Angular variations of reflectance and fluorescence from paper - the influence of fluorescent whitening agents and fillers

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Abstract

It has earlier been shown that light reflected from the body of paper exhibit anisotropic behavior. On the other hand, fluorescence emission is often assumed to be distributed in a Lambertian manner. The angular behavior of light reflected and fluoresced from paper is examined using measurements from a spectral goniophotometer. The angular dependency of the radiance factors was measured for a range of excitation wavelengths. Moreover, the influence of fillers and fluorescent whitening agents (FWA) on the anisotropy was studied. The measurements show that the anisotropy of the total radiance factor of paper decreases when an increasing amount of FWA is added to the paper. The same effect was also observed when an increased amount of filler was added to the paper. In addition, it was shown that the presence of fillers reduce the effect of the FWA. The results show that in comparison to the anisotropy of the total radiance factor from the paper samples, the anisotropy of the fluorescence alone is negligible. Hence, for paper samples containing FWA evenly distributed in the bulk, the fluorescence alone should not induce significant differences between color measuring instruments of different measurement geometries.

Introduction

We frequently encounter fluorescence in our daily lives. Fluorescent lighting is widely used in public environments and fluorescent paints are used to improve the visibility of traffic signs and for attention-grabbing effects. Fluorescent dyes are also widely used to alter or improve the appearance of paper products and textiles. These special types of dyes are referred to as fluorescent whiteness agents (FWAs) or optical brightening agents (OBAs) and are specifically used to increase the whiteness of the products. The latter application is a reason why FWAs can be found in detergents. These dyes absorb ultraviolet (UV) light from the illumination and emit light in the blue region of the visible spectrum. In the paper industry, whiteness is a widely used quality parameter of paper products and the whiteness value is an important sales argument. To achieve higher whiteness levels, producers of paper and board use more bleaching of the pulp and increased amounts of FWA added in the papermaking process. Paper products with a slightly bluish shade are perceived as being whiter than papers having a more neutral color by most humans [1]. Therefore, the addition of FWAs increases the perceived whiteness by increasing both the lightness and the bluishness of the paper. Among the many whiteness formulas proposed, the CIE Whiteness formula [2] is the most widely used for paper products. This formula does also reward slightly bluish papers and most commercially available printing papers contain FWAs. To accurately measure fluorescence requires the use of a two-monochromator instrument, e.g. a spectrofluorimeter or bispectrometer [3, 4]. These instruments make it possible to record a discrete, illuminant independent, matrix representation of the bispectral radiance factor for each excitation wavelength and emission wavelength, the Donaldson Matrix [5]. Coppel et al used bispectrometer measurements to characterize the quantum efficiency of FWAs in paper samples with different compositions in terms of FWA concentration, filler concentration, and fiber content [6] and to examine the dependence of the CIE whiteness of uncoated and unfilled papers on the FWA concentration [7]. Previous work on fluorescence in the field of paper and print is dominated by studies related to the influence of FWAs on color measurements with different instruments using polychromatic illumination, in particular studies dealing with the UV-content of the illumination [8, 9, 10]. To the authors' knowledge, only little work related to fluorescence in paper and print has involved angularly resolved measurements, although most materials to some extent display angular variations in color (goniochromism) [11]. Furthermore, Neuman and Edström [12, 13] showed that the light reflected from turbid media will exhibit anisotropic behavior in all realistic situations encountered. Holopainen et al. [14] used a goniofluorimeter to show that the fluorescence emission of a spectralon fluorescence reference standard, which in similarity to paper can be regarded as a solid amorphous material (amorphous $\approx$ non-crystalline) deviates significantly from the lambertian distribution. Wilkie et al. presented an analytical BRDF model based on layered micro-facets for fluorescent materials where the fluorescent component was assumed to be perfectly diffuse [15]. In a more recent study by Hullin et al.[16] the results indicated that the luminance from fluorescent materials such as paint, fabrics and paper displayed small angular variation of the fluorescence. The aim of the work presented here is to determine how the addition of fluorescence (FWAs) and light scatterers (filler pigments) to the fiber network of a paper influence the overall anisotropy of the scattered light. Anisotropy of scattered light could lead to differences in color measurement readings obtained with instruments having different measurement geometries.

Method

To study the angular distribution of light reflected and fluoresced from paper, a set of paper samples with different amounts of filler and FWA, but otherwise identical were produced. The total radiance factor was measured with a spectral goniophotometer for a set of viewing angles ranging from -20^{o} to $+75^{o}$, in steps of 5^{o} for a fixed angle of incident light of 45^{o} relative to the surface normal of the sample. The definition of the

angles is illustrated in figure 1.
The spectral goniophotometer used is of single-monochromator type, where the sample is illuminated with monochromatic light and the entire radiation of all wavelengths from the sample is detected. When illuminating the sample with light of wavelengths within the absorption band of the FWA, the detected radiation consists of light reflected from the substrate as well as fluorescence. This type of configuration will from here on be referred to as monochromatic/polychromatic. The opposite configuration, polychromatic/monochromatic, where the sample is illuminated with polychromatic light and the fluoresced and reflected light is measured monochromatically, is a more common single-monochromator setup for color measurements. The different configurations measure the same spectral reflected radiance factor, but differ in how the fluorescence is measured, and thus how the total radiance factor is measured.

For the polychromatic/monochromatic configuration, the spectral total radiance factor $\beta_{\mathrm{T}}(\lambda)$ is given by:

$$\beta_T(\lambda) = \beta_R(\lambda) + \beta_L(\lambda) \tag{1}$$

where $\beta_{\mathrm{R}}(\lambda)$ is the spectral reflected radiance factor and $\beta_{\mathrm{L}}(\lambda)$ is the spectral luminescent radiance factor. The spectral luminescent radiance factor is given by:

$$\beta_L(\lambda_2) = \int_{\lambda_1} E(\lambda_1) b(\lambda_1, \lambda_2) d\lambda_1 / E(\lambda_2) \tag{2}$$

where $\mathrm{E}(\lambda)$ is the relative spectral power distribution of the illumination and $\mathrm{b}(\lambda_1, \lambda_2)$ is the bispectral radiance factor for excitation wavelength λ_1 and emission wavelength λ_2.

For a monochromatic/polychromatic configuration, we cannot obtain spectrally resolved measurements of the fluorescence. Hence, the measured spectra cannot be used for colorimetric purposes [3]. What we can measure is the total fluorescence as a function of excitation wavelength, provided that we can separate the fluorescence from the reflected light. The fluorescent component is in our case given by:

$$\beta_L^*(\lambda_1) = \int_{\lambda_2} b(\lambda_1, \lambda_2) d\lambda_2 \tag{3}$$

where the excitation wavelength λ_1 is the wavelength of the monochromatic incident light. The integration is performed over the emission wavelengths λ_2 of the fluorophore, which in our case corresponds to polychromatic detection conditions. (In a real measurement situation, the spectral response $\Re(\lambda)$ of the detector must also be taken into account.) The total radiance factor measured is thus given by:

$$\beta_T^*(\lambda_1) = \beta_R(\lambda_1) + \beta_L^*(\lambda_1) \tag{4}$$

where the usage of λ_1 and superscript (*) denotes that we are measuring the total radiance factor as a function of excitation wavelength and that the entire fluorescence emission is included, in difference to the radiance factors defined in Eqs. (1) and (2).

After measuring the total radiance factor $\beta_{\mathrm{T}}^*(\lambda_1)$, the fluorescent component β_{L}^* was measured by equipping the detector with a UV-blocking filter. Finally, the reflected radiance factor was obtained by subtracting the luminescent radiance factor from the total radiance factor. The samples were measured for a range of excitation wavelengths and the angular dependency of the radiance factors was studied as well as the influence of filler and FWA on the anisotropy.

Material

The paper samples were produced on a small-scale experimental paper machine (XPM) at MoRe Research AB, Sweden, using a chemical pulp blend of 25% softwood and 75% hardwood fibers, sulphate-bleached at ISO-brightness of 90. Precipitated calcium carbonate (PCC) was used as filler and Percol (0.01%) and Bentonit (0.05%) as retention agents. The FWA, tetrasulpho Blankophor-P01, was added in three different levels, see table 1. However, the actual amount of FWA in the final paper might differ from the amounts fed into the process due to varying retention.

Table 1. Paper samples used in the study

Sample	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
FWA [%]	0.0	0.6	0.9	1.8	0.0	0.0	1.8	1.8
Filler [%]	0	0	0	0	15	30	15	30

All the samples used in this study have the same basis weight of 80 $\mathrm{g/m^2}$. No surface treatment was performed on the samples to maintain a high surface roughness, thereby reducing first surface reflections.

Measurements

The samples were measured with a spectral goniophotometer, Perkin Elmer Lambda 1050, equipped with ARTA goniophotometer accessory from OMT Solutions BV. The sample was illuminated with monochromatic light incident at an angle of 45° relative the surface normal of the sample. For the visible and IR part of the spectra, the light source is a tungsten halogen light bulb, whereas a deuterium lamp is used for the UV range. The switching point between the two illuminations was set to 340 nm. Monochromatic light is obtained by letting the light pass through double holographic grating monochromators and into the sample compartment via a system of mirrors. The sample is placed in on a motorized rotation stage, and the angle of the incident light relative the normal of the sample surface is varied by rotating the sample, see fig 1. The reflected light is detected with an integrating sphere detector, with a diameter of 60 mm and equipped with a photomultiplier tube for UV/VIS and an InGaAs detector for NIR. The sphere is mounted on a second motorized rotation stage, allowing the detector to be positioned at any angle relative the normal of the sample surface, except for ±10°in proximity to the light source. The distance between the sample surface and the aperture of the integrating sphere is 91 mm. Measurements were carried out using excitation wavelengths in the range 280 to 440 nm in steps of 5 nm. The size of the illuminated area was 5 x 8 mm at normal incidence, and the solid angle subtended by the detector when viewed from the sample plane was $0.025\mathrm{sr}^{-1}$. This solid angle can be varied

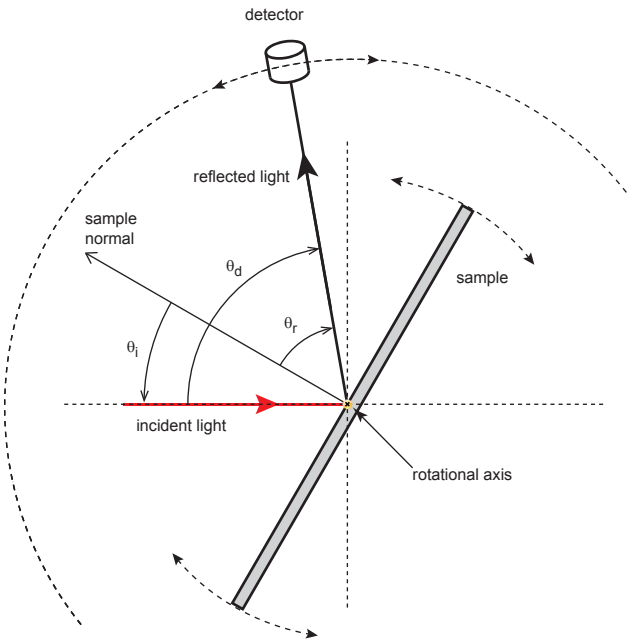

Figure 1. *Defining angles in goniophotometric measurement*

by adjusting the width of the detector aperture, which was set to 12.7 mm for, corresponding to a polar acceptance angle of 7.7°. Reducing the size of the illuminated spot would allow a smaller detector aperture to be used while still capturing the entire illuminated spot, and result in a higher angular resolution of the measurements. This would, however, result in worse signal-to-noise ratio, insufficient for measurements on matte samples.

The reflected light was measured at polar angles ranging from -20°to +75°, in steps of 5°. The measurements were carried out for both s- and p-polarized incident light, and the average of these measurements were taken to represent unpolarized illumination. All measurements were confined to the plane of incidence, i.e. the plane defined by the incident beam and the normal to the surface, and performed on the top sheet of an opaque pile of paper sample sheets.

In order to filter out the fluorescence from the total radiation, an UV-blocking filter, Hoya HMC UV(0) was attached to the detector. This enables angularly, but not spectrally resolved measurements of the total fluorescence for different excitation wavelengths. The transmittance of the UV-blocking filter was measured and is shown in figure 2.

The fact that the absorption band and emission band of the FWA overlap limits the number of suitable excitation wavelengths. In addition to this, the characteristics of the UV filter put further restrictions to the number of suitable excitation wavelengths. From Coppels bispectrometer measurements of the emission spectra of the FWA [6] we see that the emission at wavelengths below 400 nm is very small. As the passband of the UV filter used stretches down below 400 nm, see figure 2, the major part of the emitted fluorescence is captured.

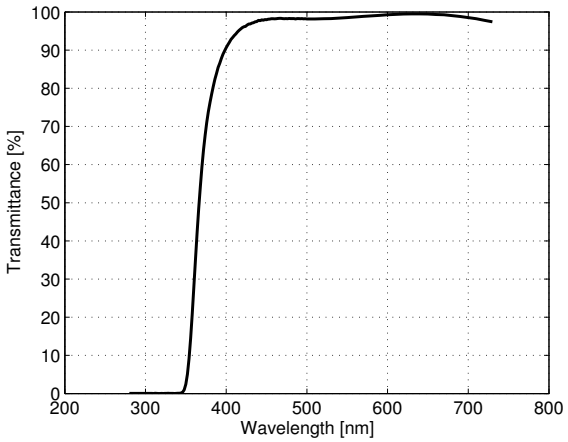

Figure 2. *Measured transmittance of UV-filter, Hoya HMC UV(0)*

The goniophotometer is a double-beam instrument, were a reference beam is lead directly to the detector, allowing simultaneous determination of both the incident and reflected power (or flux) [watts]. The output signal V (voltage) from the detector is related to the detected power according to:

$$V = \int_{\lambda} \Re(\lambda)\Phi(\lambda)d\lambda \tag{5}$$

where $\Re(\lambda)$ is the responsivity of the detector. Even when using monochromatic incident light, integration is still carried out due to the finite spectral bandwidth of the monochromator.
Treating the light as truly monochromatic with a wavelength λ_1, the measurement signal can be written as:

$$V(\lambda_1) = \Phi(\lambda_1)\Re(\lambda_1) \tag{6}$$

In the absence of fluorescence, when there is no wavelength shift between the incident and reflected flux, the responsivity factors cancel each other out and the reflectance is given by:

$$\frac{\Phi_R}{\Phi_I} = \frac{V_R \cdot \Re(\lambda_1)}{V_I \cdot \Re(\lambda_1)} = \frac{V_R}{V_I} \tag{7}$$

The measured quantity is then the ratio of the reflected and incident power Φ_r/Φ_i, which makes it possible to carry out absolute bidirectional reflectance measurements. The reflectance was converted to radiance factor via the bidirectional reflectance distribution function (BRDF), defined by Nicodemus et al. [17] as:

$$f_r(\theta_i, \phi_i, \theta_r, \phi_r, \lambda) = \frac{dL_r(\theta_i, \phi_i, \theta_r, \phi_r, \lambda)}{dE_i(\theta_i, \phi_i, \lambda)} \tag{8}$$

where $\mathrm{dL_r}(\theta_\mathrm{i}, \phi_\mathrm{i}, \theta_\mathrm{r}, \phi_\mathrm{r}, \lambda)$ is the reflected radiance in the direction $(\theta_\mathrm{r}, \phi_\mathrm{r})$ and $\mathrm{dE_i}(\theta_\mathrm{i}, \phi_\mathrm{i}, \lambda)$ is the irradiance from the direction $(\theta_\mathrm{i}, \phi_\mathrm{i})$. The defining angles used in bidirectional measurements are illustrated in figure 3. The detector aperture was set large enough to cover the entire illuminated spot. With this measurement situation, it can be shown that the BRDF can be calculated from the measured reflectance $\Phi_\mathrm{R}/\Phi_\mathrm{I}$ according to:

$$f_r(\lambda) = \frac{\Phi_R(\lambda)}{\Phi_I(\lambda)} \cdot \frac{1}{\omega_r \cos\theta_r} \tag{9}$$

where ω_r is the detection solid angle and the directional dependence has been omitted for clarity. The differential quantities have been replaced by their finite counterparts, which is inevitable in real measurement situations.

The spectral reflected radiance factor is related to the BRDF according to:

$$\beta_R(\lambda) = \pi \cdot f_r(\lambda) = \frac{V_R(\lambda)}{V_I(\lambda)} \cdot \frac{\pi}{\omega_r \cos\theta_r} \tag{10}$$

using Eq. (7) and that the BRDF of the perfect reflecting diffuser (PRD) is equal to $1/\pi$.

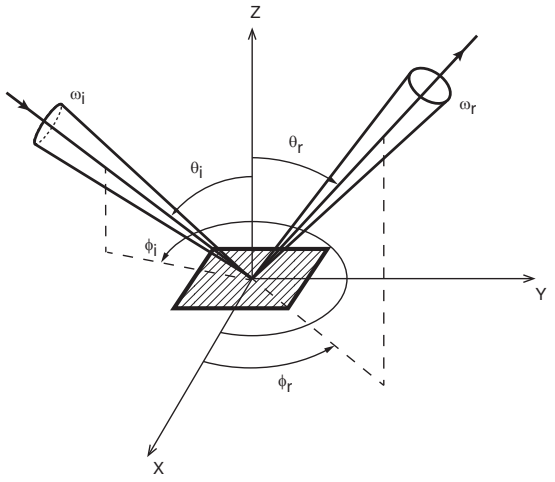

Figure 3. *Defining angles for bidirectional reflectance*

For fluorescent samples, the responsivity of the detector must be taken into account. The measurement signal for the total radiance V_T, and total fluorescence V_L are given by:

$$V_T = \int_\lambda \Phi_T(\lambda)\Re(\lambda)\,\mathrm{d}\lambda \tag{11}$$

$$V_L = \int_\lambda \Phi_T(\lambda)\Re(\lambda)\Psi(\lambda)\,\mathrm{d}\lambda \tag{12}$$

where $\Phi_T(\lambda)$ is the spectral total radiance, and $\Psi(\lambda)$ is the transfer function of the UV-blocking filter. Inserting Eqs. (11) and (12) in Eq. (10), we get the following expressions for the measured total and luminescent radiance factors:

$$\beta_T^*(\lambda_1) = \frac{\int_\lambda \Phi_T(\lambda)\Re(\lambda)\mathrm{d}\lambda}{\Phi_I(\lambda_1)\Re(\lambda_1)} \cdot \frac{\pi}{\omega_r \cos\theta_r} \tag{13}$$

$$\beta_L^*(\lambda_1) = \frac{\int_\lambda \Phi_T(\lambda)\Re(\lambda)\Psi(\lambda)\,\mathrm{d}\lambda}{\Phi_I(\lambda_1)\Re(\lambda_1)} \cdot \frac{\pi}{\omega_r \cos\theta_r} \tag{14}$$

Radiance factor is per definition determined for infinitesimal solid angles. The detector solid angle of 0.025 sr^{-1} used here is relatively large. However, the measured radiance factors are still regarded as good representatives of the true radiance factor, since the uncoated, matte samples are not expected to exhibit any dramatic changes in reflectance over the angular range covered by the aperture.

Results

Figure 4 shows the luminescent radiance factor measured at 0° for samples with three different levels of FWA content. The results are in agreement with the absorption coefficient measurements carried out by Coppel [6] on the same set of samples. Figures 5-7 shows the total, luminescent and reflected radiance

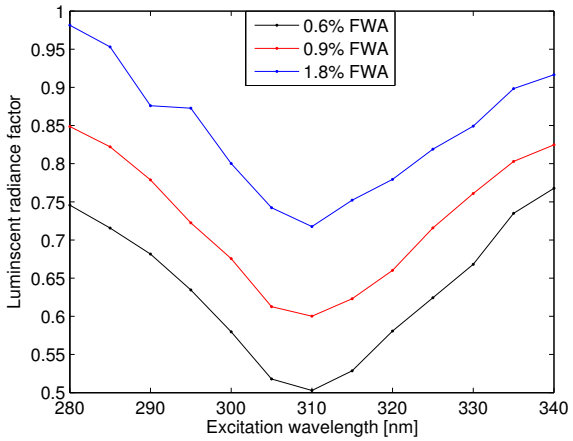

Figure 4. *Luminescent radiance factor at viewing angle 0° and illumination angle 45°.*

factors for samples having different levels of FWA for an excitation wavelength of 320nm. The results show that the luminescent radiance factor (the effect from FWA) is fairly isotropic in comparison to the reflected radiance factor which displays a significant forward scattering effect. As a reference, the PRD would have a radiance factor equal to 1 for all viewing angles.

Figures 8-10 shows the total, luminescent and reflected radiance

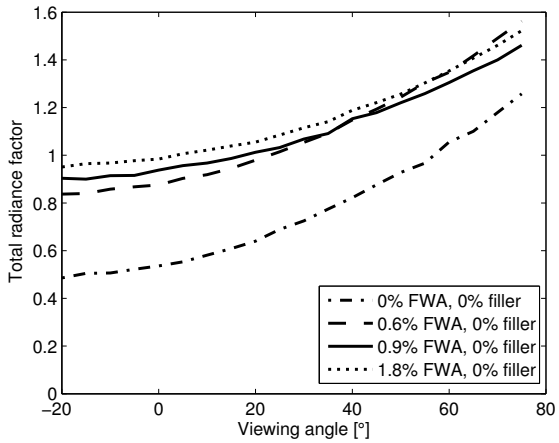

Figure 5. *Total radiance factor at excitation wavelength 320 nm and illumination angle 45°.*

factors for samples having two levels of FWA and three levels of filler content for an excitation wavelength of 320nm. The results once again show that the luminescent radiance factor (the effect from FWA) is fairly isotropic in comparison to the reflected radiance factor which displays a significant forward scattering effect.

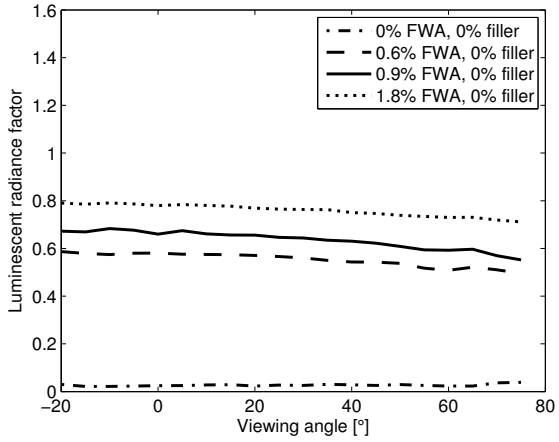

Figure 6. *Luminescent radiance factor at excitation wavelength 320 nm and illumination angle 45°.*

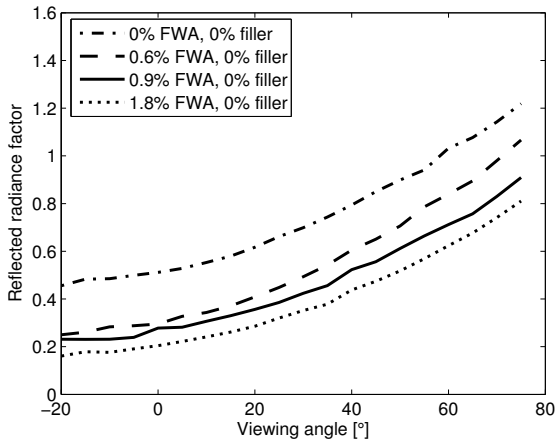

Figure 7. *Reflected radiance factor at excitation wavelength 320 nm and illumination angle 45°.*

In figure 8, it can be observed that the anisotropy of the total radiance factor decreases with increasing filler content, regardless of FWA content. However, when FWA is present, the angular dependence of the total radiance factor for different filler contents is altered.

Discussion

The results shows that for the uncoated papers used in this study, the fluorescence display an isotropic behavior while the reflectance from these papers displays a significant forward scattering as earlier reported by [13]. As a consequence of this, the total anisotropy of the papers is reduced when the amount of FWA is increased. Moreover, figure 9 shows that with an increasing addition of filler to the paper, the luminescent radiance factor is reduced for a constant FWA content. A plausible explanation to this observation could be that the filler is screening the FWA from part of the UV radiation due to increased scattering. This assumption is further strengthened by figure 10 where the reflected radiance increases with an increasing amount of fillers.

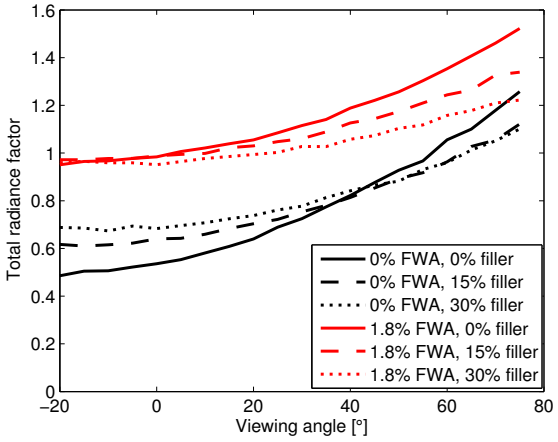

Figure 8. *Total radiance factor at excitation wavelength 320 nm and illumination angle 45°for samples with different amount of filler.*

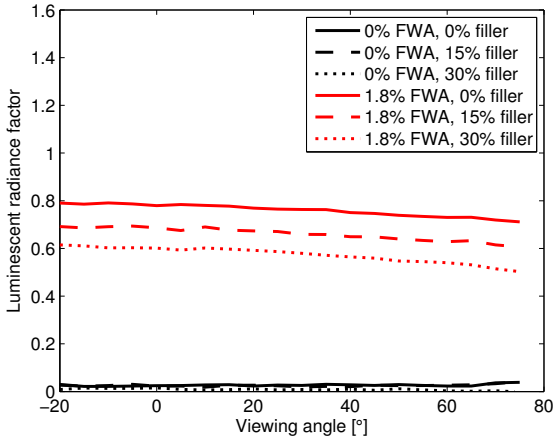

Figure 9. *Luminescent radiance factor at excitation wavelength 320 nm and illumination angle 45°for samples with different amount of filler.*

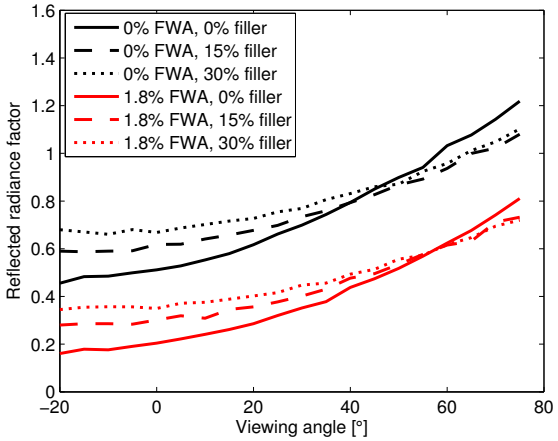

Figure 10. *Reflected radiance factor at excitation wavelength 320 nm and illumination angle 45°for samples with different amount of filler.*

In addition, the reflected radiance displays a more isotropic behavior with increasing amount of fillers. The same behavior can also be observed for the total radiance factor in figure 8.

In the manufacturing of the paper samples, the FWA was added to the stock. In commercial paper production, it is common practice to add the major part of the FWA (tetrasulpho) to the surface of the paper. It should be pointed out that when using tetrasulpho in the surface layers and stock, total levels above 1.0% FWA content are rarely used in the production of commercial papers, neither are filler contents of 30%. A final remark regarding the samples used here is that the effect of the FWA might also been reduced due to aging, however all samples were manufactured at the same occasion and stored under the same conditions.

As an extension of the work carried out here we plan to include paper samples where FWA is added to the top layer only or coated samples having FWA only in the coating, thus using paper samples that better resembles commercial printing papers of other type than office grades. Furthermore, the measurement setup could be further improved with a set of narrowband filters which could be utilized to resolve the spectral characteristics of the fluorescent emission.

Conclusions

The results show that in comparison to the anisotropy of the total radiance factor from uncoated paper samples, the anisotropy of the fluorescence alone is negligible. Hence, for paper samples containing FWA evenly distributed in the bulk, the fluorescence should not induce significant differences between color measuring instruments of different measurement geometries.

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