Pummer *et al*. (1973) and Crouse *et al*. (1981) found that some of the retention aids used at the wet end have negative effects on OBA efficiency; for instance polyethylene imine (PEI) is a notable high-charge cationic polymer that quenches OBA, thus reducing its efficiency. He *et al*. (2009) also found that PEI exhibits a quenching effect on OBA efficiency in HYP-containing furnish.

Gratton and Pruszynski (2005) reported that the hybrid coagulants, various co-polymers of DADMAC and acrylamide, show low impact on OBA efficiency and are effective in turbidity reduction. Wild *et al*. (2008) found that the DDA drainage time also increases with the increase of OBA addition because of the quenching effect.

Effect of Fillers

Fillers, including PCC and GCC, are widely used in fine paper production. Fillers have higher brightness and higher light scattering coefficient than fibers; thus they can improve the brightness of filled paper products. At the same time, fillers have higher specific surface area, which can absorb more OBAs, and thus decrease OBA retention efficiency.

Zhang *et al*. (2009) showed that the fluorescent composition of the filled samples was significantly lower than that of the un-filled samples at the same OBA dosage. They contributed the decrease in OBA efficiency to a UV light-diverting effect by filler particles, thus preventing it from travelling through the sheet thickness to reach OBA there.

Size Press Application

OBA size press addition is the most economical application technique for uncoated papers, as it gives 100% OBA retention and keeps OBA on the paper surface. UV light can come into contact with OBA on the sheet surface before encountering materials other than starch; in this way the OBA efficiency is maximized.

In alkaline-sized papers all the incompatibility problems related to cationic wet-end sizing ingredients may be avoided by size press addition. Figure 5 shows that OBA size press application can improve paper brightness very effectively in HYP-containing paper. However, it should be noted that the OBA efficiency still depends on the HYP substitution levels.

OBA can migrate into the sheet when paper is surface sized. Forsström *et al*. (2003) found that the penetration of liquid phase increased with increasing base sheet porosity, as shown in Fig. 6. OBA penetrated less deeply into a dense base paper structure than into a porous structure.

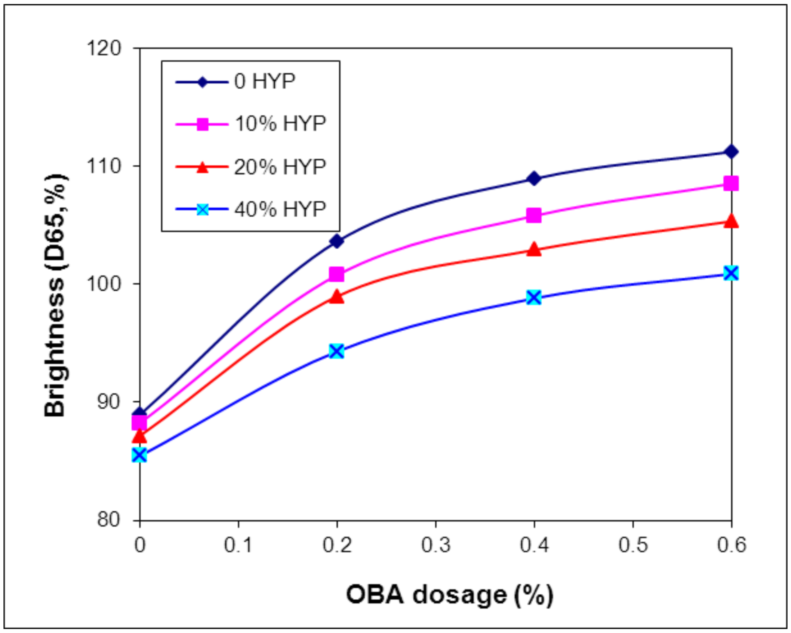

Fig. 5. Effect of OBA addition on brightness at the surface sizing (OBA: Tinopal ABP-A, starch solution: 5%, sizing pickup: $3g/m^2$, figure not previously published)

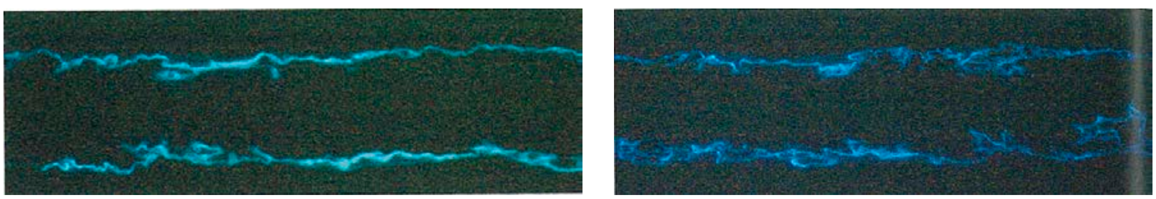

Fig. 6. Cross-sectional image of a dense base sheet (left) and a porous base sheet (right) (Forsström *et al*. 2003, by permission of the author)

NEW TECHNOLOGIES FOR ENHANCING OBA EFFICIENCY

New concepts have been developed to enhance the OBA efficiency and there now three such technologies available commercially. The main challenge is how to balance the cost and performance when using these technologies provided by the suppliers.

ColorLok©

Colorlok technology was first unveiled by HP and International Paper late in 2005 (Jackon 2009). This technology places special demands on OBA size press application. Since the formulation is usually applied by a size press, OBA carriers, such as PVOH, are usually present, which help in maintaining OBA on the paper surface. When the pigments come into contact with a divalent cationic (or positively charged) salt ion they rapidly come out of suspension or coagulate. When the salt is added during size press application, it provides a means to rapidly immobilize the inkjet pigment particles while they are near to the paper's surface, soon after an inkjet droplet lands on the paper. This technology also helps enhance inkjet printability of uncoated fine paper, but it needs to be licensed from HP. This technology has been widely used for producing inkjet printing papers.

Extra White

Extra white is an aqueous solution that was designed to reduce thermal reversion, and it was found that it also can enhance the performance of certain OBAs by changing the molecular level conformation . The objective of this technology is to prevent paper web brightness loss as the paper progresses through the paper machine system due to exposure to heat and moisture. The net effect of suppressing thermal darkening, chemically modifying pulp, and activating OBAs often noticeably exceeds compensation of thermal darkening alone (Smith 2008). This product needs to be added at the size press and has good compatibility with traditional size press additives. Any paper mill that has a size press can take advantage of this technology, which is an ideal candidate for production of high-brightness grades of paper (>92% ISO brightness). A 1.0 increase in ISO brightness coupled with a 40 to 50% reduction in OBA consumption has been achieved at a usage level of 1.5 to 2.0 kg/t at the size press, and 15% reduction in long term brightness reversion.

Organic Coagulant

Traditional coagulants, such as polyaminoamido glycol, polyethylene imine, polyamines, polyDADMACs, alum, and polyaluminum chloride, are necessary to achieve suitable characteristics of paper. Unfortunately, many of these coagulants can adversely affect the performance of OBAs used in the same systems. In particular, traditional coagulants can dull the effect of OBAs, thus reducing the OBA efficiency. Buckman laboratories has introduced a new organic coagulant that can provide the added benefit of increasing OBA efficiency (Covarrubias 2007). This coagulant will not quench OBAs to the same extent as polyamines and polyDADMACs do. It can be fed by thin or thick stock application. An increase of 2 to 5 brightness units and 4 fluorescence units can be obtained at a dosage of 1 to 2 kg/t of organic coagulant.

CONCLUSIONS

Significant progress has been made in recent years to better understand the factors affecting OBA efficiency and find ways of increasing it when HYP is used as part of the furnish in uncoated fine papers:

1. OBA efficiency is determined mainly by the base sheet brightness, the presence of UV light absorbing competitors such as lignin and TiO_2, the retention of the OBA, the presence of dissolved and colloidal substances, and fines. Fillers can boost the brightness of the HYP-containing furnish, but the OBA efficiency is adversely affected by UV light scattering by filler particles. OBA size press addition is an efficient way to improve the brightness and whiteness of HYP-containing paper. OBA migration depends strongly on the porosity of the base sheet.

2. New technologies to improve the OBA efficiency are now commercially available. However, the optimization of the performance and cost is always a challenge. Technologies that are more cost effective and more compatible with wet end and size press operations are still desirable in the future.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the National Natural Science Foundation of China (31100435), Foundation for the Development of Science and Technology in Tianjin Universities (No. 20100509), Tianjin University of Science & Technology Research Fund (20100222), Innovation Fund of Science and Technology of Tianjin Committee of Science and Technology (10SYSYJC28000), and International Scientific and Technological Joint Project of China and Canada (2008DFA91290).

REFERENCES CITED

Blum, T., Linhart, F., Kaub, H., Champ, S., Wendker, M., Mech, D., and Geiger, S. (2004). "Method for increasing the whiteness of paper by means of cationic polyelectrolytes," *US patent*, US2004/0182533 A1.

Bobu, E., Ciolacu, F., and Parpalea, R. (2002). "Effective use of FWAs in papermaking by controlling their interactions with other chemicals," *Wochenblatt für Papierfabrikation* 130(22), 1510.

Branston, R. (2007). "FWAs and dyes in coating applications," *TAPPI Coating Short Course*.

Chen, Q., Zhang, H., Li, Z., and Ni, Y. (2010). "Effect of an optical brightening agent on the optical properties of aspen, birch and maple high-yield pulps," *Journal of Pulp and Paper Science* 36 (1-2), 35-41.

Covarrubias, R. M., and Headrick, G. A. (2007). "New advances in wet end chemistry for high bright OBA applications," *93rd PAPTAC Ann. Mtg.*, Montreal, Canada, A89-A94.

Crouse, B. W., and Snow, G. H. (1981). "Fluorescent whitening agents in the paper industry-their chemistry and measurement," *Tappi J.* 64(7), 87-89.

Forsström, U., Fagerholm, K., and Saharinen, E. (2003). "The role of base paper porosity in MSP coating," *Paperi ja Puu-Paper and Timber* 85(8), 454-459.

Gauto, M. (2007). "Increasing whiteness: The key is in your hands," *TAPPI Papermakers Conference*, March, Jacksonville, US, PPT.

Gratton, R., and Pruszynski, P. (2005). "Potential incompatabilities in the wet end of paper machines," *6th PIRA Wet End Chemistry Conference*, Boston, US, PPT.

He, Z., Zhang, H., Ni, Y., and Zhou, Y. (2009). "Adding optical brightening agents to high-yield pulp at the pulp mill," *Pulp & Paper Canada* 110(3), 18-23.

He, Z., Zhang, H., Chen, Q., and Ni, Y. (2010). "Comparison of peroxide bleaching and the combined peroxide/OBA brightening of an aspen CTMP: Pulp properties and effluent characteristics," *Journal of Pulp and Paper Science* 36(1-2), 49-54.

Hui, L., Liu Z., and Ni, Y. (2009). "Characterization of high-yield pulp (HYP) by the

solute exclusion technique," *Bioresource Technology* 100(24), 6630-6634.
Ionides, G. (2004). "Adding value for improved market competitiveness of mechanical printing papers," *Pulp & Paper Canada* 105(4), 40-44.
Jackson, A. (2009). "Optical brightening agents: Past, present and future," *Pulp & Paper International* 5, 32-34.
Levlin, J. E. (1990). "On the use of chemi-mechanical pulps in fine papers," *Paperi ja Puu – Paper and Timber* 72(4), 301-307.
Li, H., Ni, Y., and Sain, M. (2002). "The presence of dissolved and colloidal substances in BCTMP and their effect on sizing," *J. Pulp Paper Sci.* 28(2), 45-49.
Liu, H., Yang, S., and Ni, Y. (2010a). "Effect of pulp fines on the dye-fiber interactions during the color-shading process," *Ind.Eng. Chem. Res.* 49(18), 8544-8549.
Liu, H., Yang, S., and Ni, Y. (2010b). "Comparison of dye behavior from aspen HYP: Dyes added in the HYP manufacturing process versus dyes added at the papermaking wet end," *Journal of Wood Chemistry and Technology* 30(2), 118-128.
Liu, H., Yang, S., and Ni, Y. (2007). "Using dyes for improving the optical properties of high yield pulps," *Pulp & Paper Canada* 108 (10), 25-29.
Liu, H., Ni, Y., and Yang, S. (2008). "Applying dyes to HYP-containing paper grades," *Appita J.* 61(2), 128-140.
Pummer, H. (1973). "Optical properties of papers manufactured using various retention agents," *Tappi J.* 56(4), 112-115.
Rocik, T., and Hunke, B. (2003). "New generation of FWAs (OBAs) for the paper industry-improved fluorescent whitening agents for size press application," *Wochenbl. Papierfabr.* 131(10), 572-575.
Smith, C. (2008). "Extra white, extra bright can be achieved cost effectively," *Pulp and Paper International* 50(2), 34-36.
Tindal, A. (2001). "New developments in optical brightening agents," *Papier* 2, 49-51.
Wild, M. P., and Urbantas, R. (2008). "An innovative approach to higher brightness and whiteness," *Tappi PaperCon 2008*, Atlanta, GA, US, May 2-5, PPT.
Zhou Y. (2004). "Overview of high yield pulps (HYP) in paper and board," *PAPTAC 90th Annual Meeting*, Montreal, Quebec, B1429-B1434.
Zhang, H., Hu, H., He, Z., Ni, Y., and Zhou, Y. (2007). "Retention of optical brightening agents and their brightening efficiency on HYP-containing paper sheets," *Journal of Wood Chemistry and Technology* 27,153-167.
Zhang, H., He, Z., Ni, Y., Hu, H., and Zhou, Y. (2009). "Using optical brightening agents (OBA) for improving the optical properties of HYP-containing paper sheets," *Pulp & Paper Canada* 110(8), 20-24.
Zhang, H., Hui, L., and Ni, Y. (2010). "Adsorption behaviors of optical brightening agents and precipitated calcium carbonate onto pulp fibers," *Industrial & Engineering Chemistry Research* 49(19), 9407-9412.
Zhang, R., Ni, Y., Wong, D., Schmidt, J., Heitner, C., and Jordan, B. (2009). "Interactions of optical brightening agents with high yield pulps," *Journal of Wood Chemistry and Technology* 29, 358-370.

Article submitted: Feb. 6, 2012; Peer review completed: March 17, 2012; Revised ver. received: March 20, 2012; Accepted: March 23, 2012; Published: March 26, 2012.