EFFECT OF CO-BINDERS FOR COATING ON THE PERFORMANCE OF FLUORESCENT OPTICAL BRIGHTENING AGENTS

YUAN-SHING PERNG, EUGENE I-CHEN WANG* and CHIH-PING CHANG

Da Yeh University, Department of Environmental Engineering, Changhua 51591, Taiwan
**Taiwan Forestry Research Institute, Division of Wood Cellulose, Taipei 10066, Taiwan*
✉ *Corresponding author: Yuan-Shing Perng, ysperng@mail.dyu.edu.tw*

Received March 21, 2013

The proportions of bleached chemi-thermomechanical pulp (BCTMP) in the pulp mix need to increase with the trend toward lighter paper grammage, leading to a decrease in the brightness of coated paper, which also influences the quality of the paper. Adding fluorescent optical brightening agents (OBAs) to coating formulas can increase the whiteness of the coated paper. If suitable co-binders can be found as carriers of the OBAs to exert a synergistic effect, then the whiteness of the paper can be further increased. Our experimental design selected a typical coating formula for art paper, and three kinds of typical co-binders (starch, carboxymethyl cellulose (CMC), and soy protein) were tested. Four different types of OBAs (di-, tetra-, and 2 kinds of hexa-sulpho-OBAs) were applied at dosages of 0.25, 0.5, 1.0, 2.0, and 4.0 parts (with the total coating pigment as 100 parts). The brightness, whiteness, and CIE L*a*b* values of the coated papers were then evaluated. The experiments comprised 63 sets of treatments. Results indicated that for the starch co-binder, and relatively low brightness demand, 4S-OBA was optimal, while for relatively high brightness demand, however, 6S-B-OBA was more suitable. With CMC as the co-binder, the respective OBAs of choice were 2S-OBA and 6S-B-OBA; and with soy protein as the co-binder, these were either 2S- or 4S-, and 6S-B-OBA, respectively. As for the choice of co-binders, when using 2S-OBA, the option of soy protein was optimal, followed by starch; in matching 4S-OBA, starch was the co-binder of choice, followed by CMC. When 6S-A-OBA was used, for relatively low-whitening demands, soy protein was optimal; and for high-whitening demands, starch was the choice. When 6S-B-OBA was used, the lower brightness requirements called for soy protein, while higher requirements called for soy protein or starch as co-binders.

Keywords: fluorescent brightening agent, brightness, whiteness, co-binder, starch, carboxymethyl cellulose (CMC), soy protein

INTRODUCTION

Fluorescent optical brightening agents (OBAs) absorb ultraviolet light and reemit it as bluish light, which is perceived by the eyes as whiteness gain. OBAs used in the paper industry often include di-, tetra-, and hexa-sulpho-OBAs. Di-, and tetra-sulpho-OBAs are the main types applied at the papermaking wet end; for coated paper, then tetra- and hexa-sulpho-OBAs are the choices.[1-3] When irradiated by sunlight or UV-containing office light, paper containing OBA absorbs this portion of the spectrum and reemits it at longer wavelengths of blue light, and the UV intensity decreases, which is conducive to reducing the effect of color reversion of the paper.[4-6]

There is a trend in papermaking toward lighter grammage. Thus, for many printing and writing grades, if conventional chemical pulps mixes are maintained, then there will be problems of insufficient bulk, caliper, and opacity. Adding bleached chemi-thermomechanical pulp (BCTMP) can often counter such problems, but with their addition, coated paper tends to have decreased brightness that can lower the quality of the products.[4-11]

Makinen and Eklund[12] observed the effects of different co-binders, such as polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC), on the performance of OBAs. By altering the mixing sequences, they noted that a shock was always detected when PVA was added as the first chemical into the clay slurry. If OBA and/or CMC were metered before PVA, the shocks were partially or almost totally eliminated. Robringer and Fletcher[13] evaluated the maximum optical absorbance of various OBAs (di-, tetra- and hexa-sulpho-OBAs, and distyryl biphenyl (DSBP)) and dosages (0.05%, 0.1%, and 0.2%) in coating formulations and found that different OBAs exhibited differing tendencies toward yellowing. The correlation between light absorption and fluorescence was independent of the kind of OBA chosen in the wet end applications. Furthermore, for application as a coating, the use of conventional OBAs resulted in increased yellowing and reduced fluorescence. DSBP offered substantial advantages for use in high-brightness applications. Barnard[14] described the role of OBAs and cross-linking agents in the brightness of paper. If high brightness is the target in coated papers, there is no alternative to OBAs. OBA dosages can be reduced by using co-binders and cross-linking agents, e.g., starch, resins, ammonium zirconium carbonate (AZC), etc. Nordstrom *et al.*[6] observed how the optical properties of coated thick paperboard were affected by temperature and humidity and found that moisture had little effect. Heat caused the hue of the paper to move in the direction of less white and towards the red-yellow area, and the b* value was the most difficult to control. Sturm and Chen[15] showed that most white grades of paper, especially high-whiteness fine writing grades, use OBA to enhance the product appearance. They described what is unique to high-whiteness paper grades and discussed recent advances in measurement and control solutions.

In this study, we investigated the effects of adding various OBAs, including di-, tetra-, and 2 hexa-sulpho-OBA types at different dosages to a typical art paper coating formula in combination with three types of co-binders, including starch, CMC, and soy protein, on the optical properties of the coated paper both before and after calendering. In order to compare the results, we measured the solids content, pH, low-shear viscosity, and water-retention values of the color, as well as the brightness, whiteness, and CIE L*a*b* parameters of the coated papers.

EXPERIMENTAL

Materials

- Coating base paper: wood-free sheets made by Yuen-Foong-Yu Paper (Kaohsiung, Taiwan), with a basis weight of 91.5 g/m^2, and brightness of 85.39% ISO.
- Coating color pigments: a) grade A clay, α-Gloss, supplied by Huber (Edison, NJ, USA); and b) calcium carbonate, C-90, supplied by Imery (Par Cornwall PL24 2SQ, UK).
- Binder: styrene-butadiene resin (SBR) latex, 380 SF. made by Shen-Feng (Kaohsiung, Taiwan).
- Co-binders: a) starch, A-45 by Abeve (Veendam, Netherlands); b) CMC, Finnfix 5, by Huber; c) soy protein, PC 4200 by Dupont (Wilmington, Delaware, USA).
- Additives: a) lubricant: LB-50 by Hopax (Kaohsiung, Taiwan); b) dispersant, PA-40, by Hopax; c) wet-strength agent: SR-302 by Sumitomo (Tokyo, Japan); and d) violet dye: Blue R-L by Klein (New York, USA).
- Fluorescent OBAs: a) 2S type, anionic liquid, Tinopal UP; b) 4S type, Tinopal ABP, anionic liquid; c) 6S types, (A) Tinopal SPP, anionic liquid; and (B) Tinopal SHP, anionic liquid. All were supplied by Ciba Specialty Chemicals now a part of the BASF group (Ludwigshafen, German).

Experimental design and methods

A typical art paper coating formulation was adopted. With conventional coating color formulations, the total pigment solids are regarded as 100 parts, and all other additives are dosed with reference to these. The experimental variables included varying four OBAs at different dosages (0.25, 0.5, 1.0, 2.0, and 4.0 parts) in combination with three co-binders (starch 3 parts, CMC 2 parts, and soy protein 1 part). In total, 63 sets of test specimens were prepared. The optical properties, such as the brightness, whiteness, and CIE L*a*b* values, of the resulting coated paper specimens were then measured. The coating formulations for the study are detailed in Table 1. Comparisons were made on coating color parameters of solids content, pH, low-shear viscosity, and water-retention values. Each experimental set was replicated twice to allow calculation of the means and standard deviations (SDs). Then the 63 SDs were pooled to produce a pooled SD with 63 degrees of freedom. The pooled SDs of brightness, whiteness, and L*, a*, and b* values were 0.13% ISO, 0.11% ISO, 0.25, 0.012, and 0.015, respectively.

Experimental procedures

- Coating color preparation sequences and conditions were the following:

water → calcium carbonate/clay → (high-speed dispersion for 30 min) → dispersant + dyestuff → (mixing for 5 min) → sodium carbonate → (adjusting the pH to 9.0~9.2) → co-binder → (mixing for 20 min) → wet-strength agent → (mixing for 5 min) → binder → (slow dispersion for 30 min) → coating color ready for use.

- Property testing of the coating color:

1) Solids content.
2) Low-shear viscosity: tested using a Brookfield DV-II+ model viscometer (Greifensee, Switzerland) with a #4 spindle at 60 rpm.
3) Water retention values: tested using a Kaltec model AA-GWR unit (Novi, MI, USA) applied with a fixed pressure of 1.5 bar, duration of 120 s, and with filter paper having a pore diameter of 5 μm.
4) pH meter: In accordance with NIEA W424.51A (EPA, Taiwan), using a Mettler-Toledo model MP 220 unit (Greifensee, Switzerland), which was accurate to ±0.01 units.

- The coating operation was conducted using a semiautomatic coater, Multicoater, model K-303 by Testing Machines (New Castle, DE, USA). The coating was done at a fixed pressure of 6 bars; the coating spindle used was #16M; and the coat speed was 6 m/min.
- Calendering operation: coated specimens were cut to a size of 20 x 20 cm and calendered using a model 25FF-200E supercalender by KRK (Tokyo, Japan). The applied linear pressure was 100 kgf/cm and temperature was 80 °C.
- Measurements of the optical properties: a Technidyne model Micro S-5 unit (Dorval, QC, Canada) was used to test the brightness, whiteness and CIE L*a*b* values of the coated paper specimens.

RESULTS AND DISCUSSION

This study mainly aimed for a comprehensive understanding of how various OBAs currently in use interact with coating co-binders in color formulations and affect the optical properties of the coated paper. The evaluation of coating color properties entailed observing the effects of various co-binders on the solids content, low-shear viscosity, pH, and water-retention value of the colors. The effects on the optical properties of the coated paper entailed comparing their brightness, whiteness, and CIE L*a*b* values.

Table 1
Coating formulations

Chemical		Addition ratio (part)	Concentration (%)
Pigments	Grade A clay	70	71
	Calcium carbonate	30	75
Binder	SBR latex	12	50
Co-binder	Starch, 3 parts; CMC, 2 parts; soy protein, 1 part		
Additives	Lubricant	0.5	50
	Dispersant	0.1	10
	Na_2CO_3	0.2	10
	Wet-strength agent	0.5	30
	Violet dyestuff	0.0015	1
	OBA	0.25, 0.5, 1.0, 2.0, and 4.0 parts	

SBR, styrene-butadiene resin; OBA, optical brightening agent

Table 2
Effects of 3 different co-binders on coating color properties

Co-binder	pH	Solids content (%)	Water retention value (s)	Low-shear viscosity (cps)
Starch (3 parts)	8.94±0.02	62.32±0.53	129±2.4	2799±13.1
CMC (2 parts)	9.50±0.05	60.43±0.42	129±3.1	3029±12.5
Soy protein (1 part)	9.65±0.03	60.73±0.36	179±4.5	1620±24.2

CMC, carboxymethyl cellulose

Properties of the coating color

The effects of the three co-binders on coating color properties are summarized in Table 2. Starch and CMC generally had comparatively smaller effects on the water-retention values and low-shear viscosity; however, despite its lower fractional ratio, soy protein had notable effects on the water-retention value and low-shear viscosity. Due to the experimental setup, a lower water-retention value actually means a greater tendency for the color to hold water, and thus the color drains poorly. The significantly lower low-shear viscosity also means that during application, the rheological property of the color may become too flowy.

Brightness and whiteness

The effects of the four types of OBAs and three co-binder types on the coated paper brightness are shown in Figs. 1 and 2 and on whiteness are shown in Figs. 3 and 4. The figures show that adding OBAs whitened the paper, but different types of OBAs performed differently in terms of brightness and whiteness, particularly upon reaching the saturation point. These are discussed below.

OBA types

As shown in Fig. 1A, in coating formulations incorporating 2S-OBA, the brightness gain effect among the co-binders was the best with CMC, followed by soy protein and starch. In Fig. 3A, however, the whiteness gain of soy protein was the best, followed by starch and CMC.

As for 4S-OBA formulations, Figs. 1B and 3B indicate that at a 4S OBA dosages of < 1 part, soy protein was the best, followed by CMC and starch; at dosages of > 1 part, however, the whitening effect of starch was the best followed by soy protein and CMC in that order. Regardless of brightness or whiteness, at 4S-OBA dosages of > 1 part, the soy protein co-binder reached saturation, and the gain tended to decrease with a further increase in the OBA dosage.

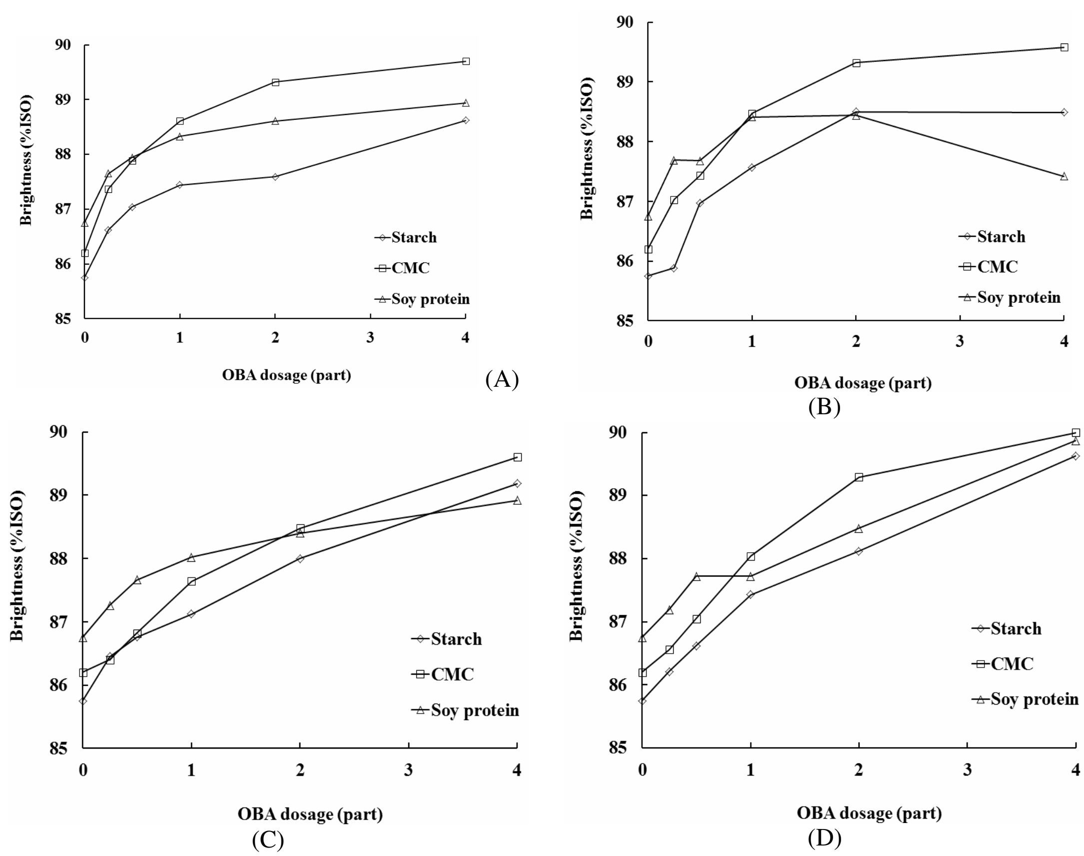

Figure 1: Effects of optical brightening agent (OBA) dosage and type of co-binder on the brightness of coated papers; (A) 2S-OBA, (B) 4S-OBA, (C) 6S-A-OBA, and (D) 6S-B-OBA

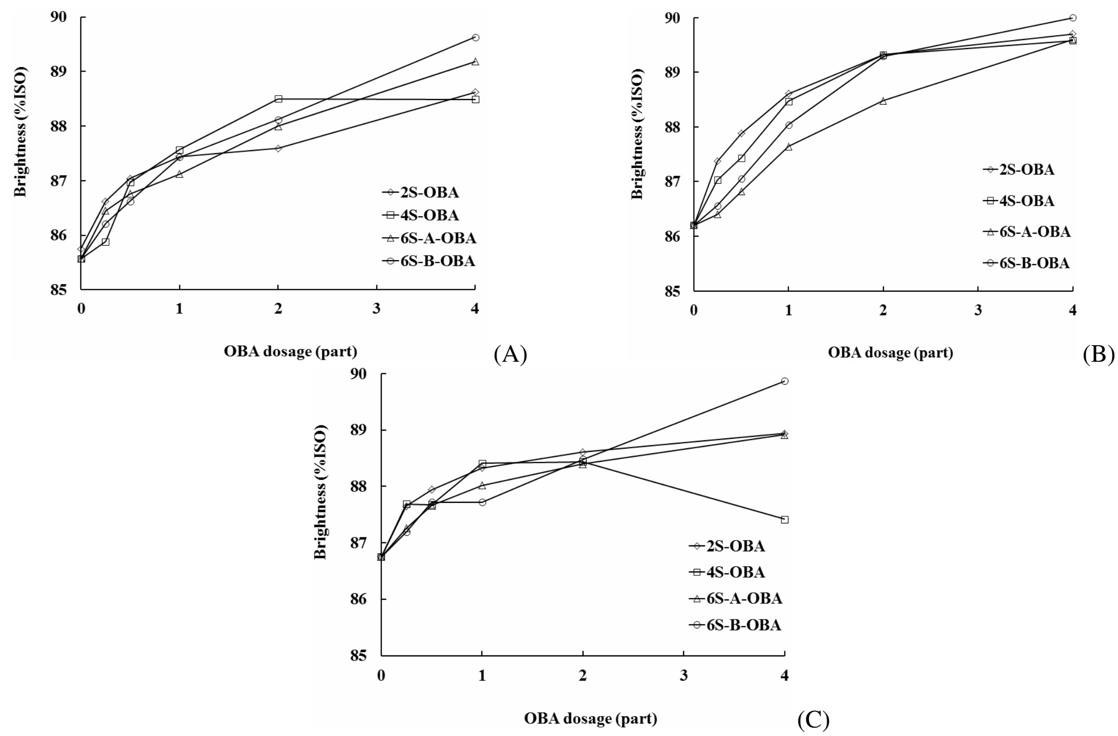

Figure 2: Effects of optical brightening agent (OBA) dosage and type of OBA on the brightness of coated papers; (A) starch, (B) carboxymethyl cellulose (CMC), and (C) soy protein

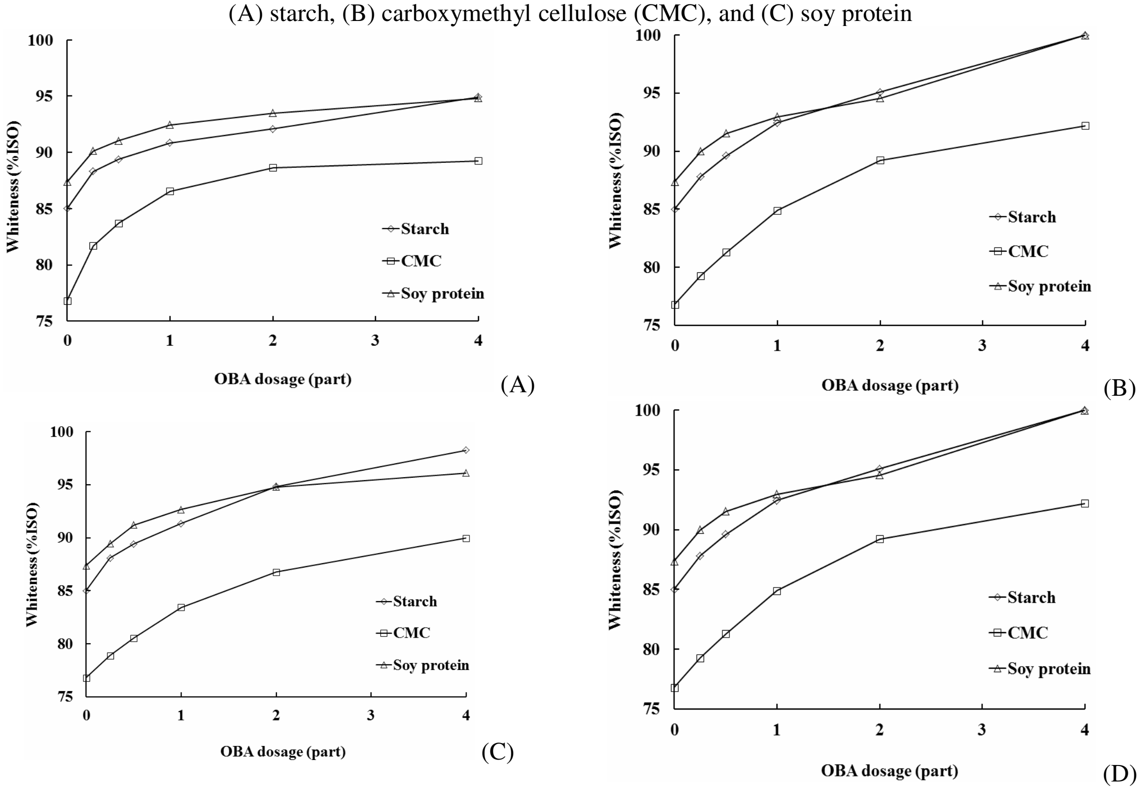

Figure 3: Effects of optical brightening agent (OBA) dosage and type of co-binder on the whiteness of coated papers; (A) 2S-OBA, (B) 4S-OBA, (C) 6S-A-OBA, and (D) 6S-B-OBA

With respect to whiteness of the coated papers in Fig. 1C, for formulations including 6S-A-OBA, at dosages of < 1 part, the soy protein co-binder was the best in terms of brightness gain, followed by CMC and starch in that order; at dosages of > 1 part, however, CMC was the best co-binder, followed by starch and soy protein. With regard to whiteness in Fig. 3C, on the other hand, with 6S-A-OBA dosages of < 1 part, soy protein was the optimal co-binder, followed by starch and CMC; at dosages of > 1 part, however, starch was the best, followed by soy protein and CMC.

In coating formulations with 6S-B-OBA, the effect of co-binder types on the brightness gain in Fig. 1D suggested that at dosages of < 1 part, soy protein was the best, followed by CMC and starch in that order; at dosages of > 1 part, however, CMC was the best, followed by soy protein and starch. With respect to coated paper whiteness in Fig. 3D, at dosages of < 1 part, soy protein was the best co-binder, followed by starch and CMC; at dosages of > 1 part, starch and soy protein fared equally well, with CMC trailing behind.

Co-binder types

When starch was used as co-binder in coating formulations, Figs. 2A and 4A indicate that at 4S-OBA dosages of < 2 parts, the best whitening efficacy was attained. At an OBA dosage of > 2 parts, however, 6S-OBAs had better whitening efficacies, with 6S-B-OBA reaching a whiteness of 100% ISO. The 2S-OBA formulation fared the poorest, in agreement with the conventional concept of OBA applications.[1] For relatively low brightness demands, the starch co-binder worked well with 4S-OBA; at a relatively high brightness demand, however, the starch and 6S-B-OBA match was optimal.

When CMC was the co-binder, Figs. 2B and 4B indicate that at OBA dosages of < 2 parts, 2S-OBA had the best brightening effect; at an OBA dosage of > 2 parts, however, 6S-B-OBA had the best performance. In such a situation, the 2S- and 4S-OBAs often tended to have decreased whiteness instead. In formulations with CMC as the co-binder, a relatively low brightness demand was best met by 2S-OBA; but for high brightness demands, 6S-B-OBA was more suitable.

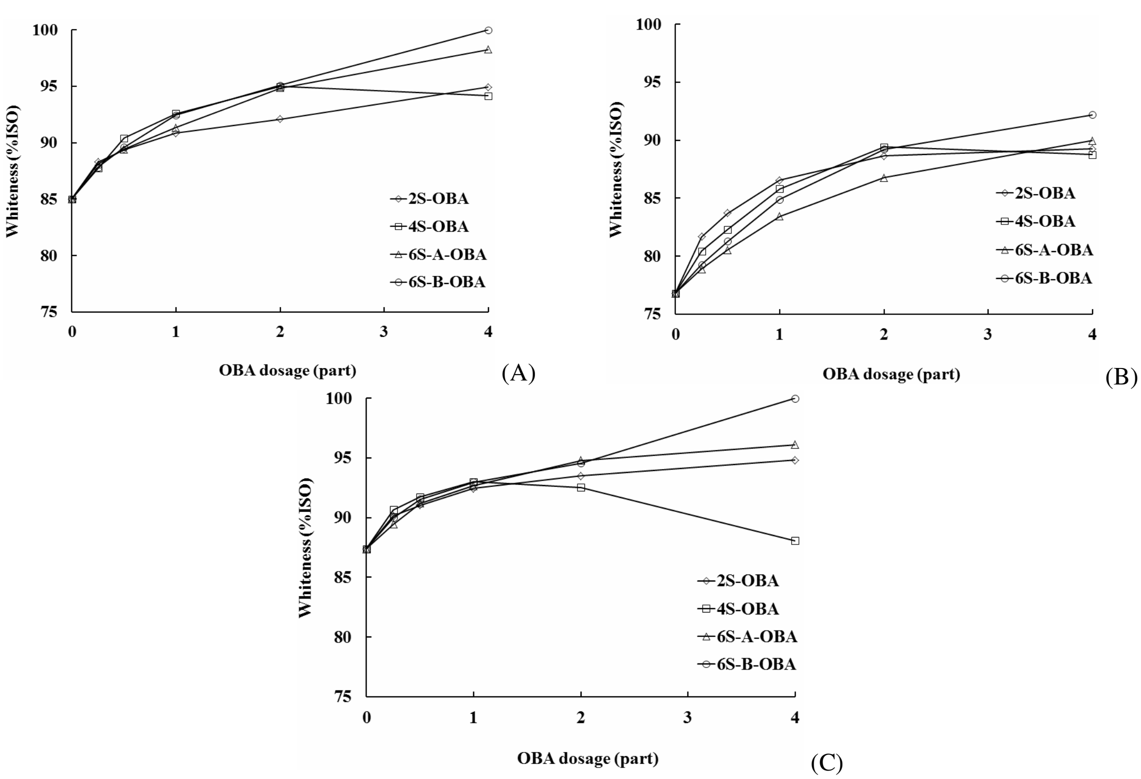

Figure 4: Effects of optical brightening agent (OBA) dosage and type of OBA on the whiteness of coated papers; (A) starch, (B) carboxymethyl cellulose (CMC), and (C) soy protein

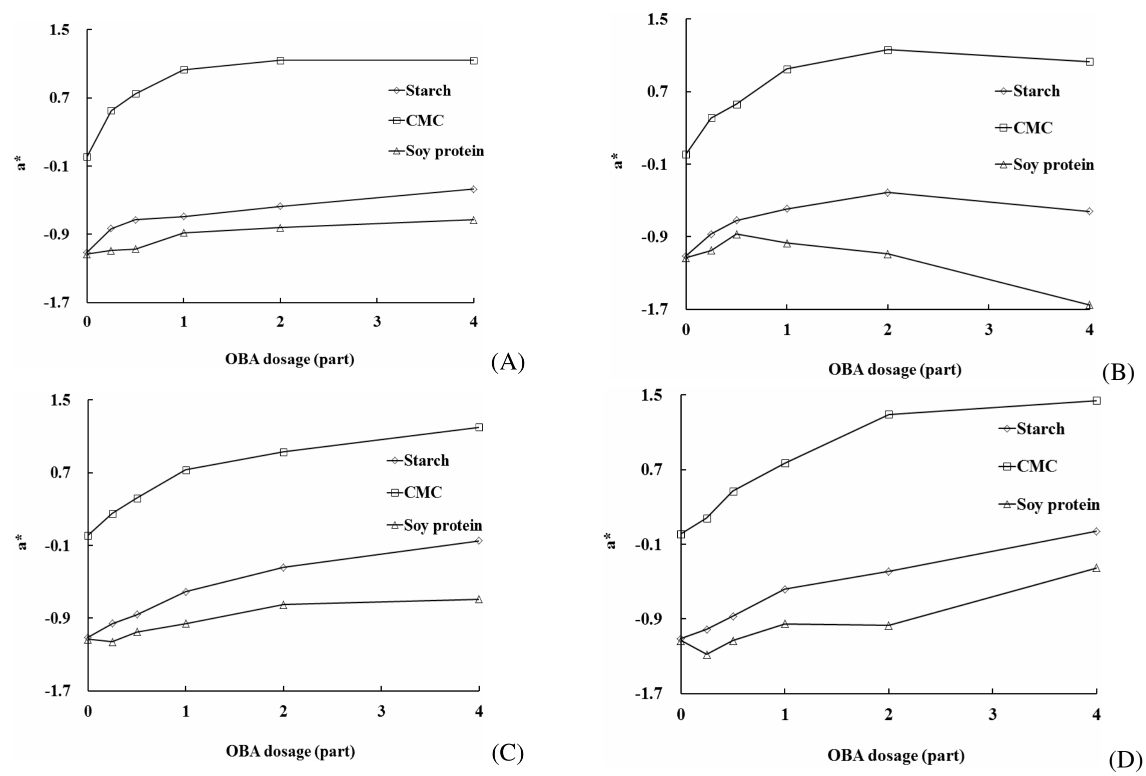

Figure 5: Effects of optical brightening agent (OBA) dosage and type of co-binder on the a* value of coated papers; (A) 2S-OBA, (B) 4S-OBA, (C) 6S-A-OBA, and (D) 6S-B-OBA

With soy protein as the co-binder, Figs. 2C and 4C show that at OBA dosages of < 1 part, all four OBAs performed similarly; at a dosage of > 2 parts, however, regardless of the brightness or whiteness, 4S-OBA's performance plummeted. Thus for an OBA dosage of > 2 parts, 6S-B-OBA outperformed the others, particularly in terms of whiteness which could reach 100% ISO. All other OBAs tended to have leveled-off up to the saturation points. Thus, for color formulations with soy protein as the co-binder, 2S-OBA or 4S-OBA best met the low brightness demand, while 6S-B-OBA did well for high brightness demand situations.

a* and b* Values

Among the 4 types of OBAs examined, the effects of dosage and co-binder types on the a* values of coated paper are shown in Figs. 5 and 6, and those on b* values are shown in Figs. 7 and 8. a* denotes the redness-greenness axis, + values indicate redness, and – values indicate greenness; while b* denotes the yellowness-blueness axis, + values indicate yellowness and – values indicate blueness. The figures show that adding OBAs tended to shift a* to higher values and b* to lower values, indicating that the tone of the coated paper changed from greenness-yellowness to redness and blueness, which effectively increased the brightness and whiteness perceptions. Among the four OBA groups, Figs. 5 and 7 indicate that the CMC co-binder was intrinsically produced more of a redness-yellowness tone compared to starch and soy protein. Thus, it tended to have a more-muted effect toward the whiteness gain, but it often had the best brightness gain.

OBA types

In coating color formulations with 2S-OBA (Figs. 5A, 7A) and CMC as the co-binder (Figs. 6B, 8B), an OBA dosage of > 2 parts often exceeded the saturation point (greening point), wherein the tone no longer shifted from greenness-yellowness to redness-blueness, and there was no more whitening efficacy. Thus, soy protein appeared to be a more suitable co-binder for 2S-OBA formulations, followed by starch.

In coating color formulations with 4S-OBA in Figs. 5B and 7B, at OBA dosages of > 1 part for soy protein, and > 2 parts for CMC and starch, saturation points were exceeded, and no further brightening gain existed. Thus, for 4S-OBA groups, starch appeared to be more suitable as a co-binder choice, followed by CMC.

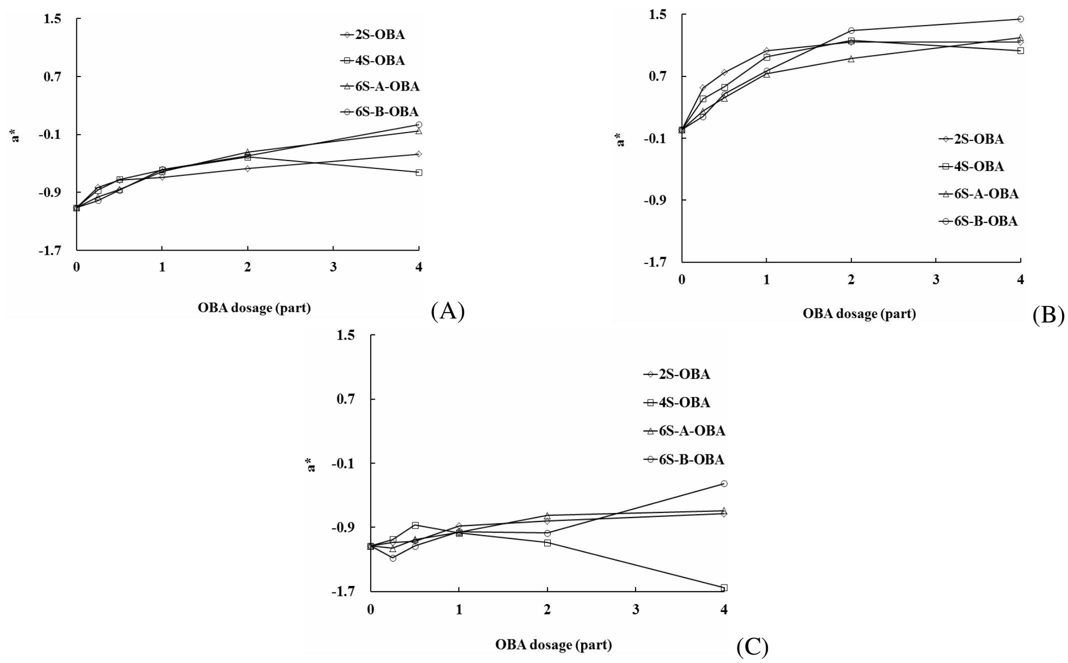

Figure 6: Effects of optical brightening agent (OBA) dosage and type of OBA on a* values of coated papers; (A) starch, (B) carboxymethyl cellulose (CMC), and (C) soy protein

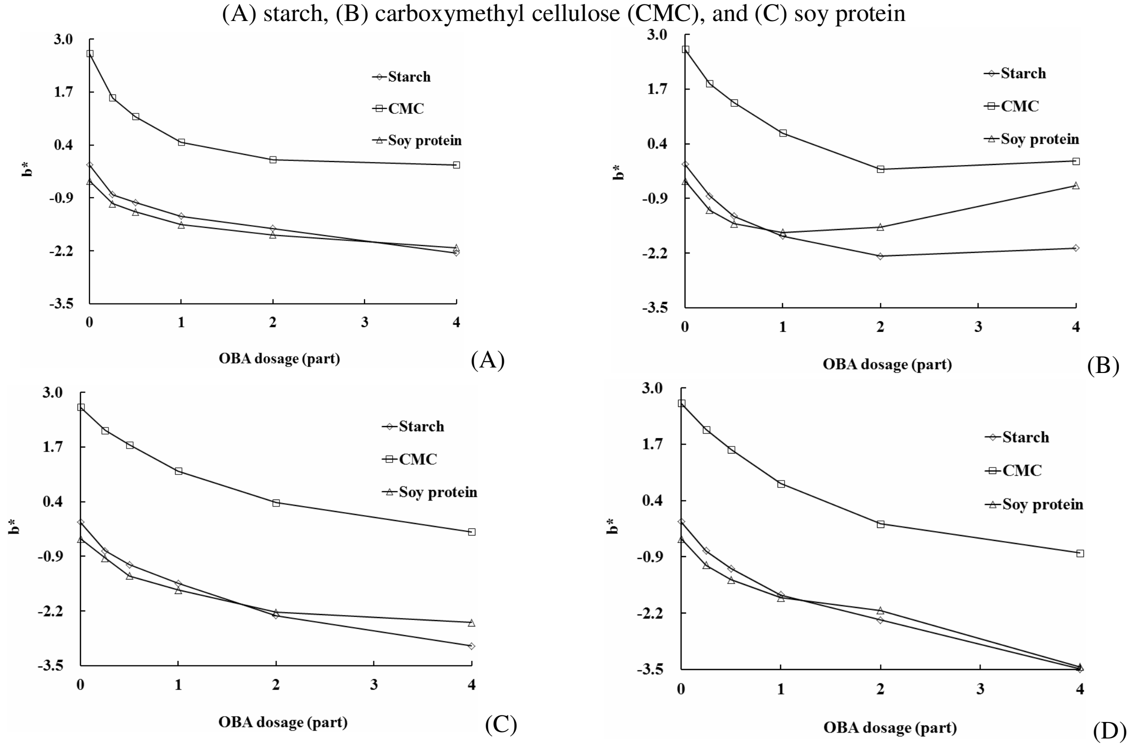

Figure 7: Effects of optical brightening agent (OBA) dosage and type of co-binder on b* value of coated papers; (A) 2S-OBA, (B) 4S-OBA, (C) 6S-A-OBA, and (D) 6S-B-OBA

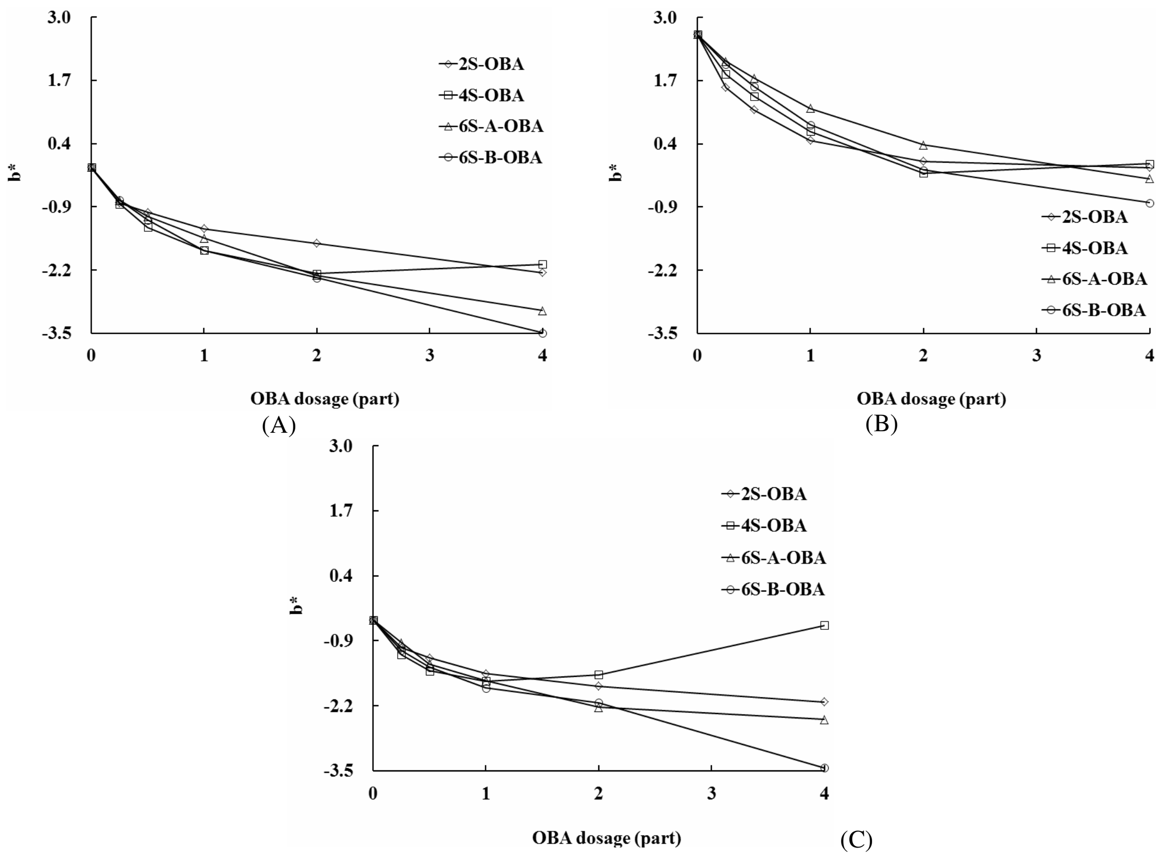

Figure 8: Effects of optical brightening agent (OBA) dosage and type of OBA on b* value of coated papers; (A) starch, (B) carboxymethyl cellulose (CMC), and (C) soy protein

In coating colors containing 6S-A-OBA in Figs. 5C and 7C, and with relatively low brightness demands, soy protein appeared to be optimal; but for higher brightness demands, starch was a better choice.

In coating color using 6S-B-OBA in Figs. 5D and 7D, all three co-binders showed similar tonal trends, and for lower brightness demands, soy protein appeared to be better; while for higher brightness demands, both soy protein and starch worked well.

Co-binder types

Figures 6A and 8A show that when starch was the co-binder, and at OBA dosages of < 2 parts, the 4S- and 6S-OBAs had similar tonal responses; at a dosage of > 2 parts, however, 6S-B-OBA shifted more toward redness-blueness, hence, a better brightening efficacy, particularly for relatively higher brightness demands.

When CMC was the co-binder in Figs. 6B and 8B, and at OBA dosages of < 2 parts, 2S-OBA had a more pronounced tonal effect; at a dosage of > 2 parts, however, 6S-B-OBA shifted the tone of the coated paper more toward redness-blueness, and hence had a better brightening efficacy in the higher brightness demand region. The 2S- and 4S-OBAs at a dosage of > 2 parts all tended to have tone reversal from redness-blueness to greenness-yellowness, suggesting that the saturation points had been reached, and no further brightening effect with a higher dosage was possible.

For coating colors using soy protein as co-binder in Figs. 6C and 8C, at OBA dosages of < 1 part, all four OBAs had similar tonal responses; at a dosage of > 2 parts, however, the 6S-B-OBA group still maintained the redness-blueness drive and hence the best brightening efficacy at the higher brightness requirement end. Even at dosages of > 1 part, the 4S-OBA group had reached the saturation point with no further brightness gain possible.

The above results indicate that different co-binders appeared to exert fairly significant effects on the whitening efficacy of coated paper containing different OBAs. However, the reasons for different OBA performances with different co-binders may be quite complicated and difficult to delineate. The intrinsic color (yellowish in the case of CMC, and white powders in the other two) might be one of these. Dosages differed among the co-binders (2 parts for CMC, 1 part for soy protein, and 3 parts for starch), so the different solids contents affected the OBAs differently. In addition, the molecular morphology of the co-binders differed as well. CMC is a linear long-chain polymer, soy protein – a globular structure, and starch – a branched polymer, so their interactions with the binder, pigment, OBA, and particularly UV light component in the light source thus differed. The above causes underlie the subtle differences in brightness perceptions as measured by the whiteness instrument.

CONCLUSION

We examined interactions among co-binders used in typical art paper coating formulations with various types and dosages of OBAs. The results indicated that for starch co-binder formulations, 4S-OBA appeared optimal for relatively lower brightness demand applications; for higher brightness demands, however, 6S-B-OBA was the better choice. With CMC as the co-binder, 2S-OBA did well for lower brightness requirement applications, and for higher brightness requirements, 6S-B-OBA was more suitable. For soy protein-formulated coating colors, 2S- or 4S-OBAs, and 6S-B-OBA were suitable choices, respectively. Conversely, for 2S-OBA, the co-binder of choice was soy protein, followed by starch. For 4S-OBA, starch appeared more suitable, followed by CMC. For 6S-A-OBA, the co-binders of choice at the lower and higher brightness requirements were soy protein and starch, respectively. For 6S-B-OBA color formulations, the lower and higher brightness requirements called for soy protein and soy protein or starch as co-binders, respectively.

ACKNOWLEGEMENTS: The authors wish to acknowledge financial support from the National Science Council (now the Ministry of Science and Technology, NSC95-2313-B-212-012-MY3) and help rendered by the staff of the Research Center of Yuen-Foong-Yu Paper Co. during the experimental work conducted there. Help with chemicals and information from the former Ciba Specialty Chemicals (now a group of BASF), Taiwan is hereby acknowledged as well.

REFERENCES

[1] C. C. Roltsch and T. A. Lioyd, in *Procs. TAPPI Papermakers Conference*, Atlanta, April 6-8, 1987, pp. 87-99.

[2] B. W. Crouse and G. H. Snow, *Tappi J.*, **64**, 87 (1981).

[3] A. K. Sarkar, in "Fluorescent Whitening Agents", Merrow, England, 1971.

[4] S. Bourgoing, E. Leclerc, P. Martin and S. Robert, *J. Pulp Paper Sci.*, **27**, 240 (2001).

[5] A. J. Ragauskas, L. Allison, L. A. Lucia and C. Li, *Solutions/Tappi J.*, **84**, 55 (2001).

[6] J. E. P. Nordstrom, J. P. Nordlund and J. P. L. Gron, in *Procs. TAPPI Coating Conference*, Philadelphia, May 11-14, 1997, pp. 260-277.

[7] H. J. Zhang, H. R. Hu, Z. B. He, Y. H. Ni and Y. J. Zhou, *J. Wood Chem. Technol.*, **27**, 153 (2007).

[8] M. Sykes, F. Y. Tan and S. Abubakr, in *Procs. TAPPI Pulping Conference*, Montreal, October 25-29, 1998, pp. 539-545.

[9] H. Zhang, Z. He, Y. Ni, H. Hu and Y. Zhou, in *Procs. PAPTAC Annual Meeting*, Montreal, February 6-8, 2007, pp. B235-240.

[10] E. Drzewińska, *Fibers Text. East. Eur.*, **16**, 105 (2008).

[11] E. Drzewińska, *Fibers Text. East. Eur.*, **16**, 103 (2008).

[12] M. Makinen and D. Eklund, in *Procs. TAPPI Coating Conference*, Nashville, May 19-22, 1996, pp. 61-78.

[13] P. Rohringer and I. Fletcher, in *Procs. TAPPI Coating Conference*, Nashville, May 19-22, 1996, pp. 239-251.

[14] J. D. Barnard, *Paper Technol. Ind.*, **33**, 24 (1992).

[15] S. Sturm and S. C. Chen, in *Procs. TAPPI Practical Papermaking Conference*, Milwaukee, May 22-26, 2005, pp. 61-81.