Preparation of Highly Brightened Papers*

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【Abstract】Paper dyed with fluorescent agent will convert ultraviolet light to a longer wavelength and thereby produce additional white light and increase the apparent brightness or whiteness. To achieve a higher whiteness of paper, many papermakers include a fluorescent whitening agent (FWA) or shading dyestuff in the paper. In this study, we attempt to prepare a highly brightened alkaline $CaCO_3$ filled paper in which color will be comparable to imported one at a request of Taiwan papermaker. It was found out that whiteness of brightened paper was not markedly affected by the varying freeness of bleached pulps. A matched highly brightened hand sheet (whiteness 146.27%, CIE L*a*b* 94.14/2.25/-13.43) could be prepared by selecting certain FWAs, bluish shading dyestuffs, high brightness $CaCO_3$ and bleached sulfite pulp (brightness>90% ISO) and $NaBH_4$ treated bleached pulp, when compared to the color (147.17%, 94.26/1.95/-13.58 standard) of imported brightened printing paper.

【Key words】Fluorescent whitening agent, Brightness, Whiteness, Shading dye, Filler

高白度螢光增白紙之配方

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【摘要】白紙中添加可吸收紫外光反射成帶藍色強烈可視光及少量藍色染料中和白漿之微黃色，使紙視之益白。某紙廠委妥本試驗室研製可比美歐洲進口高視白度之白紙配方。試驗結果顯示紙漿游離度對紙視白度影響不大；利用含強紫外光之氙光源測色儀找出完全對色之白紙配方爲利用高白度進口亞硫酸鹽紙漿(白度大於 90% ISO)，添加不吸收紫外光之高白度碳酸鈣塡料，高螢光增白效果之螢光染料及帶藍色提色劑所抄出之鹼性手抄紙之顏色値：視白度 146.27% ，CIEL*a*b*94.14/2.25/-13.43 足堪比美進口之高視白度紙之顏色値：視白度 147.17% ，CIEL*a*b*94.26/1.95/-13.58 .

【關鍵詞】螢光增白劑，白度，視白度，提色劑，塡料

I. INTRODUCTION

Whiteness differs fundamentally from paper brightness in that whiteness includes the entire visible spectrum in its assessment whereas brightness includes only the blue portion of the spectrum, as Figure 1 shown (T-562 pm-96,1996; Malthouse 1995). When white papers are commonly ranked subjectively by customer or supplier, it has been shown that people prefer bluish whites to grayish, yellowish, greenish, or pinkish whites. As a consequence, papermakers often add fluorescent whitening agent (FWA) to enhance the appearance of their papers (Kuo,1996).

High brightness or whiteness papers are getting

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popular to the consumer or printer, due to their attractive color printing effect. Unfortunately most of white papers present yellowish tint with the residual lignin in bleached pulps, so it is difficult to prepare highly brightened paper in Taiwan paper mills. There are about 5,000 distinguishable colors which would be called white by a normal human observer and about 30,000 more whites are called '...ish' whites, i.e., bluish whites, yellowish whites, etc (Hunter, 1987). When a human being visually compares two or more white materials to each other, it is known that most people give preference to the bluish whites. Commonly blue whites are perceived as being clean, fresh or pure in comparison to grey whites, yellow whites, pink whites, etc. This bias made it difficult to select the right FWA and shading dyestuff for the preparation of a matched highly brightened white paper. However, when FWAs are present in paper samples being investigated, the FWA will absorb energy from the ultravilolet wavelengths present in the source of illumination and re-emit that energy in the form of visible light (see Fig.1). In other words, FWAs are selected to re-emit their energy in the blue portion of the visible spectrum to counteract the loss of blue energy due to the lignin yellowing, thereby making the paper appear whiter and brighter. The re-emitted light adds to the light energy normally reflected from the base stock providing a 'boosting' to the reflectance of the sheet. Additionally, bluish shading dyestuff is the complementary color of yellow that was caused by the presence of lignin, which can make the paper appear whiter. Up to a point, the more UV available the bigger whiteness 'increase'.

How to prepare a highly brightened paper as our customer required? Of course, we are taught that the color of this paper (white paper is color paper as well (Kuo, 1986) can be made by the addition of FWA together with some bluish shading dyestuffs in a bleached pulps. However, a color matching problem encountered with FWA containing sample is that the reflectance of brightened paper over 100% in the range of 400-450 nm shows a sharp peak in which makes color matching difficult. As a consequence, we attempt to prepare a highly brightened printing paper (whiteness : 147.17, CIE L*a*b* : 94.26/1.95/-13.58) which

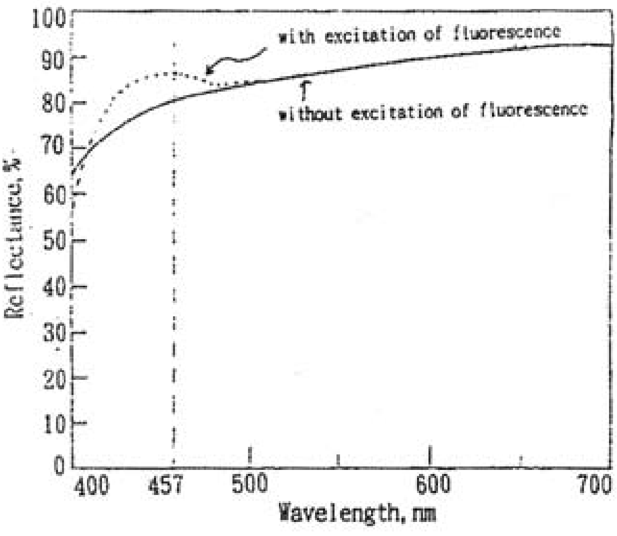

Fig. 1. Spectral reflectance of brightened paper with or without the addition of FWA.

can be matched the color of standard (whiteness : 147.17, CIE L*a*b* : 94.26/1.95/-13.58) with modern spectrophotometer at a Taiwan papermaker's request.

II. MATERIALS AND METHODS

Bleached softwood sulfate pulp, bleached hardwood sulfate wood, and bleached softwood sulfite pulp were obtained from the USA and Canada, and the pulps were refined using a PFI to 450 mL CSF. Drained the water of each refined pulp to a moiture content of ca 25% by a centrifuge and stored in a 50℃ refrigerator. Refine each pulp to 350, 450 and 550 mL CSF respectively by PFI and then prepare a 100 g/m^2 hand sheet in accordance with TAPPI standard T205 to investigate the effect of extent of refining upon the brightness, whiteness and chromatic characteristics.

Fluorescent whitening agents - Leucophor U LTD (L-U), Leucophor NS LIQ (L-NS), and Taflomol X-MP (TX-MP) and shading dyestuffs - Printofix Violet H-3B LIQ. (H-3B), Cartasol Blue 3RF LIQ (Car.3RF), Carta Violet 3B 70LIQ (Car. 3B) Cartasol BR-Violet 5BFN LIQ (Car.5BFN), Cartaren Blue C-BR LIQ (Car.BR) and Direct Violet 51 (DV-51) were obtained from one of Taiwan paper mills. Add various combinations of FWAs and shading dyestuffs into the stock until we obtain over all match (color difference (E <1.0) between standard and sample. Change the order of addition FWAR→shading dyestuff into shading -dyestuff → RFWA for the comparison of brightening effect.

Although TiO_2 has high refractive index of 2.5-2.7, it will absorb ultraviolet in the range of 400-450 nm and can not reemit it as visible light at the blue end of spectrum (Casey, 1981), so we determine the whiteness of TiO_2- filled paper to elucidate TiO_2 effect on the optical whiteners.

Measuring the brightness, CIE whiteness, CIE L*a*b* and scattering coefficient (s) of paper specimens with spectrophotometer (Macbeth Color-Eye 3000, USA) incorporating direction (d/0) and UV-containing xenon lamp.

In principle, overall color-matched FWA brightened pair (sample and reference) should have the same or similar spectral reflectance, brightness and whiteness under the illumination of UV-containing light source.

The overall color difference ΔE (= $(\Delta L^* + \Delta a^* + \Delta b^*)^{1/2}$) take into account lightness/ darkness, as well as chromatic differences. Usually overall color difference less than 1.0 will be acceptable by our visual eyes during color matching of paper. In order to achieve the best possible agreement between customer and supplier on visual color matching, a spectrophotometer with same illuminating and viewing conditions must be employed.

III. RESULTS AND DISCUSSION

(I)*Effect of pulp freeness on whiteness*

Beating gives a repeated crushing action to the wet fibers and causes a breakdown of fibers. Table 1 shows no marked effect on the whiteness of papers with the addition of various FWAs at different levels of freeness i.e. in the range of 350-550 mL CSF.

The highest admiral whiteness of over 120% paper samples with UV containing light source was achieved for FWA TX-MP, so we select TX-MP as the unique FWA in this study. It is interesting to note that an UV out source produces much lower whiteness for the lack of ultraviolet as Table 1 shown. However, in order to maintain optimum strength, we take 450 mL freeness for all stock preparations.

(II)*Shading dyestuff selection*

Table 1. Effect of pulp freeness on the optical properties of brightened papers.

Freeness, ml C.S.F.	FWAs	Brightness, %	Whiteness, %	CIE L*a*b* (L*/a*/b*)	smax(λ), cm^2/g
350	TX-MP	102.63[a]	120.82	96.87/1.75/-6.47	763
		86.44[b]	71.33	95.10/-0.84/3.64	253
	L-U	91.76[a]	93.64	96.15/0.80/-0.73	274
		81.22[b]	67.41	93.71/-0.40/3.74	241
	L-NS	87.24[a]	77.49	96.06/-0.23/2.82	248
		74.90[b]	64.61	93.67/-0.48/3.67	238
450	X-MP	100.85[a]	121.34	5.83/1.71/-7.10	751
		86.20[b]	72.72	94.73/-0.95/3.13	249
	L-U	90.32[a]	93.00	95.44/0.76/-0.96	281
		81.34[b]	68.73	94.50/-0.42/3.44	239
	L-NS	87.62[a]	78.76	96.04/-0.16/2.52	253
		74.83[b]	65.84	92.92/-0.42/3.63	244
550	TX-MP	102.00[a]	122.18	96.31/1.72/-7.05	776
		87.60[b]	72.58	95.59/-0.92/3.63	254
	L-U	89.10[a]	93.05	94.67/0.84/-1.32	262
		80.07[b]	68.36	93.19/-0.30/3.69	236
	L-NS	87.77[a]	78.59	96.20/-0.05/2.65	245
		75.62[b]	64.35	94.96/-0.47/3.52	239

a :measured with UV-in.
b :measured with UV-out.
smax(λ) is the highest s value in the range of 400-700nm.

Shading dyestuffs are the colorants that adding into white stock to make color perceived as not at all yellow (see Figure 2). Since the objective was to match the color i.e., brightness and whiteness of standard sample, two methods - FWA and shading dyestuff additions - were considered as a means of achieving this.

For undyed stock having an initial brightness 82.19% and whiteness 75.43%, excepting dyestuffs H-3B and C-BR, shading in the range of 10-40 ppm (on dried pulp) often produced whiteness gains of 3-36 points as shown in Table 2. Various shading dyestuffs charges may not produce apparent scattering coefficient increments which accounted for the high absorption power of dyestuffs rather than scattering power (see Table 2). Negative b* values of all paper samples showed that bluish whiteness is the marked preference for human being.

(III)***Order of addition***

During the paper preparing process, adding FWA (TX-MP) before shading dyestuff (5BFN) gives lower whiteness and higher brightness papers than that of shading-FWA one as shown in Table 3. Nevertheless, considering the color of the standard (147.17%, 94.26/1.95/-13.58) to be matched, it is advisable to choose the FWA-shading sequence. As a result, it is necessary to add the dyes sequentially to keep the shade of brightened paper relatively constant.

Table 4. shows that either the filler ($CaCO_3$: 10%) - FWA (TX-MP:1%) - shading dyestuff (5BFN: 40 ppm) - retention aid (polyacryl amide: 300 ppm) or FWA-shading dyestuff- filler-retention addition sequences gives the similar bright-

Table 2. Effect of various shading dyestuffs' dosages on the optical properties of brightened papers.

Dyestuffs ppm	Brightness %	Whiteness %	CIE L*a*b* (L*/a*/b*)	^{s}max(λ) cm^2/g
Blank	82.19	75.43	93.31/0.23/1.79	245
H-3B	10	80.96	69.2893.52/-0.35/3.23	244
20	83.91	71.22	94.98/-0.37/3.60	234
30	83.35	72.14	94.49/-0.35/3.13	233
40	82.38	70.38	94.18/-0.25/3.35	267
3RF				
10	78.96	81.69	90.26/-1.12/-1.02	253
20	80.44	88.68	89.95/-1.59/-2.63	248
30	78.69	92.85	88.22/-1.86/-4.21	253
40	79.29	97.81	87.82/-2.01/-5.40	287
3B				
10	82.28	85.17	91.60/1.35/-1.14	256
20	80.82	92.37	89.41/2.50/-3.64	253
30	79.62	97.47	87.97/3.10/-5.29	246
40	78.76	104.05	86.44/4.43/-7.23	251
5BFN				
10	77.88	87.09	88.56/0.01/-2.88	268
20	80.27	98.57	88.08/0.32/-5.47	253
30	78.20	103.63	86.08/0.76/-7.24	256
40	79.36	111.51	85.52/1.13/-9.04	291
C-BR				
10	80.27	69.66	93.05/-0.43/2.90	234
20	80.42	69.48	93.13/-0.54/2.98	229
30	81.27	69.63	93.63/-0.55/3.21	250
40	80.18	66.91	93.38/-0.56/3.67	259
D-V 51				
10	82.64	78.66	92.84/-0.13/0.85	258
20	82.35	82.22	92.04/0.30/-0.30	256
30	81.31	85.33	90.90/0.55/-1.50	250
40	81.47	88.68	90.41/0.43/-2.43	264

Measured with UV-in.
smax(λ) is the highest s value in the range of 400-700nm.
H-3B: Printofix Violet H-3B LIQ.
3RF: Cartasol Blue 3RF LIQ.
3B: Carta Violet 3B 70 LIQ.
5BFN: Cartasol BR Violet 5BFN LIQ.
C-BR: Cartaren Blue C-BR LIQ.
D-V 51: Direct Violet 51.

Table 3. Effect of the order of FWA and shading dyestuff addition on the optical properties of brightened papers.

Order of addition	Brightness %	Whiteness %	CIE L*a*b* (L*/a*/b*)
F1 → D	101.51a	138.83	92.32/1.64/-12.48
	85.39b	84.39	91.05/-1.89/-1.24
D → F_1	98.55a	145.50	89.45/1.37/-14.93
	83.71b	91.53	88.94/-1.66/-3.65
F2 → D	99.71a	145.58	90.82/2.42/-14.52
	84.79b	94.05	89.59/-1.16/-3.91
D → F_2	99.11a	151.86	89.35/2.33/-16.36
	83.85b	98.81	88.43/-0.90/-5.38

a: measured with UV-in.
b: measured with UV-out.
F1: T X-MP 1% ・ F2: T X-MP 0.5% ・ D: 5BFN 40ppm.

Table 4. Effect of the order of FWA, dyestuffs and filler addition on the optical properties of papers.

Order of addition	Brightness %	Whiteness %	CIE L*a*b* (L*/a*/b*)	$^{s}max(\lambda)$
F → FWA → D → R	98.28a	149.57	88.88/2.10/-16.00	2265
	84.14b	98.73	87.83/-1.59/-5.58	360
FWA → D → F → R	98.58	150.15	88.94/2.07/-16.11	10191
	84.27	98.57	88.02/-1.44/-5.48	375

a: measured with UV-in.
b: measured with UV-out.
smax(λ) is the highest s value in the range of 400-700nm.
F: $CaCO_3$ added : 10% ・ FWA : Fluorescent T X-MP added : 1% ・ D: Dyestuffs 5BFN added : 40ppm ・ R: retention aid.

ness and whiteness results. Provided filler adding (the latter case in Table 4) in the pulp far behind the dyes may lead to higher scattering coefficient (10191 cm^2/g) when comparing the first one.

(IV)***Effect of fillers on the whiteness gains***

Fillers such as talc, clay, calcium carbonate may improve the opacity, brightness, printability of paper and replace part of expensive pulps. Because of their excellent scattering coefficient and brightness, most of fillers are used both as filler and in coating. As commonly known, the high scattering power of titanium dioxide resulting from its high refractive index (2.5-2.7) and uniformly fine particle. However, titanium dioxide containing brightened paper shows the lowest optical properties as shown in Table 5. It is generally accepted that the absorption of ultraviolet light by titanium dioxide inhibits the effect of FWA in developing maximum brightness, because this effect depends on the ability of the dye to convert ultraviolet to visible light. So the calcium carbonate is the only filler used in this experiment.

(V)***Relatively high brightness pulps***

During color matching process, the use of FWA and shading dyes as whitening agents for increasing the optical properties of softwood

Table 5. The optical properties of various filled brightened paper.

Fillers %	Brightness %	Whiteness %	CIE L*a*b* (L*/a*/b*)	$^{s}max(\lambda)$ cm^2/g
Blank	82.19a	75.43	93.31/0.23/1.79	245
	76.55b	66.30	91.26/-0.19/2.71	238
$CaCO_3$				
10	97.85	151.55	88.32/2.29/-16.60	10191
	83.61	98.50	87.60/-1.64/-5.62	359
20	99.29	149.74	89.54/2.18/-15.84	n.d
	85.84	99.32	88.80/-1.46/-5.55	527
30	100.77	146.89	90.92/2.14/-14.76	n.d
	87.35	99.60	90.03/-1.34/-4.90	709
Talc				
10	98.16	144.51	89.72/2.01/-14.65	3164
	84.33	95.93	88.47/-1.64/-4.76	350
20	99.29	143.36	90.51/1.89/-14.13	35696
	85.48	95.12	89.55/-1.47/-4.15	465
30	99.13	141.57	90.80/1.83/-13.64	n.d
	86.11	95.36	90.03/-1.39/-4.01	532
Clay				
10	98.21	151.75	88.32/1.98/-16.63	8314
	83.79	101.30	87.22/-1.55/-6.34	408
20	100.05	149.35	89.80/2.05/-15.67	n.d
	86.10	100.66	88.91/-1.36/-5.57	633
30	101.14	145.89	91.05/1.97/-14.50	n.d
	87.14	98.97	89.98/-1.26/-4.79	776
TiO_2				
10	94.24	119.88	91.61/0.97/-8.62	4113
	88.41	96.45	91.52/-0.97/-3.60	815
20	92.50	107.36	92.91/0.78/-5.34	2486
	89.86	95.88	92.99/-0.60/-2.81	1544
30	93.59	105.13	93.99/0.64/-4.36	3495
	91.4	95.61	93.95/-0.56/-2.29	2213

a: measured with UV-in.
b: measured with UV-out.
smax(λ) is the highest s value in the range of 400-700nm.
Order of addition : NBKP 100% → Tafluonol X-MP Liquid 1% → Cartasol BR. Violet 5BFN 40ppm → Filler(10 · 20 · 30%) → PAM 300ppm.
n.d : no detection.

bleached kraft pulp has been demonstrated that an acceptable matched sample can not be easily attained for the dull bluish tint ($b^* = -13.58$) of standard. It is believed that the decrease in brightness gains is concomitant with adding more bluish shading dye in stock. Too many failure in color matching discourage us to the utmost.

In addition to FWA and dye addition, we also investigated the brightness of commercial high-brightness pulps. How high is the brightness of pulps suitable for brightened papermaking? Are they high enough to prepare a high-brightness paper as the standard? If not, can we improve the brightness of pulps with some bleaching agents such as $NaBH_4$ or something else?

Keeping the NaOH loading at 1% (pH 10) and increasing the sodium borohydride loading from 0.1 to 0.5 % resulted in a brightness increase to 90% at 0.2% loading as shown in Figure 2. In general, relatively high-brightness pulps i.e., > 90% can lead to a successfully preparing the admirable brightened papers.

(VI)***Dyestuff formulation for preparing high-brightness paper***

As mentioned above, whiteness is a combination of total reflectance of white light and uniformity of the reflectance. Because all paper has a yellow cast, a small amount of FWA and dye added to the stock in making whiter paper. The effect is pleasant because the average person prefers a bluewhite to a yellowish white.

A comparison of the brightness ,whiteness, CIE $L^*a^*b^*$ values between the match and standard showed that Match 71 (see Table 6 and Figure 3) gave the small color difference ($\Delta E = 0.36$) which can not be discernible by visual eyes.

Dyestuff formulation in match 71 displayed as a perfect color matching when compared to that of standard. Furthermore, we added optimum amounts of strongly brightening FWA (Tafluonol X-MP) and bluish shading dyestuff (Cartasol BR. Violet 5 BFN) into relatively high-brightness pulps such as $NaBH_4$ treated pulp and bleached sulfite pulp (brightness> 90%) which could result in fully color-matched brightened $CaCO_3$-filled paper (whiteness = 147.17%, CIE $L^*a^*b^*$ = 94.26/1.95/

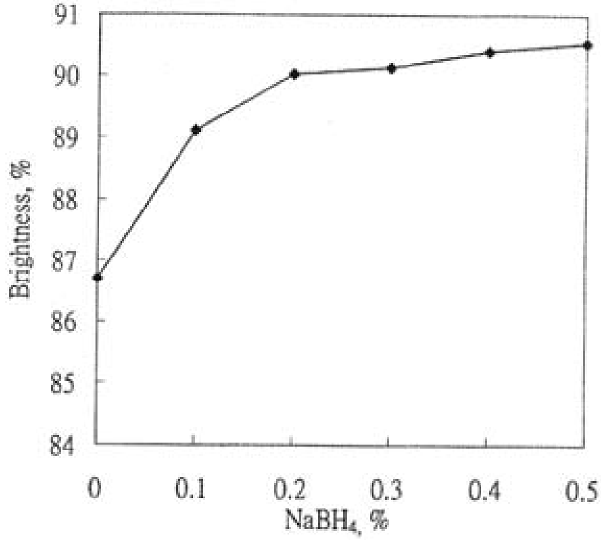

Fig. 2. Brightness gain of LBKP versus $NaBH_4$ treatment at different levels.

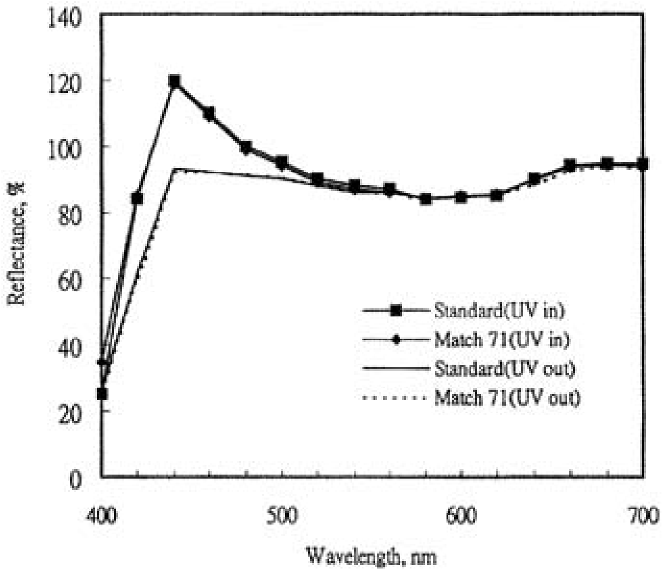

Fig. 3. Reflective curves of standard and match 71 paper samples.

-13.58, acceptable color difference = 0.36).

IV. CONCLUSIONS

Paper dyed with fluorescent agent will convert ultraviolet light to a longer wavelength and thereby produce additional white light and increase the apparent brightness or whiteness. To achieve a higher whiteness of paper, many papermakers include a fluorescent whitening agent (FWA) or shading dyestuff in the paper. In response to prepare a highly brightened alkaline $CaCO_3$ filled paper, of which color was matching to an imported one at a request of one Taiwan papermaker, first of all we found that the whiteness of brightened paper was not markedly affected by the varying freeness of bleached pulps. And then, a color- matched highly brightened hand sheet (whiteness: 146.27%, CIE L*a*b*: 94.14/2.25/-13.43) can be achieved by optimizing certain highly brightening FWAs, bluish shading dyestuffs, high-brightness $CaCO_3$, bleached sulfite pulp (brightness>90% ISO) and $NaBH_4$ treated bleached pulp, when compared to the color (147.17%, 94.26/1.95/-13.58) of imported brightened printing paper (standard).

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