Effect of Carrier Chemicals on the Optical Properties of Paper Surface-Sized with Fluorescent Whitening Agents

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Fluorescent whitening agents (FWAs) are important chemicals for improving the CIE whiteness and ISO brightness of papers. However, papermakers must reduce the amount of FWAs added to their products because FWAs present many disadvantages associated with the papermaking process, as well as paper quality; the public also has concerns about these chemicals in papers. Because the first step to reducing FWAs in the papermaking process is to improve their whitening effect, a new strategy for the effective use of FWA carrier chemicals must be developed. In this study, the whitening effects of tetra-sulpho FWA (T-FWA) and hexa-sulpho FWA (H-FWA) are compared in surface sizing, as well as with carrier chemicals. H-FWA showed a greater whitening effect than T-FWA in surface sizing, and carrier chemicals improved the optical properties of the paper when surface-sized with FWAs. It is concluded that carboxymethyl-celluloses (CMCs) were a more effective carrier chemical for T-FWA; polyvinyl alcohol (PVOH) is effective with H-FWA in the surface-sizing process to increase paper sheet whiteness.

Keywords: Fluorescent whitening agent (FWA); Carrier chemical; polyvinyl alcohol (PVOH); Carboxymethylcellulose (CMC); CIE whiteness; ISO brightness

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INTRODUCTION

Recently, CIE whiteness and ISO brightness have been considered important optical properties because they determine the value added to paper products (Gaudreault and Bouvier 2006); paper that is more white and bright can be sold at a higher price than less white and bright varieties. Many techniques have been reported to improve the optical properties of paper (Fairchild 1992; Laufmann and Forsblom 2000; Zhao *et al*. 2005; Headrick and Covarrubias 2007; Connell *et al.* 2014; Cho and Won 2005). Nonetheless, the use of fluorescent whitening agents (FWAs) has proven to be the most practical and effective in paper production (Lee *et al*. 2012, 2015a). However, FWAs are some of the most expensive chemicals used in papermaking and can negatively impact the efficiency of retention aids or other additives because of their anionic character (Hunke and Roich 2005; Cho and Won 2005; Smith 2008). In addition, many consumers have considered FWAs to be toxic, despite the lack of clear evidence for this assessment. Therefore, papermakers should minimize the amount of FWAs added in the papermaking process by improving the FWAs' whitening effect; they should also expect the simultaneous reduction in production costs (Jeong *et al*. 2014) and improvement of paper quality (Lee *et al*. 2015b) in the surface-sizing process.

The FWAs used in paper mills can be classified into three types, according to their applications (Weaver 1997; Holmberg 1999; Lee *et al*. 2015b). Internal FWAs, such as di-sulpho FWA (D-FWA), are added into the stock directly. For the surface-treatment of paper, FWAs such as tetra-sulpho FWA (T-FWA) and hexa-sulpho FWA (H-FWA), are added to the starch solution or the coating color formulation. The amount of surface-treated FWAs added is higher than that of internal FWA added into the stock because the surface-treated FWAs can show greater improvement for the CIE whiteness and ISO brightness of paper than internal FWA (Weaver 1997; Kim and Lee 2012). According to many reports, the use of carrier chemicals improves the CIE whiteness and ISO brightness of paper that has been surface-treated with T-FWA or H-FWA (Holmberg 1999; Hentzschel 2000; Kloow 2000). In our previous study (Kim and Lee 2012), it was reported that the surface holdout of an FWA is a key factor for a high level of whitening; furthermore, polyvinyl alcohol (PVOH) increased the effectiveness of FWAs by improving the surface holdout of FWAs. However, we did not investigate the effect of carboxymethylcelluloses (CMCs) with T-FWA on the optical properties of paper, nor did we investigate the synergetic effect between PVOH or CMCs and H-FWAs for surface sizing.

In this study, the whitening effects of T-FWA and H-FWA are compared in surface sizing, and the effects of carrier chemicals on improving the whitening efficiency of FWAs are determined. Confocal laser scanning microscopy was used to acquire images from the cross sections of paper samples to observe the distribution of FWAs in the sized surface, as well as the agent's holdout.

EXPERIMENTAL

Materials

Two types of commercially available FWAs were used: T-FWA and H-FWA (Samshin Chemical Co. Ltd., Korea). Never-sized fine paper with a grammage of 95 g/m^2 was used as the base paper for surface sizing with T-FWA and H-FWA. Oxidized starch, polyvinyl alcohol (PVOH), and two types of carboxymethyl cellulose (CMC1 and CMC2) which had different molecular weight were used for surface sizing. Poly-(diallyldimethylammonium chloride) (Poly-DADMAC) was used to analyze charge densities of polymers and FWAs.

Methods

The preparation of polymers and the measurement of their basic properties

PVOH powder was added to distilled water, and the PVOH slurry was then heated at 90 to 95 °C until the PVOH powder was completely dissolved. After heating, the final concentration was controlled at a concentration of 5% with the addition of distilled water. CMC solutions were also prepared in the same way as the PVOH solution. However, the final concentration of the CMC solutions was adjusted to 1%. All the solutions were cooled to 25 °C before they were added to the starch solution.

Table 1. Basic Properties of the Polymers

Polymer	Viscosity (cPs) (Measured concentration)	Charge density (meq/g at pH 5.9)
Oxidized starch	16 (10%)	-0.24
PVOH	84 (1%)	0.00
CMC1	66 (1%)	-0.21
CMC2	713 (1%)	-0.21

The Brookfield viscosity of the polymers was measured at 25 °C, and the charge density for a 0.1% solution, including polymers and FWAs, was measured using a streaming current detector (PCD, BTG, Germany) with 0.001 N Poly-DADMAC. The basic properties of the polymers used are summarized in Table 1.

Surface sizing of paper with a starch solution including FWAs and polymers

The preparation of the starch solution and surface sizing were carried out in the same manner as described in our previous study (Kim and Lee 2012). The starch solution at a concentration of 10% was made by cooking the oxidized starch at 90 to 95 °C for 30 min. Afterwards, the temperature of the starch solution was cooled to 50 °C, the carrier chemicals were added, and the solution was mixed for 5 min. Then, the FWA concentrates were added, and the starch solution was mixed for 30 min.

The surface sizing process was carried out using a rod coater (HT-BC-ST, Hantech, Korea). The top side of a never-sized paper was surface sized, and the paper was then dried in an air dryer for 150 s. To prevent the surface-sized paper from curling, it was passed through a cylinder dryer twice at 120 °C. After the top side of the base paper was surface sized, the bottom side of the paper underwent the same treatment. The final pickup weight was controlled at 2.0 to 2.5 g/m^2 for each side. The surface-sized paper was conditioned at 23 °C and 50% relative humidity prior to measuring its CIE whiteness and ISO brightness.

Measurement of the optical properties and distribution of FWAs in the cross section of surface-sized paper

After surface-sizing application with FWAs and polymers to the sheet, the sheet's CIE whiteness and ISO brightness were measured using a spectrophotometer (Elrepho, Lorentzen and Wettre, Sweden). The light sources used for the measurements are summarized in Table 2 according to ISO 11475:1999 and ISO 2470:1999. A confocal laser scanning microscope (CLSM) (JP/FW 1000, Olympus, Japan) was utilized to observe the FWAs distribution within the surface holdout of FWAs in the surface-sized paper.

Table 2. Light Sources Used for Measured Optical Properties

Item	Light source
CIE whiteness	D65
ISO brightness	C

RESULTS AND DISCUSSION

Whitening Effects of T-FWA and H-FWA in Surface Sizing

T-FWA and H-FWA are usually applied on wet-end and surface applications, respectively. However, recent strategies for additives applications have tended to diverge from conventional processes, especially if the new methods are more effective for improving paper quality or at reducing paper production costs. Therefore, the possibility for FWAs' application at the surface size press and their whitening efficiency were investigated in this study.

The CIE whiteness and ISO brightness of the paper surface sized with T-FWA and H-FWA are shown in Figs. 1 and 2. As the amounts of T-FWA and H-FWA added to the starch solution were increased, the CIE whiteness increased logarithmically.

When the level of FWAs added was at the same amount, the CIE whiteness of the paper surface sized with H-FWA was higher than that of paper surface sized with T-FWA. The ISO brightness of the paper showed the same trend as the CIE whiteness; also, H-FWA showed higher values than T-FWA. Weaver (1997) reported a greater whitening efficiency for H-FWA than for T-FWA and D-FWA. In addition, the whitening efficiencies of H-FWA can be explained by examining the CLSM images of the *z*-direction of paper (Fig. 3). A previous study showed that a key factor for improving CIE whiteness and ISO brightness is surface holdout (Kim *et al*. 2012). H-FWA showed relatively higher surface holdout when compared to T-FWA. This may be related to the fact that H-FWA has a higher anionic charge because of the higher number of sulfonic acid groups on the H-FWA molecule versus the T-FWA molecule (Table 3). Cellulosic fibers also have an anionic charge as a result of the carboxylic acid groups (Bley and Winder 1997). It follows that the repulsive force between the cellulosic fibers and H-FWA would be higher than for T-FWA. It is also reasonable to expect that higher degree of sulfonation renders H-FWA more soluble, leading to less self-association and higher optical efficiency. Therefore, not only can H-FWA be used as an FWA in surface sizing, but it also can improve the whitening effect better than T-FWA.

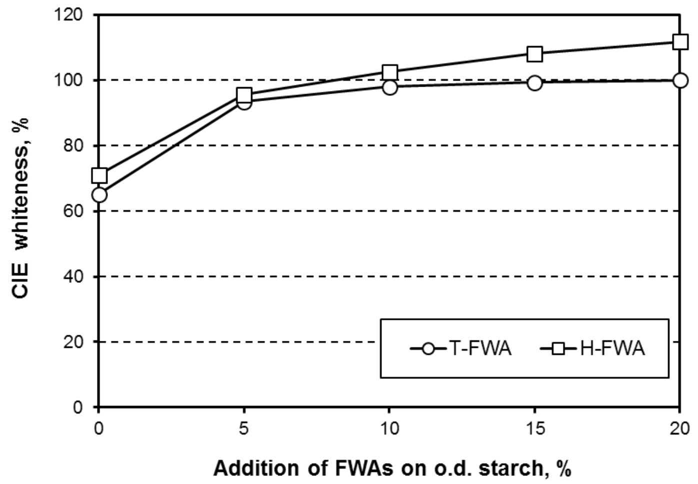

Fig. 1. CIE whiteness of paper sheets surface-sized with T-FWAs or H-FWAs

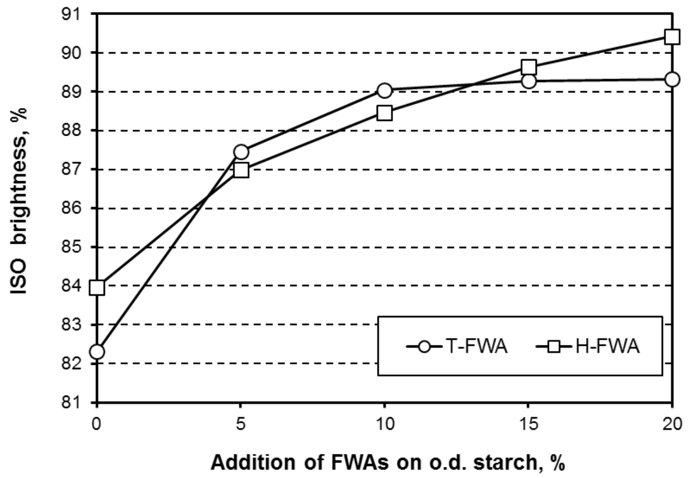

Fig. 2. ISO brightness of paper sheets surface-sized with T-FWAs or H-FWAs

Table 3. Charge Densities of FWAs

pH	T-FWA	H-FWA
5.5	-5.0	-6.5
7.5	-5.2	-6.6

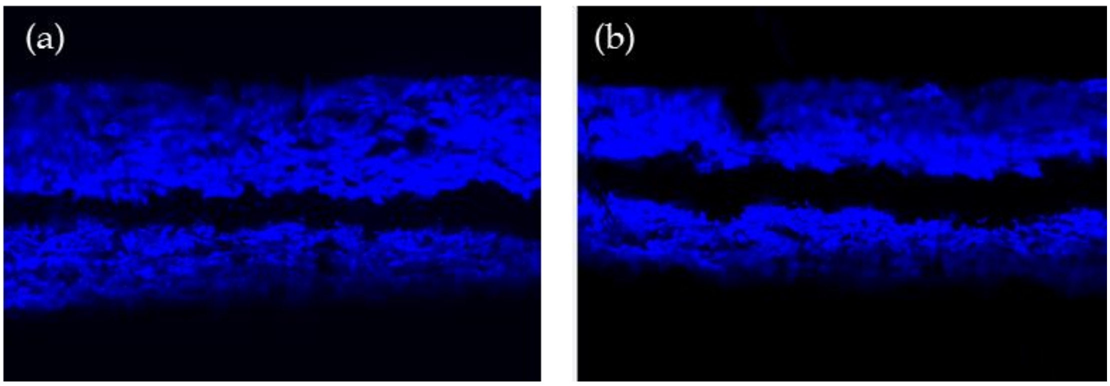

Fig. 3. FWA distribution of paper surface-sized with (a) T-FWAs and (b) H-FWAs

Improvements of CIE Whiteness and ISO Brightness for Paper Surfaces Sized with FWAs and Carrier Chemicals

The CIE whiteness and ISO brightness of paper surface-sized with T-FWA and carrier chemicals are shown in Figs. 4 and 5. The level of T-FWAs added to the starch was 10% (on an oven-dried basis). When the addition level of carrier chemicals was increased, so were the CIE whiteness and ISO brightness values of the paper. Although both optical measurements showed different absolute values, they both exhibited similar trends. The CIE whiteness and ISO brightness of paper applied with T-FWA and PVOH also showed a trend similar to that reported in the authors' previous study (Kim *et al*. 2012). When the carrier chemicals were added at the same level, sheets utilizing CMCs had higher whiteness values than sheets utilizing PVOH. However, a substantial difference between CMC1 and CMC2 on whitening was observed; the two CMCs used had different molecular weights. The CIE whiteness and ISO brightness of paper sheets surface-sized with H-FWA and carrier chemicals are shown in Figs. 6 and 7. The addition of H-FWA to the starch was also 10% (on an oven-dried basis). The CIE whiteness and ISO brightness of paper sheets treated with

H-FWA and carrier chemicals increased as a function of the amount of carrier chemicals added. Although CMCs showed higher values for optical properties for paper surface sized with T-FWA, the use of PVOH with H-FWA resulted in a higher whitening effect than CMCs with H-FWA.

The FWA distribution in the cross section of the paper sheet was imaged by CLSM (Figs. 8 and 9) to analyze how carrier chemicals improved optical properties. The CLSM images indicated that CMCs and PVOH had T-FWA and H-FWA stay on the paper surface respectively. This can be explained by the interactions between the FWAs and carrier chemicals. H-FWAs have relatively higher anionic charges than T-FWAs, so the anionic CMCs cannot interact with H-FWAs effectively due to the repulsive forces. In addition, T-FWA has a relatively lower anionic charge than H-FWA, so the opposition interactions between CMCs and T-FWAs can be expected to be lower.

Therefore, CMCs can be an effective carrier chemical for T-FWAs, and PVOH interacts well with H-FWA; the carrier chemicals combined with FWAs showed higher whitening efficiency in the surface-sizing process.

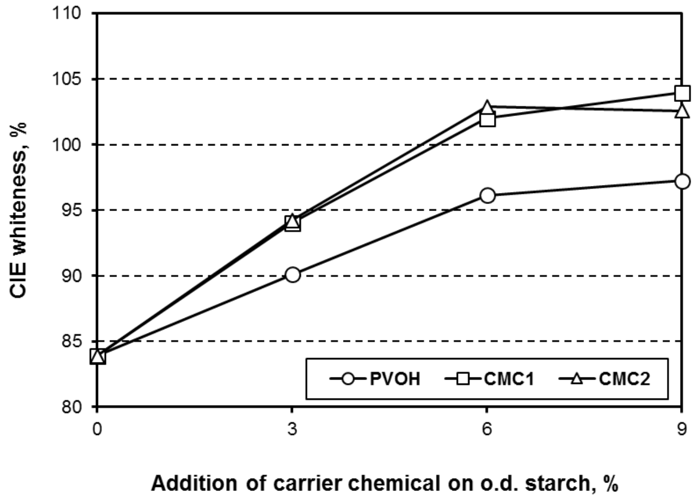

Fig. 4. Effect of carrier chemicals addition on the CIE whiteness of the paper sheets treated with T-FWAs (10% on o.d. starch)

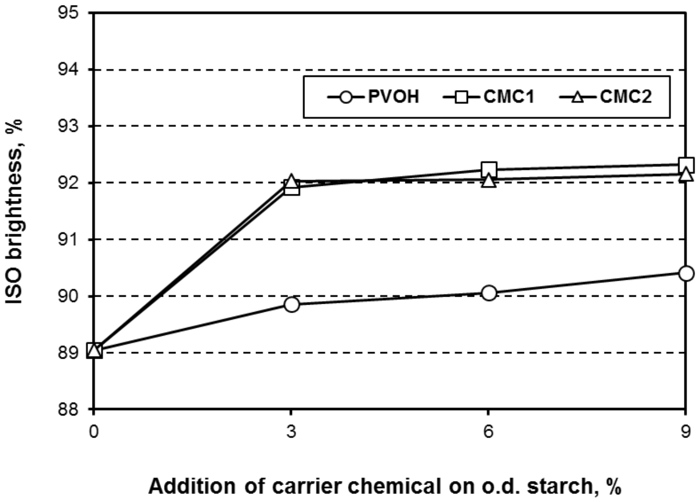

Fig. 5. Effect of carrier chemicals addition on the ISO brightness of the paper sheets treated with T-FWAs (10% on o.d. starch)

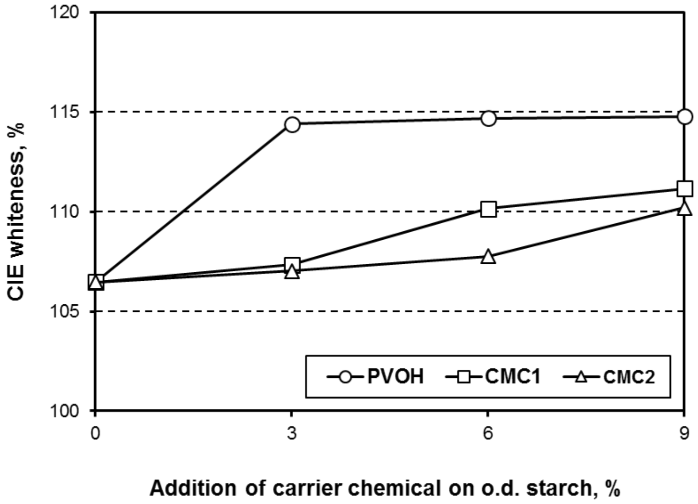

Fig. 6. Effect of carrier chemicals addition on the CIE whiteness of the paper sheets treated with H-FWAs (10% on o.d. starch)

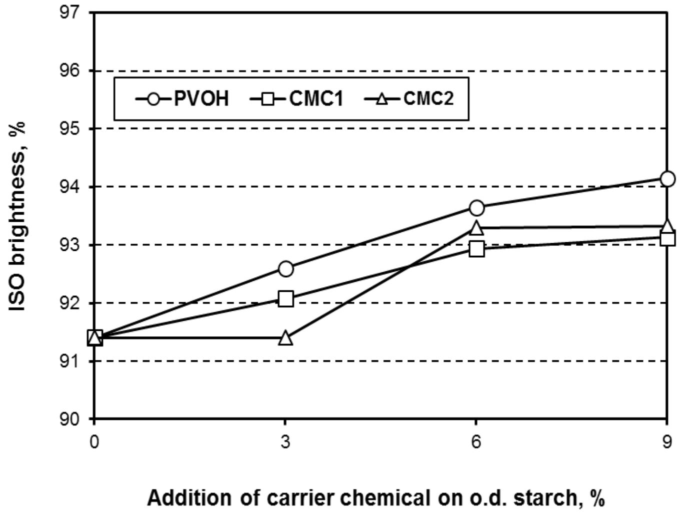

Fig. 7. Effect of carrier chemicals addition on the ISO brightness of the paper sheets treated with H-FWAs (10% on o.d. starch)

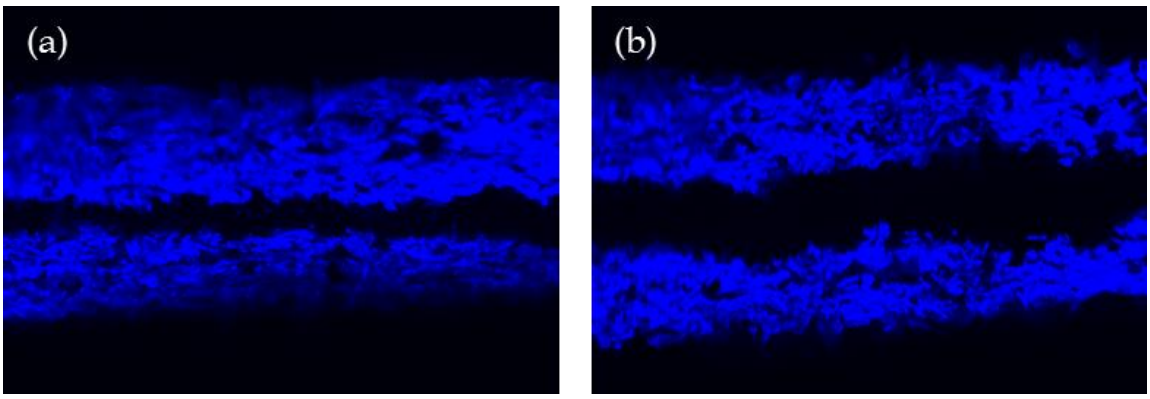

Fig. 8. FWA distribution in the cross section of paper sheets surface-sized with T-FWAs (10%; a) and T-FWAs (10%) and CMC1 (6%; b)

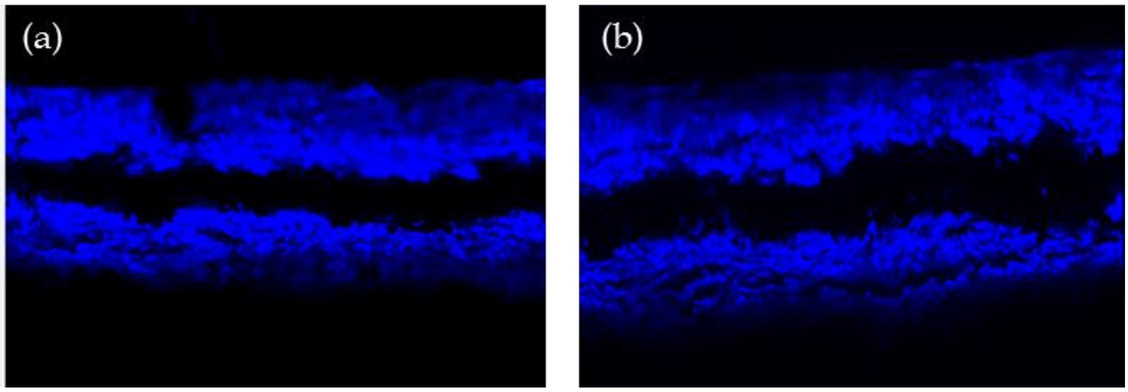

Fig. 9. FWA distribution in the cross section of paper sheets surface-sized with (a) H-FWAs (10%) and (b) H-FWAs (10%) and PVOH (6%)

CONCLUSIONS

1. T-FWA and H-FWA improved the CIE whiteness and ISO brightness of paper sheets that were surface sized. H-FWA proved to be more effective at boosting paper whiteness than T-FWA, which was attributed to H-FWA's higher whitening efficiency. Therefore, H-FWA can be used as an effective FWA in surface sizing.
2. H-FWA had a relatively higher anionic charge than other FWAs, which did not interact as well with anionic CMCs because of the repulsive forces; this impaired the effectiveness of additives to impact optical sheet properties. Meanwhile, because T-FWA had a relatively lower anionic charge than H-FWA, CMCs can be more effective carrier chemicals with T-FWA. PVOH is effective with H-FWA in the surface-sizing process to increase paper sheet whiteness.

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