EXPLORING MYTHS OF MEASURED AND PERCEIVED WHITENESS

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Abstract

Fluorescent Whitening Agents (FWA), dyes and colored pigments are used extensively in the paper industry to enhance the appearance and optical performance of coated and uncoated papers. There are several different systems in use for the description and specification of color and optical properties of paper. CIE and TAPPI are the most commonly used color systems in the paper industry. In this study, three different colorants (blue, black and red), and a FWA were added into a coating formulation at three to five addition levels. Coated LWC papers were measured for their optical properties with two different spectrophotometers and a brightness meter. The CIE whiteness formulation (1986) was analyzed on slightly colored papers.

Introduction

Other than physical properties of a paper, its appearance is most important, especially to the printer and to the final reader. Today, many free sheet and groundwood containing offset, gravure, and ink jet grades contain FWAs.[1,2] Appearance is also important in several other paper grades such as tissue papers. For this reason, there have been many efforts to produce paper with high whiteness levels. The bleaching of pulp and addition of fillers into the paper serve to increase the whiteness of papers. However, their contribution to whiteness and/or brightness of the paper and paperboard is limited due to strength and porosity issues. Highly apparent white papers can only be achieved with the application of a pigmented coating and proper usage of FWAs.[3]

Whiteness and brightness are manifestations of optical properties, and they cannot be measured directly. Evaluation of whiteness in terms of its visual wavelengths can be made by visual appearance or by instrumental measurements. Only the physical property, the spectral reflectance of a sample can be measured. There are several different systems in use for the description and specification of color and optical properties of paper, using colorimeters, spectrophotometers and brightness meters. CIE whiteness [4] and TAPPI brightness [5] are the most commonly used measurements by the paper industry. Brightness is emphasized more in the Americas, while CIE whiteness is emphasized more in Europe. However, CIE whiteness, and TAPPI brightness are fundamentally different concepts and the use of TAPPI brightness to qualify papers may lead to misleading assessments of optical properties of papers that contain dyes and/or FWAs. Likewise, CIE whiteness may give a different impression of relative whiteness of two samples relative to what a human observer would conclude.

Additionally, measured spectral reflectance is not a standard fixed quantity [3]. It is influenced by a variety of factors. Geometry of the measurement device, aperture, light source, filters and measurement set up all influence the data that are acquired from an instrument. These factors may differ from one instrument to another. Thus, comparing data from at least two different instruments could be an appropriate approach to enable mills and their customers to have more accurate and reliable data for optical analyses of papers that contain dye or FWA.

Besides the configuration of the measuring device, the base paper may also complicate the usefulness of the measurement techniques and interpretation of the optical data. This is especially true for LWC (Light Weight Coated Paper) papers that contain large amounts of mechanical pulp. The high amounts of lignin present in this grade cause the product to age rapidly, which results in the yellowing of the paper with time [6]. LWC papers may also exhibit differing properties and different shades of colors from one manufacturer to another, depending on the wood species, proportions of the wood species, and the ratio of mechanical pulp to chemical pulp used in the production of the base paper. Generally speaking, papers containing high amounts of lignin, mechanical pulp or wood containing fibers, influence the optical properties of the applied coating more than for wood free papers. All these factors make the development of a standard optical measurement method for this grade very difficult. As a result, there has not been, until recently, a SWOP (Specifications for Web Offset Publications) [7] standard adopted for this grade [8]. For this reason, an LWC grade paper was selected for this study. The work herein was performed to better understand the difficulties and complications faced when trying to perform brightness and whiteness measurements on these papers in an attempt to meet the commercial specifications of the printer. In the process, some of the myths associated with interpreting brightness and whiteness of paper by the various methods were explored.

Technical Considerations

When light strikes an object, it may be transmitted, scattered, reflected, or absorbed and all these may occur separately or in combination [9]. The object appears white if it totally reflects the light, and scatters diffusively at all wavelengths of the visible spectrum [9,10]. The object appears colored if some wavelengths of the light are reflected, while the others are absorbed [9]. It is black if the object absorbs all the wavelengths of the light in the visible spectrum [1,11]. By another definition, white is the achromatic object color of greatest lightness, characteristically perceived to belong to objects that reflect diffusely nearly all the incident energy throughout the visible spectrum.[2,9,12] In general, all objects absorb illuminating light energy to some degree. The color white, as with any color, can be interpreted in a threedimensional color space [13]. For example, it can be described by hue, saturation and lightness [11]. The color white is distinguished by its high lightness, its very low (ideally zero) saturation, and it is felt to be more attractive with a bluish cast rather than yellowish cast.[10,14,15] Depending on the hues of whites, the perception may differ. For example, an object with a bluish cast will be perceived whiter than an object that has a yellow cast, where saturation and lightness are the same for both objects.[10,11,15]

1. Whiteness vs. TAPPI Brightness: Whiteness and brightness are sometimes used interchangeably, when comparing the relative whiteness of different papers or when defining how white a specific paper is. However, while these two terms are related, their scientific definitions differ (3,10,16**.** Papers having the same degree of brightness or whiteness, in fact, may differ greatly in visual appearance.[1,3]

TAPPI brightness is based on the filter chosen to measure the reflectance of the pulp in the region most sensitive to the effects of bleaching [1]. Whiteness of paper is determined by the reflectance of a paper's surface for all wavelengths of the visible spectrum. Brightness of paper is measured, typically, by comparing the amount of light, of a prescribed single wavelength (457 nm) in the blue region of the spectrum, reflected by a pad of that paper to the amount that is reflected by an arbitrary standard having a 100 reflectance at this same wavelength. The method is defined by TAPPI method T452 [5]. The selected standard is magnesium carbonate. This method states that this procedure is applicable to all naturally colored pulps, papers and paperboard. The TAPPI brightness measurement can be deceptive when papers containing dyes or FWAs are optically evaluated, because the TAPPI brightness measurement technique ignores most of the visible light spectrum. One example of this is papers that contain FWAs. Modern papers containing FWAs, tinting dyes and inks cannot be properly evaluated by a simple assessment in the blue region of the visible light spectrum.[14] Thus, brightness is not a complete description of the visual appearance of the paper.[16] CIE whiteness [4], on the other hand, includes contributions from all wavelengths, but with a complicated weighting system. As we shall see, CIE whiteness is not always a good measure of perceived whiteness, either. In particular, it gives an even higher weight to the blue region than brightness values. As stated above, blue is preferred to yellow at the same saturation, but not to the degree included in the CIE whiteness formula. In fact, the CIE whiteness measure can assign very high whiteness to very colored samples.[17]

For these reasons, the TAPPI brightness measurement method should only be used for comparing undyed and FWA free sheets, where the brightness measured depends only on the degree of blue light absorbed or reflected by the paper or coating.[11] Assessment by the TAPPI method generally functions very well only if the reflectance properties of the papers to be compared are similar.[14]

2. Whiteness Evaluation: Whiteness can be evaluated both visually and instrumentally.[11] However, neither color nor white can be measured directly. Only the physical property, the spectral reflectance, of a sample can be measured. Instrumental characterization of whiteness is made in two steps. First, reflectance spectra are measured. Then, whiteness assessments are developed through some type of graphical or numerical manipulation of the data.[3,12] Measured spectral reflectance is not a standard fixed quantity. It is influenced by the characteristics of the measurement device. The full geometry of the illuminating chamber is incorporated in the measuring results. Other factors that influence the reflectance spectra are the size of the aperture, and whether gloss is excluded or included in the measurements [11]. For this reason, not all the instruments used today give identical results. Different light sources and different filters give different and subjective assessments.[2] Therefore, sometimes comparing data from two different instruments could be an appropriate approach.

Accurate data are obtained if the incident light is strictly controlled. For this reason, special instrument design and calibration, and illuminant adaptation is required when measuring paper that contains FWAs.[1,2] Both the selection and the quantity of illuminating light is very important when instrumental evaluation of whiteness on FWA containing papers is to be made, since FWAs are only excited by UV energy. Illuminating light should match as closely as possible to the energy distribution of a daylight standard, e.g. D_{65}, both in the visible and ultraviolet spectrum. An appropriate whiteness measurement for measuring dyed or optically whitened papers should include: a) a reproducible ultraviolet rich light source like a Xenon arc lamp. [This kind of a light source is closely matched with the daylight D_{65} standard, both in UV and in the visible regions of the spectrum.] b) Software or absorbing filters to enable calibrating the UV portion of the illuminant to a constant value, c) a reverse optical system that prevents absorption of the UV and enables light from the source to reflect on the sheet before it is focused on the detector, d) a detector that measures the whole visible spectrum (400-700 nm) with at least 20 nm accuracy, e) proper software to calculate various whiteness values from measured tristimulus values [8,18]. The most effective method to measure optical properties of a FWA containing paper is with a xenon lamp, because the radiance of xenon is similar to the energy spectrum of a reference illuminant (D_{65}). Another advantage of xenon light source is that it has a relatively uniform, high-energy emission.[1,19]

Griesser, R. [20] proposed in his earlier study that the CIE whiteness formula can be significantly improved if the sample illumination is stabilized and fitted as close as possible to a desired standard illuminant. He added, in addition to illumination stabilization, the formula can also be greatly improved if the different measurement instruments are matched through adapting formula parameters specific to the instrument used. Following his proposal, Griesser made an extensive study using seven different measuring instruments and eighty- eight samples of different properties. He showed that, along with adjustment of sample illumination to a given standard to standardize the whiteness values of different measurement instrument constructions and illuminations, matching formula parameters greatly improves the whiteness assessments. This study, however, separates itself from Griesser's work by its nature. The objectives of this study were entirely different. In this study, it was aimed to further explore whiteness formulas within their contexts, investigate the correlation between the formulas and perceived appearance and the instrument effect on the formulas. This includes the construction of the instruments and illumination.

Experimental Procedures

A coating suitable for a LWC rotogravure printed-paper grade was prepared according to the formulation outlined in Table 1. The coatings consisted mostly of delaminated clay and SBR latex, and contained smaller amounts of calcined clay, TiO_2, plastic pigment, calcium stearate lubricant, and ammonium zirconium carbonate crosslinker. For the coatings containing FWA, the TiO_2 was replaced with the same volume of plastic pigment, since TiO_2 adversely influences FWA's UV absorbance and thus its whitening performance.[3,20] Three different dyes [blue (Ciba-Pergasol Blue PTD), black (Ciba-Pergasol Black LVC) and red (Ciba-Pergasol Red 2B)] were added into the coating at three different addition levels.

Table 1. Coating formulation used in the experiments. (See Appendix A for supplier information).

Coating Ingredient	Parts (dry)
Delaminated Clay	80
Calcined Clay	8
TiO_2	4
Plastic Pigment	8
SB Latex	6.5
SB Latex	1.5
Calcium Stearate	1

In order to determine the appropriate dye addition levels needed to shift the tint of the papers around in the color space, preliminary studies were made in which the dye levels added to the applied coatings were varied and measurements made on a Micro S4-M brightness meter, and datacolor Spectraflash and GretagMacbeth spectrophotometers. Dye levels that exhibited distinctive tint differences were selected for further studies. The resulting red and black dye addition levels selected for instrumental and observer evaluations were 0.1, 0.3, and 0.6 % in dry pigment weight. The selected final blue dye addition levels were 0.25, 0.05, and 0.8 % in dry pigment weight.

The same methodology was followed for the selection of fluorescent brightening agent, FWA (Bayer-Blankophor liquid P150). The selected six FWA addition levels ranged from 0.24 to 1.95% FWA on weight of dry pigment. The tinted and FWA containing coatings were applied at 6 $g/m^2$to a commercially produced base paper made from bleached Kraft and mechanical pulp (35 g/m^2 basis weight, 70 brightness) using a CLC (Cylindrical Laboratory Coater). This enabled the influence of the basesheet on coating performance of the LWC paper to be studied**.** Additional studies at higher coat weights were also performed.

The resulting LWC papers were measured for their optical properties with datacolor Spectraflash and GretagMacbeth Spectrolino spectrophotometers and a Micro S4-M brightimeter. Calculated CIE [4], Hunter [9,22] and Ganz [23,24] whiteness values and measured TAPPI brightness [5] values were compared. The CIEXYZ [25] and CIELab [26] color measurement systems for the spectrophotometers and TAPPI T452 standard for the brightness meter were used for this purpose. Coated papers were also evaluated for their optical appearance by 25 randomly selected observers. Tinted and FWA added samples were separated into four groups for the observer evaluations. Three of the four sample groups were the tinted papers with 3 addition levels of blue, black and red dyes. The last sample group was the FWA added group at 6 addition levels. Observers were asked to rank each sample group separately for their perceived whiteness in a 5000 K light booth. Samples that appeared as the whitest within the same group were ranked as extraordinary white. Samples that appeared the least white within that group were ranked as poor in whiteness by the observers. Observers were allowed to give the same rank to the samples that appeared equally white to the observers.

Results and Discussion

Preliminary results of this work were presented elsewhere [27]. Figures 1 and 2 show the color spectra of coated lightweight paper and the coated papers, where blue, black and red dyes and FWA were added into the coating. The spectral curves were acquired by a datacolor Spectraflash Spectrophotometer and a GretagMacbeth Spectrolino Spectrophotometer, respectively. Addition levels were 0.50% for blue (on dry pigment weight), 0.3% for red, and 0.3% for black, and 1.485 pph (dry/dry) % for FWA, where 1 pph PVOH as a FWA carrier was also included in the coating. Spectral curves for each dye with the two spectrophotometers were similar, as expected.

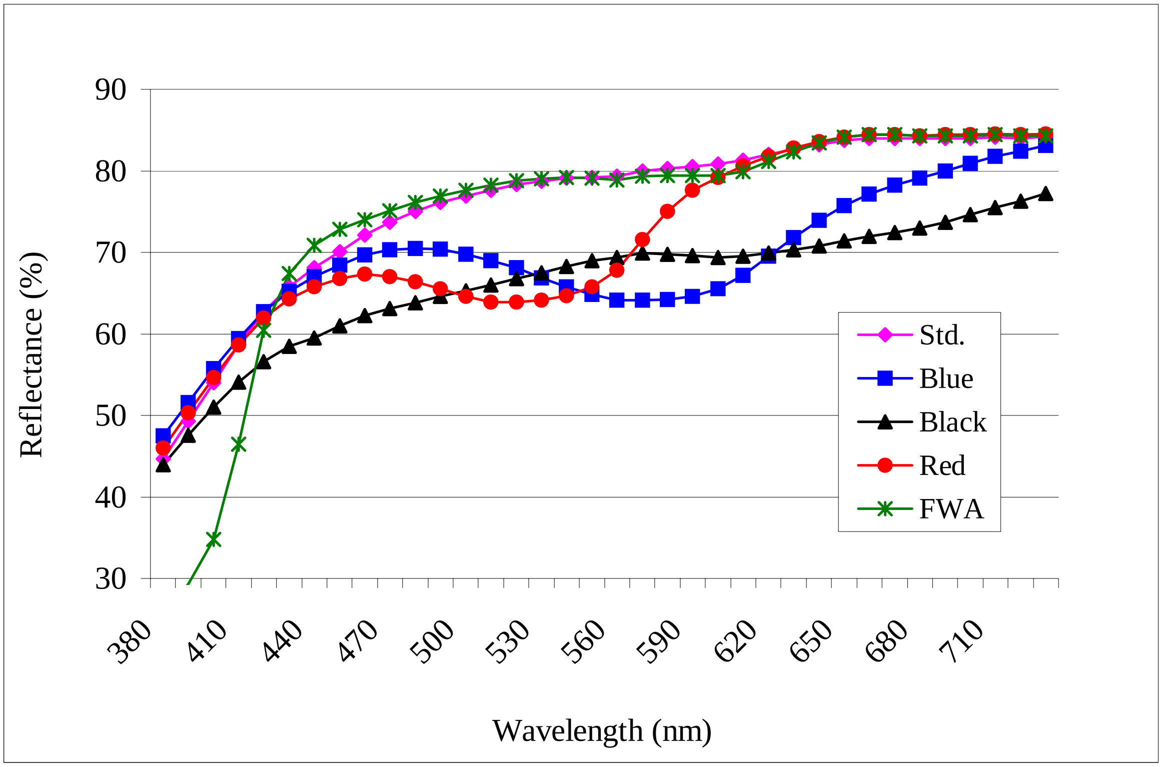

Figure 1: Color spectra of coated paper, blue, black and red dyes and FWA acquired from the datacolor Spectraflash Spectrophotometer.

As can be seen from these figures, blue dye absorbs heavily in the middle of the spectrum from green-yellow to yellow-orange regions (530-620nm). Red dye absorbs mostly in the green region (490-570 nm). The curve for black dye looks similar to the standard (coated and no dye added), but its curve falls in the lower reflectance percent scale. FWA absorbs UV light as can easily be seen from both of the figures. The apparent reflectance values for FWA are higher than any dye and the standard in the blue region (420-470 nm), suggesting reemitted UV light in the blue region by the FWA. Thus, it can be said by looking at the spectral curves in the figures, the FWA works as expected for this particular paper and coating system. The peak in the spectra observed with the FWA is smaller than expected and shows one of the current problems with using the current measuring systems for measuring the whiteness and brightness of these papers. Unfortunately, the Illuminant A light source used to illuminate the specimen in most spectrophotometers is inadequate to excite the FWA present in the coating layer, because of its very low intensity in the UV. These results in the observation of only a small peak in the spectra at the 425 nm wavelength by the instrument that does not replicate what a viewer under daylight conditions would observe. As stated above, a Xenon light source would be a better choice for measuring the effects of human observation of FWA whitened paper.

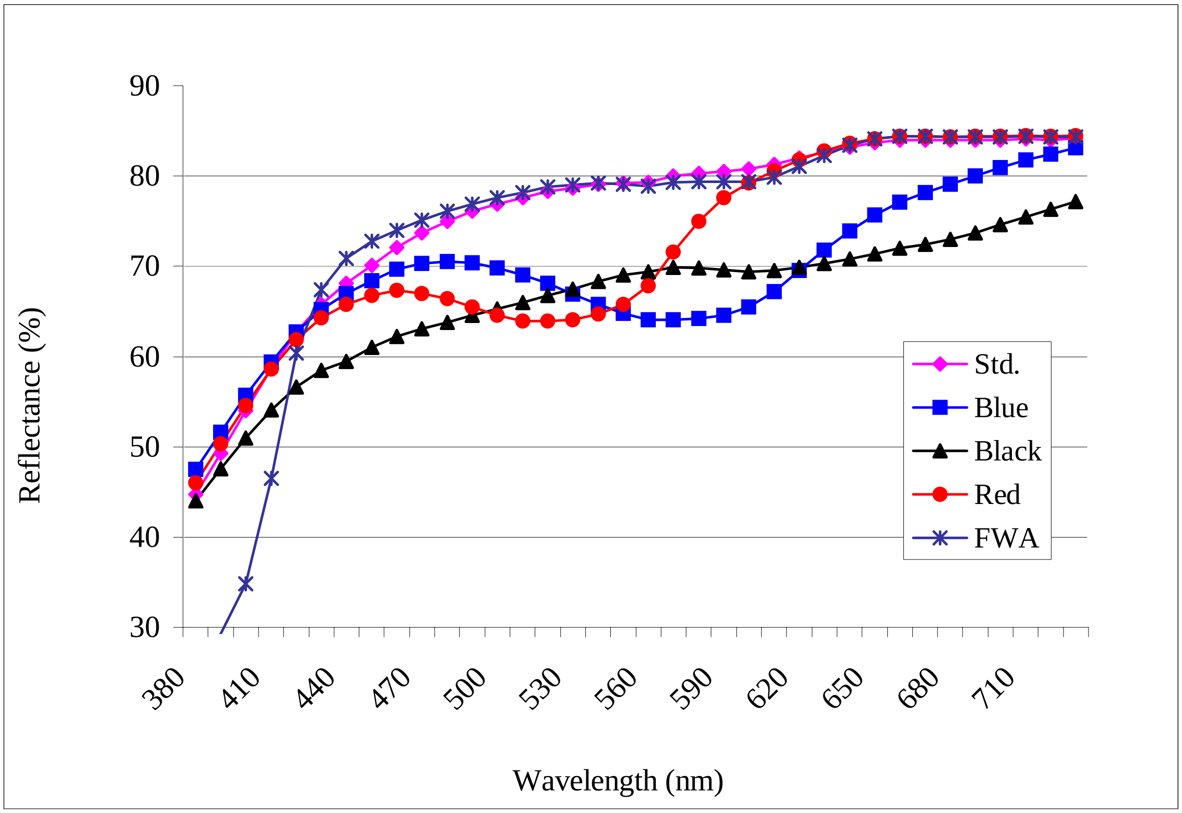

Figure 2: Color spectra of coated paper, blue, black and red dyes and FWA acquired from the GretagMacbeth Spectrolino Spectrophotometer.

Figure 3 was obtained by the statistical analyses of 25 randomly selected observers' evaluations of optical appearance of each sample (how white they observed each sample from scale of 0-very little white to 5-extremely white). All of the observations were conducted in a standard D_{50} light booth. The figure shows that only the minimal addition of blue and black dyes (0.25% for blue, 0.1% for black) appeared whiter to the observers. As the added dye level increased, coated samples appeared less and less white.

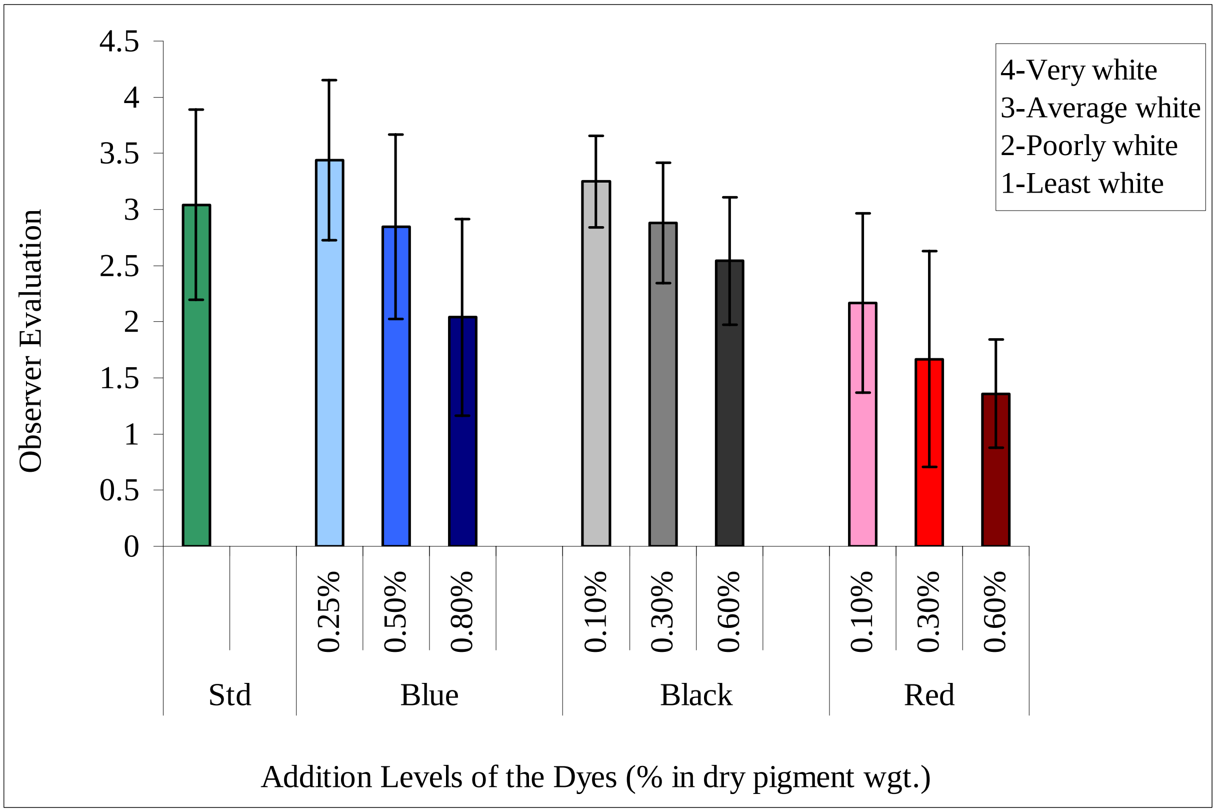

Figure 3: Observer evaluation of coated lightweight papers at varying addition levels of blue, black, and red dyes.

Figure 4 shows the representative CIE whiteness and tristimulus values for blue dye effect.

The CIE whiteness [4] is given by

$$W_{CIE} = Y + 800(x_n - x) + 1700(y_n - y), \qquad (1)$$

where

$$x = X/(X+Y+Z),$$

$$y = Y/(X+Y+Z),$$

$x_n = 0.3138$, and $y_n = 0.3310$ for $D_{65}/10$.

This equation is complemented by the tint equations:

$$T_{CIE2} = 1000(x_n\text{-}x) - 650(y_n\text{-}y), \qquad \text{for a 2 observer} \qquad (2a)$$

or

$$T_{CIE10} = 900(x_n\text{-}x)\text{-}\ 650(y_n\text{-}y), \qquad \text{for a 10 observer} \qquad (2b)$$

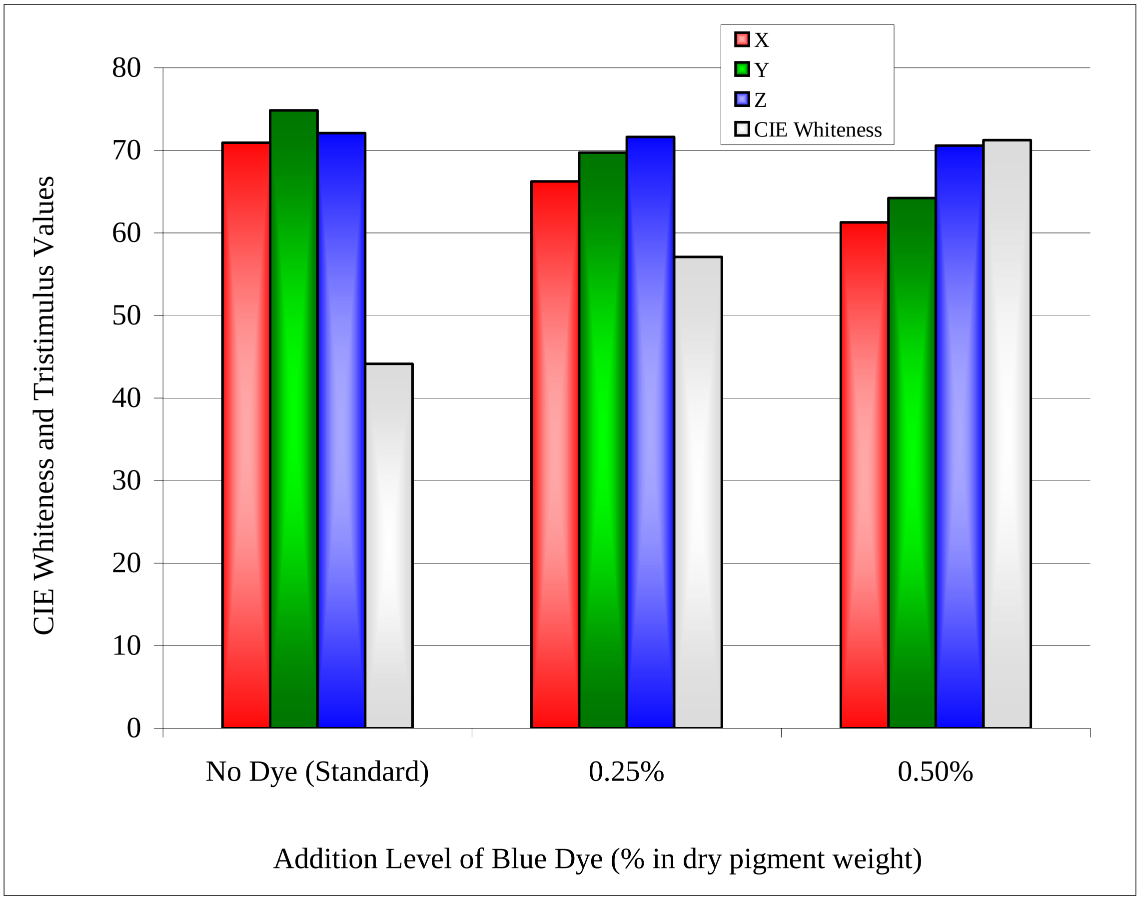

Figure 4: CIE whiteness for blue dye addition tristimulus values on CIE whiteness with the datacolor Spectraflash.

These give tint-values in the red or green direction for the 1931 or 1964 CIE standard observer, respectively. A positive value of T indicates more green and a negative value indicates more red.

According to the specification, this formula should only be used for

$$5Y-280 \quad W_{CIE} \quad 40 \tag{3a}$$

and the tint relation for 10 observer

$$3 > T_{CIE10} > -3 \tag{3b}$$

As can be seen easily and distinctively from the figure, CIE whiteness values calculated from measurements made by the datacolor Spectraflash, increased sharply with small decreases in the tristimulus values (X, Y, Z). CIE whiteness values were largely influenced, even at the smallest addition level of blue dye (0.10% in dry pigment weight). This can be explained by the large multiplication factors that are applied to x and y values in the CIE whiteness formulae (800 for x, 1700 for y). The x, and y values are acquired by the use of calculated tristimulus values. Therefore, calculated CIE whiteness values could be extremely sensitive for colored papers, even if they are slightly colored. The addition level of 0.8% blue dye was not taken into account since the calculated CIE whiteness values were outside the inequality 2a ($5Y-280 = 17.5$, $W = 290.7 > 40$). The tint values were also calculated for each sample. Although calculated tint values were slightly outside the given borders (2b), CIE whiteness results are still reported, because appearance of the samples were judged at least "fairly white" by the observers and Hunter and Ganz whiteness formulas do not specify such restrictions.

The corresponding change in CIE whiteness values, calculated from the measurements made by the GretagMacbeth spectrophotometer, as a function of added blue dye, is shown in Figure 5. The calculated values were similar to the Spectraflash values. Observers indicated that papers coated with coating formulations containing blue dye did not appear whiter or brighter as the blue dye addition level reached 0.5% (in dry pigment weight). On the contrary, they expressed that papers looked less white, less bright and more bluish from that point. This is despite the fact that the W and T values were all within the applicable range of the inequalities (3) for the GretagMacbeth measurements.

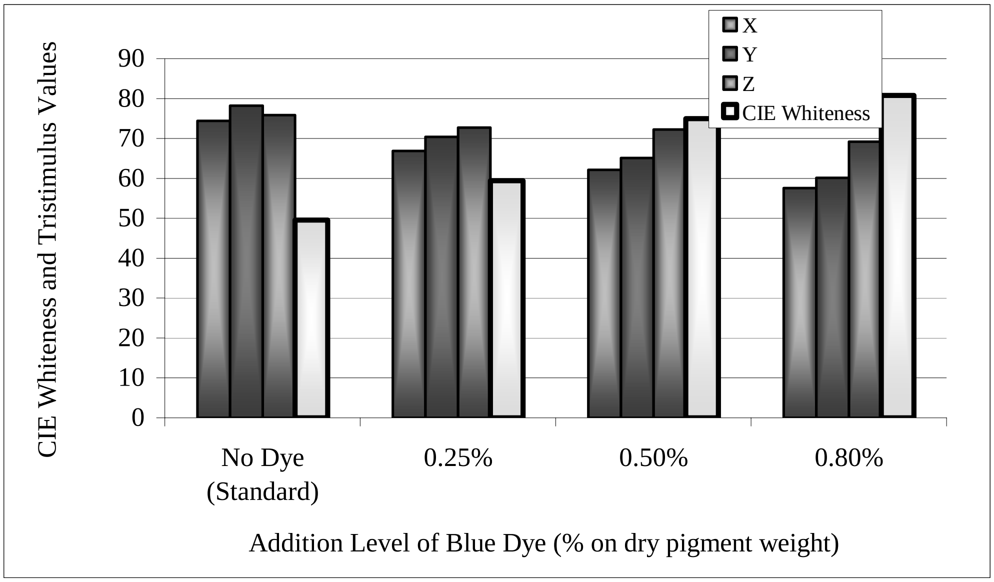

Figure 5: CIE whiteness for blue and influence of tristimulus values on CIE whiteness as measured with the GretagMacbeth spectrophotometer.

Figure 6 shows the influence of added black dye, and tristimulus values on CIE whiteness, obtained by using the datacolor Spectraflash. This figure shows an essentially random distribution of CIE whiteness values, as the amount of added black increases until the highest addition level (0.6%). However, these findings were similar to the observer evaluations that whiteness increased at the minimum addition level of black dye (0.1% on dry pigment weight), but diminishes as the black dye addition level increased.

The CIE whiteness values, obtained by the measurements made by the GretagMacbeth spectrophotometer, as shown in Figure 7, have a slight but essentially constant decreasing rate as the amount of black dye used increased. The two spectrophotometers gave similar readings and the CIE whiteness values calculated from the measured tristimulus values were also close to one another. The observers also agreed that the whiteness of the paper was significantly reduced at the highest addition level. Again, rather small deviations in the tristimulus values caused larger scale changes in the CIE whiteness, because of the aforementioned large coefficients.

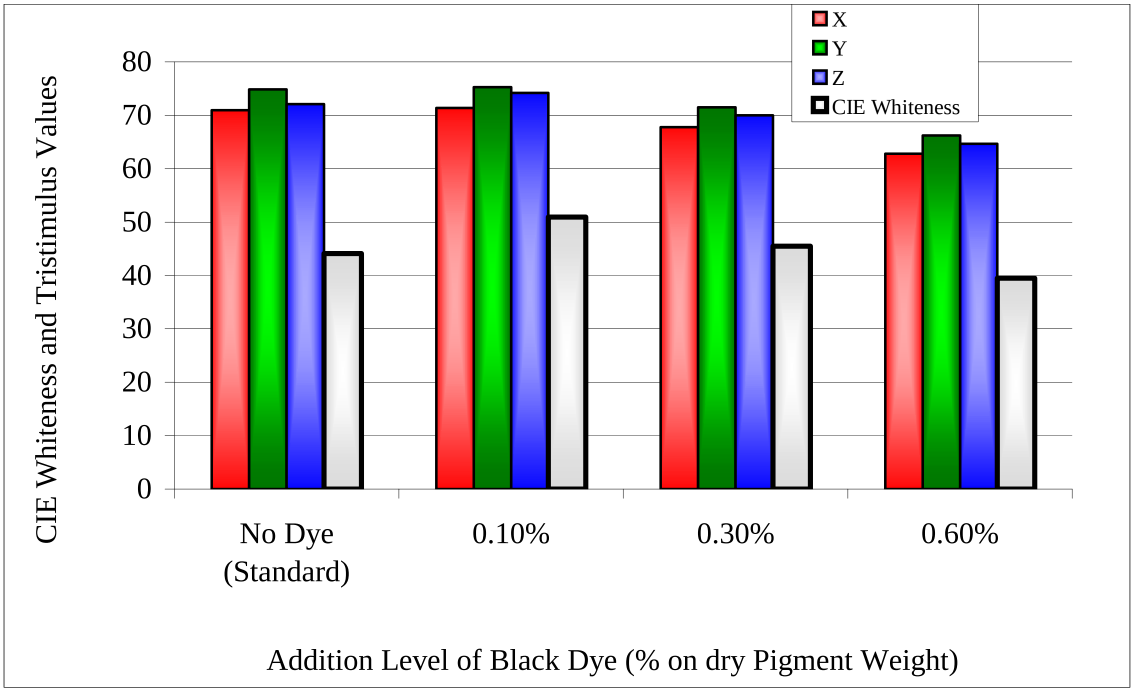

Figure 6:CIE whiteness for black and tristimulus effect on CIE whiteness with the datacolor Spectraflash spectrophotometer.

Figure 8 shows the influence of added red dye, and tristimulus values on CIE whiteness when the measurements were made with the datacolor Spectraflash. Again, small changes in tristimulus values caused significant changes in the CIE whiteness values. What is more striking is that, although the CIE whiteness values increased with increasing amounts of red dye, observers indicated again that the paper appeared reddish rather than whiter or brighter even at the minimum addition amount of red dye (0.1% dry pigment weight). CIE whiteness values were found inappropriate to be measured or calculated at the maximum addition amount (0.8% on dry pigment weight). The same optical measurements were made by the GretagMacbeth spectrophotometer, and the calculated CIE whiteness values along with tristimulus values are shown in Figure 9. CIE whiteness changed little as the addition amount of red dye increased.

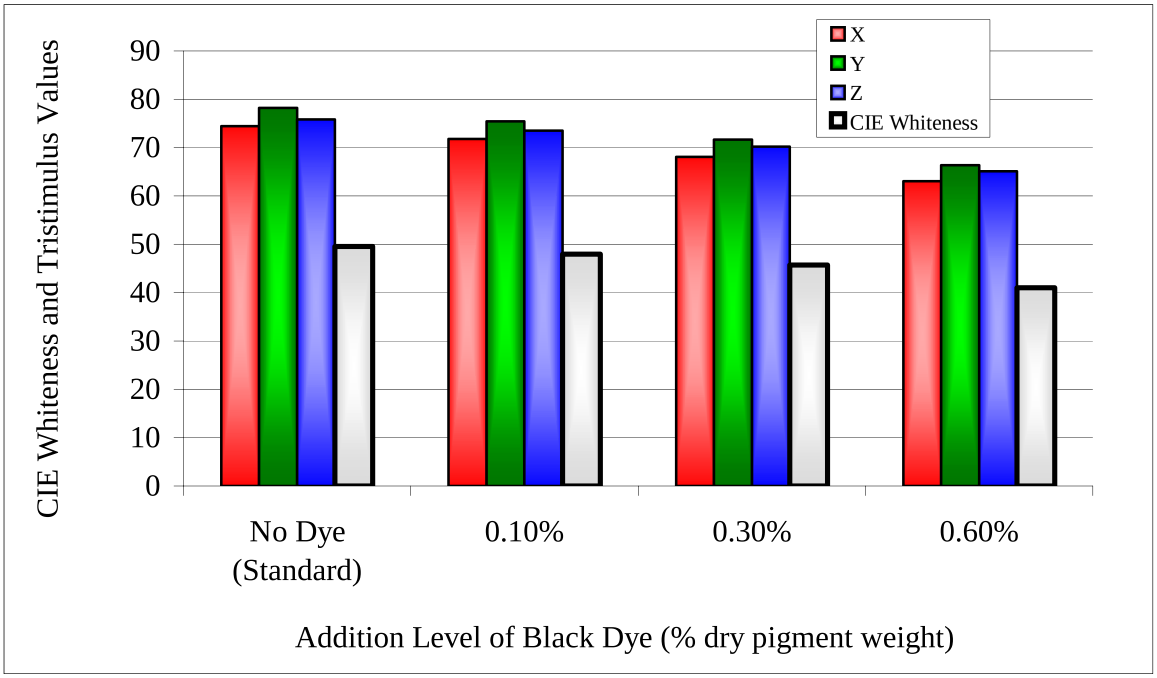

Figure7: CIE whiteness for black dye and tristimulus effect on CIE whiteness with the GretagMacbeth spectrophotometer.

Figure 10 shows the representative TAPPI brightness values for blue, black and red dyes and FWA at different addition levels measured by the Micro S4-M, and CIE, Hunter and Ganz Whitenesses from the datacolor Spectrophotometer. If compared with the CIE whiteness values for each of the colors, it is seen that the measured TAPPI brightness values and the calculated CIE whiteness measurements exhibited different patterns as the added dye amount was increased for each of the three colorants. While TAPPI brightness generally decreased with the increasing addition of each dye, the general trend in the CIE whiteness values is in the opposite direction. That is, CIE whiteness increased with increasing amount of dye in the coating formulation.

The Hunter and Ganz whiteness values for each sample were also calculated and are given in the figure. Expressions for Hunter and Ganz whiteness are given below.

For Hunter Whiteness:

Hunter WI = L- 3b, (4)

where L and b are Hunter values.[9,22]

For Ganz Whiteness

$$W_G = Y + 1869.3(x_n – x) + 3695.2(y_n – y). \qquad (5)$$

The corresponding tint formula is the Ganz Griesser [28] expression

$$T_{GG} = 1001.9(x_n – x) - 748.7(y_n – y). \qquad (6)$$

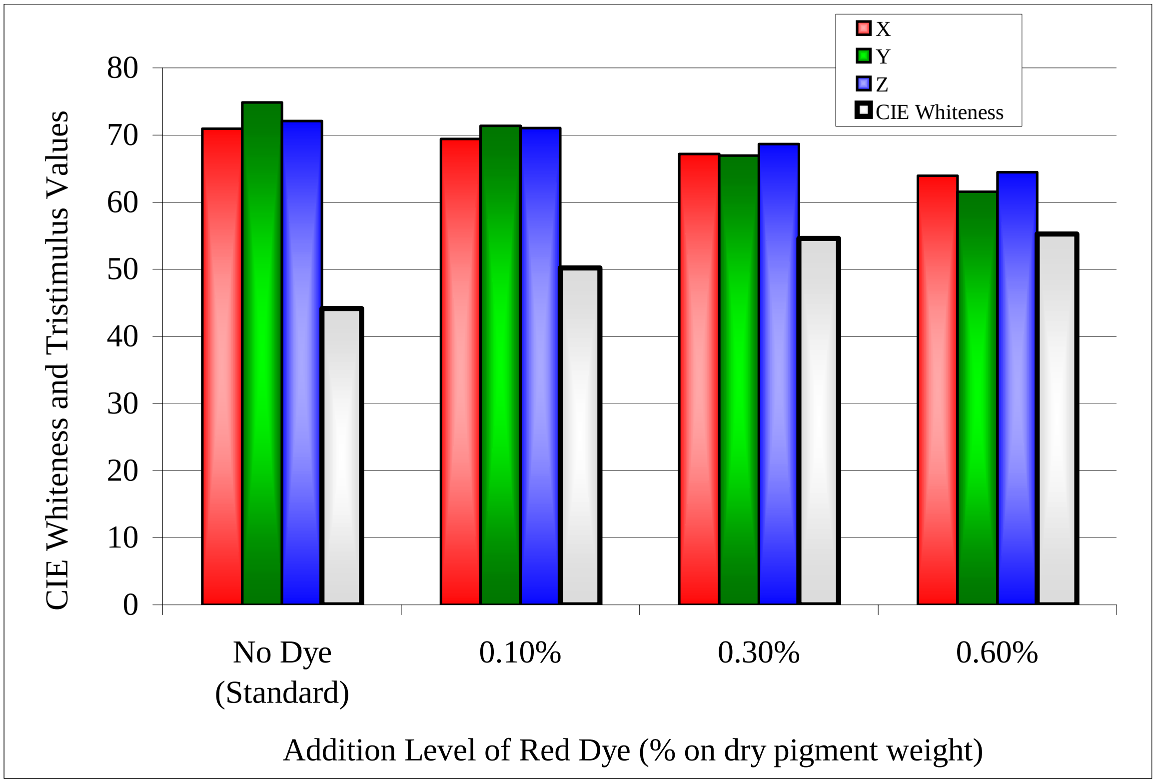

Figure 8: CIE whiteness for red dye and effect of Tristimulus Values on CIE whiteness with datacolor Spectraflash spectrophotometer.

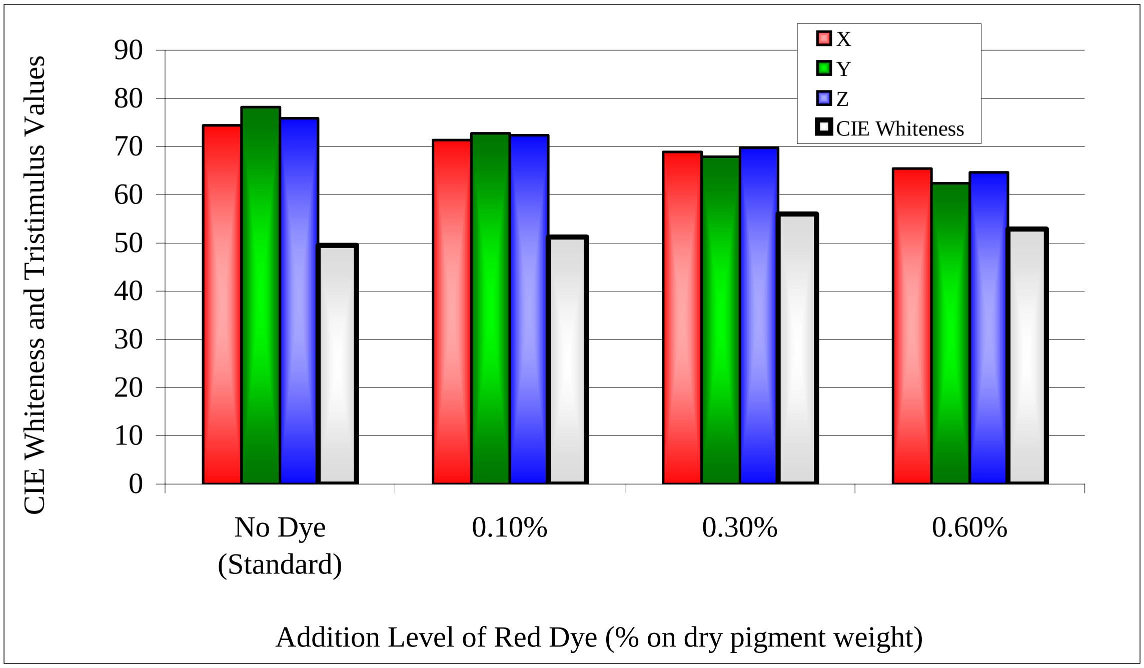

Figure 9: CIE whiteness for Red and Effect of Tristimulus Values on CIE whiteness with the GretagMacbeth spectrophotometer.

Hunter and Ganz whitenesses exhibited similar trends to CIE whiteness with dye addition, Ganz being on a smaller scale for black and red dyes, and Hunter Whiteness being on a larger scale than CIE whiteness. It seems that Ganz whiteness may be influenced less by the changes in the tristimulus values, although the multiplying factors are larger in the Ganz formulation. Observer evaluations and measured TAPPI brightness values for these colored papers were in consensus.

CIE and Ganz tint values measured by the datacolor Spectrophotometer are given in Figure 11. As seen in the figure CIE tint values are in the equality region for all addition levels of black dye, and 0.25% and 0.5% blue dye. Ganz tint values for black and the lower two levels of blue were slightly larger than CIE tint values, but are not markedly tinted from white. Tint values for 0.8% addition level of blue dye was 17 for CIE and 20.9 for Ganz. The tint values for 0.1%, 0.3% and 0.6% red dye addition levels were -8.6, -16 and -27.7 for CIE, -9.8, -17.4, and -28 for Ganz, respectively.

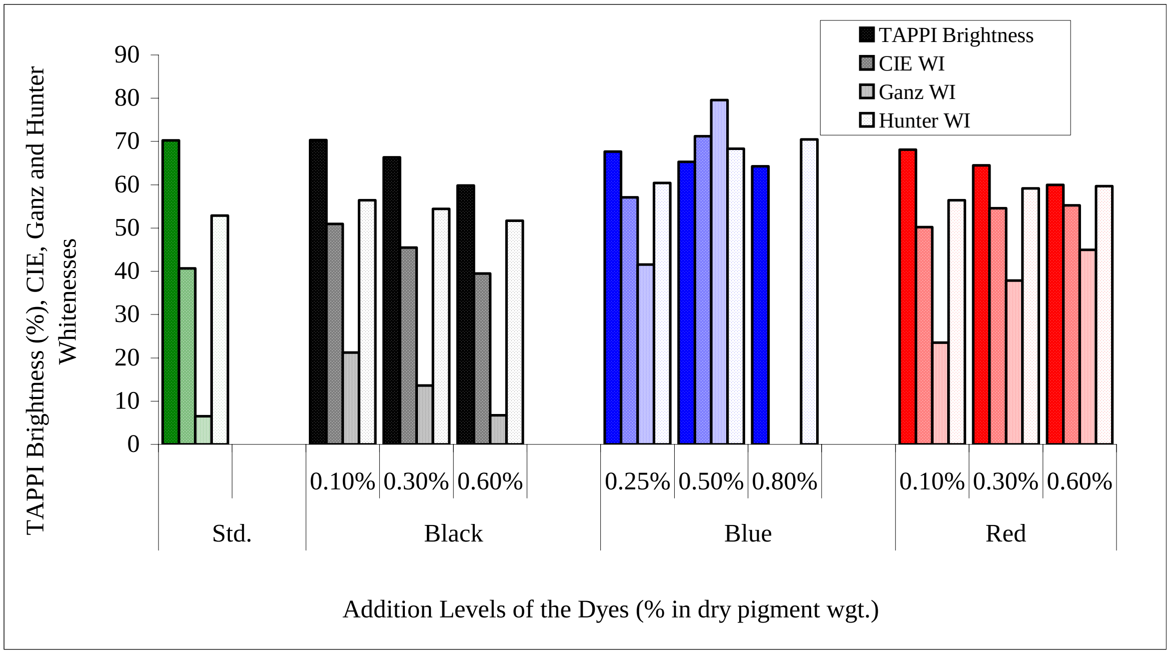

Figure 10: Blue, Black, Red Dye Effect on TAPPI Brightness and CIE, Ganz and Hunter whiteness values measured by the datacolor Spectraflash Spectrophotometer.

It should be noted that the metric is different for the two whiteness scales. The threshold for distinguishing different whiteness values is defined in the Ganz scale as being 5 points, while for the CIE whiteness it is about 2.5 points. The threshold for distinguishing different tints is about 0.5 points.

The Micro S4-M and the GretagMacbeth were used to acquire the data shown in Figure 12. Again, all the whiteness values exhibited a very similar distribution with the GretagMacbeth Spectrophotometer as with the datacolor. Ganz whiteness values seem to give the largest values, indicating that it is more influenced by the changes in the tristimulus values, when samples with blue dye are measured. On the other hand, calculated Ganz whiteness values were smaller for the black and red dyes compared to CIE and Hunter whiteness values, this time indicating that it is less influenced by the changes in the tristimulus values when samples with black and red dye are measured.

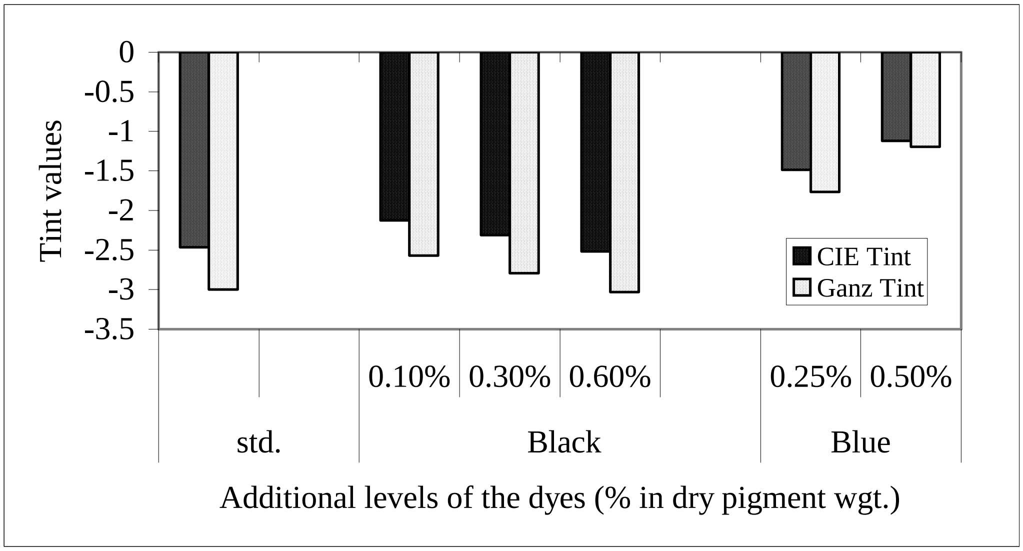

Figure 11: CIE and Ganz Tint Deviations Measured by datacolor Spectraflash Spectrophotometer.

The correlation coefficients of observer evaluations (Figure 3) and CIE, Hunter, and Ganz whiteness values and TAPPI brightness were calculated for each color dye added test sample for both datacolor Spectraflash and GretagMacbeth spectrophotometers. For the GretagMacbeth Spectrophotometer, the corresponding correlation coefficients for blue dye added test samples are 0.97 for TAPPI, -0.81 for CIE, -0.58 for Ganz, and -0.28 for Hunter. (Note that all whiteness formulas have negative signs except TAPPI brightness, indicating anti-correlation with observer data.) Corresponding ranking correlations were 1 for TAPPI, -0.8 for CIE, -0.78 for Ganz and -0.6 for Hunter. (Note that, again all whiteness formulas have negative signs while TAPPI brightness has a positive sign.) Correlation coefficients for black dye added test samples were 0.93 for Hunter, 0.92 for CIE, 0.75 for TAPPI, 0.38 for Ganz. Corresponding ranking coefficients were 0.8 for all whiteness values and TAPPI brightness. For the red tinted samples, correlation coefficients were 0.98 for TAPPI, -0.71 for Hunter, -0.58 for CIE, and -0.09 for Ganz. Corresponding ranking correlations for red tinted samples were 0.95 for TAPPI, -0.78 for Hunter and CIE, and 0.08 for Ganz.

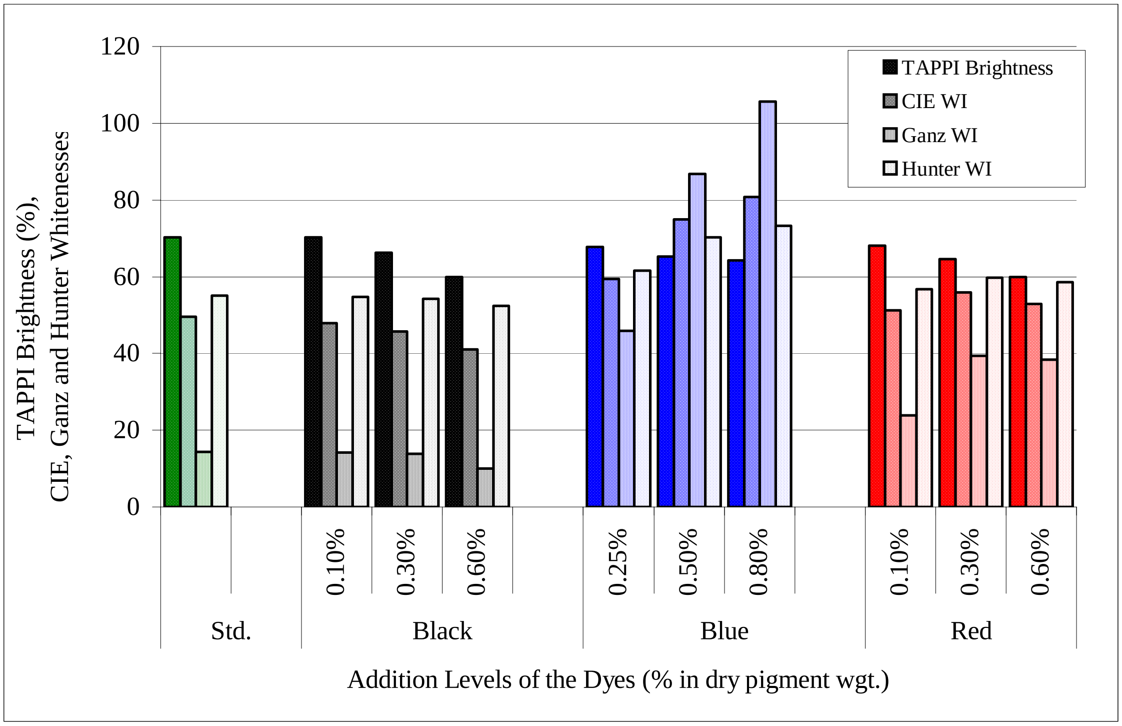

Figure 12: Blue, Black, and Red Dye Effect on TAPPI Brightness and CIE, Ganz and Hunter Whiteness values Measured by the GretagMacbeth Spectrophotometer.

For the datacolor Spectraflash Spectrophotometer, the corresponding correlation coefficients for blue dye added test samples are 0.97 for TAPPI, -0.90 for CIE, and Ganz, and -0.73 for Hunter. Negative values result from increasing whiteness corresponding to a low rank order. The ranking correlations for blue added test samples were –0.8 for Hunter, CIE and Ganz whitenesses, and 1 for TAPPI brightness. Correlation coefficients for black dye added test samples were 0.89 for CIE, 0.82 for Hunter, 0.75 for TAPPI and 0.66 for Ganz. The ranking correlations for black dye added samples are 0.8 for CIE, Hunter and TAPPI and 0.4 for Ganz. For the red dye added samples, correlation coefficients were 0.98 for TAPPI brightness, -0.86 for Ganz, 0.82 for Hunter and -0.81 for CIE. The corresponding ranking coefficients for red dye added test samples were –0.95 for Hunter, CIE and Ganz whitenesses, and 0.95 for TAPPI brightness. All the correlation coefficient values for TAPPI brightness are in the acceptable range, while those for the CIE, Hunter and Ganz formulas are generally unacceptable. The Ganz whiteness does not show good agreement with observer evaluations for any of the dye added test samples. Similarly, Hunter whiteness correlates poorly with observer evaluations for blue and red dye added test samples, while CIE whiteness does not correlate well for red dye added test samples.

To further investigate the disagreement that occurred between the two spectrophotometers with establishing correlation between observer evaluations and calculated CIE, Hunter and Ganz whiteness values, the correlation coefficients of the two spectrophotometers were calculated for each whiteness formula. The correlation coefficients found were -0.88 for Hunter whiteness, -0.76 for CIE whiteness, and -0.53 for Ganz whiteness, again representing anti-correlation. Correlation coefficients of the two spectrophotometers for tristimulus values were also calculated. The correlation coefficients were 0.98 for X, 0.99 for Y, and 0.94 for Z. As it is seen from the correlation coefficient values, although measured tristimulus values agree very well for the measurement instruments used, CIE, Ganz and Hunter whiteness values do not. This shows that even very small changes in the tristimulus values can cause significant changes especially in calculated CIE and Ganz whiteness values.

CIE and Ganz tint values measured by the GretagMacbeth Spectrophotometer are given in Figure 13. As seen in the figure CIE tint values are in the equality region for all addition levels of black and blue dyes. Ganz tint values for all addition levels of black and blue dyes were slightly larger than CIE tint values but are not markedly tinted from white. The tint values for 0.1%, 0.3% and 0.6% red dye addition levels were -10.8, -19 and -28 for CIE, -12.3, -21.4, and -31.4 for Ganz, respectively.

L*, a* and b* values are given in Figure 14. As can be seen, the two spectrophotometers are in good consensus as far as L*, a*, b* values are concerned. Figure 14.a-b. L* values (indication of lightness) decreased with increasing addition level for all three dyes. L* values are also found to be in consensus with the TAPPI brightness values and the observer evaluations. As seen in Figure 14.b, a* value increased with increasing red, also slightly increased by blue dye addition and is not influenced by black dye addition. The b* value on the other hand, decreased with the increasing addition of all three dyes, as expected.

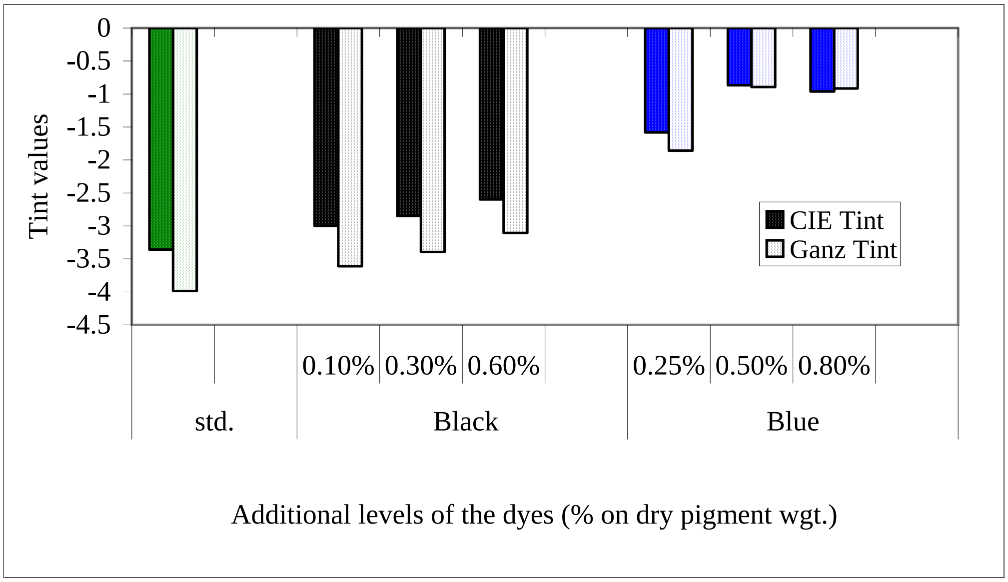

Figure 13: CIE and Ganz Tint Deviations Measured by the GretagMacbeth Spectrophotometer.

Figure 15 shows the influence of FWA on TAPPI brightness and the corresponding reflectance with the GretagMacbeth Spectrophotometer. Tests were made including and excluding the UV light source during the measurements. The measured reflectance difference at 457 nm for the two light wavelength range is given as the fluorescent effect for the Micro S4-M. Reflectance values at 460 nm were also taken for each sample using the GretagMacbeth Spectrophotometer. Measurements were made with and without the UV-filter and the difference in the reflectance values are taken as the fluorescent effect. Along with the standard coating formula with varying levels of FWA addition, the PVOH effect on FWA efficiency was measured for brightness and reflectance values for 460 nm**.** There is an increase in the reflectance difference as the FWA addition level is increased. This increase goes up by about 1.5 points for the brightness meter and more than 2 points for the spectrophotometer, when PVOH is used in the formulation as a FWA carrier. The two instruments again were found in good agreement when reflectance values at a certain wavelength are considered. The increase in reflectance is relatively small because of the above-mentioned effect of the illuminant A light source.

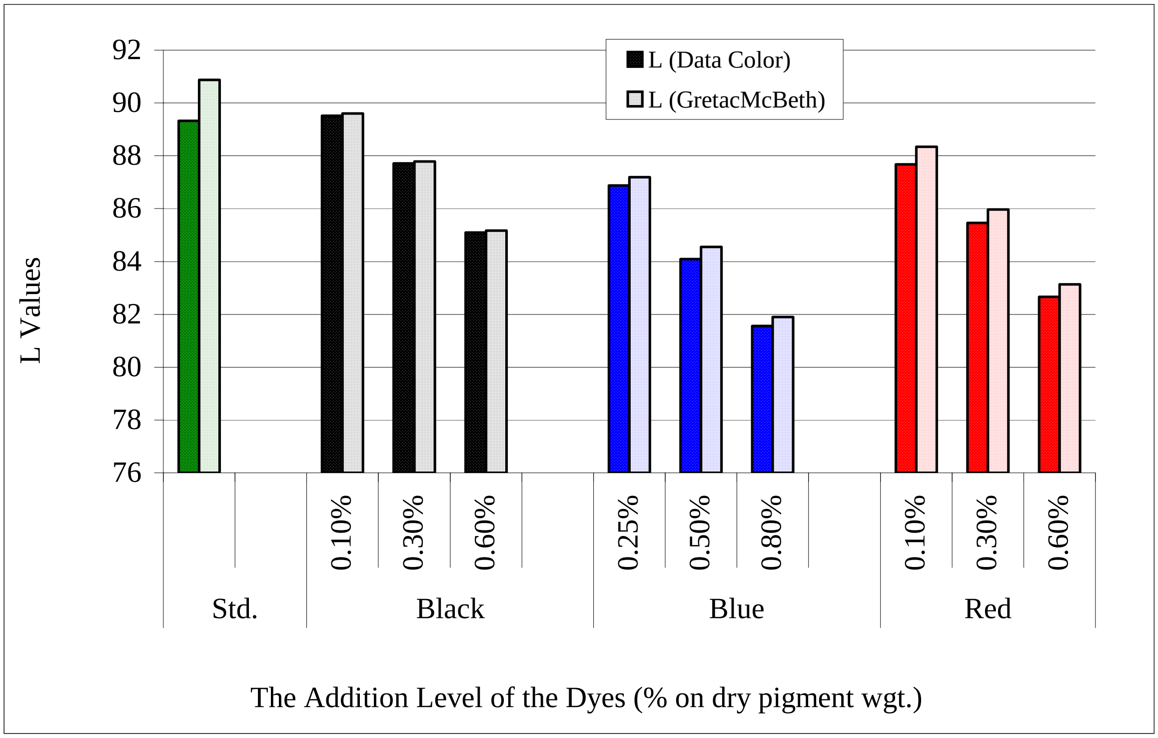

Figure 14.a: Measured L* Values Acquired by datacolor Spectraflash and GretagMacbeth Spectrophotometers.

The corresponding effects of FWA on colorimetric values are shown in Figure 16. The L* value is not significantly changed (the variations reported in Figure 16a are exaggerated by the scale used in the graph) by FWA addition, PVOH addition or use of the UV filter. The effect of FWA on L* is diminished because the light source used in the Spectrolino (Illuminant A) is very weak in the UV, and therefore, doesn't activate fluorescence to the same extent as a nominal daylight source (D_{65}, 6500 K, etc.). CIE tint deviations were calculated for each FWA addition amount and all were well within the CIE equality region.

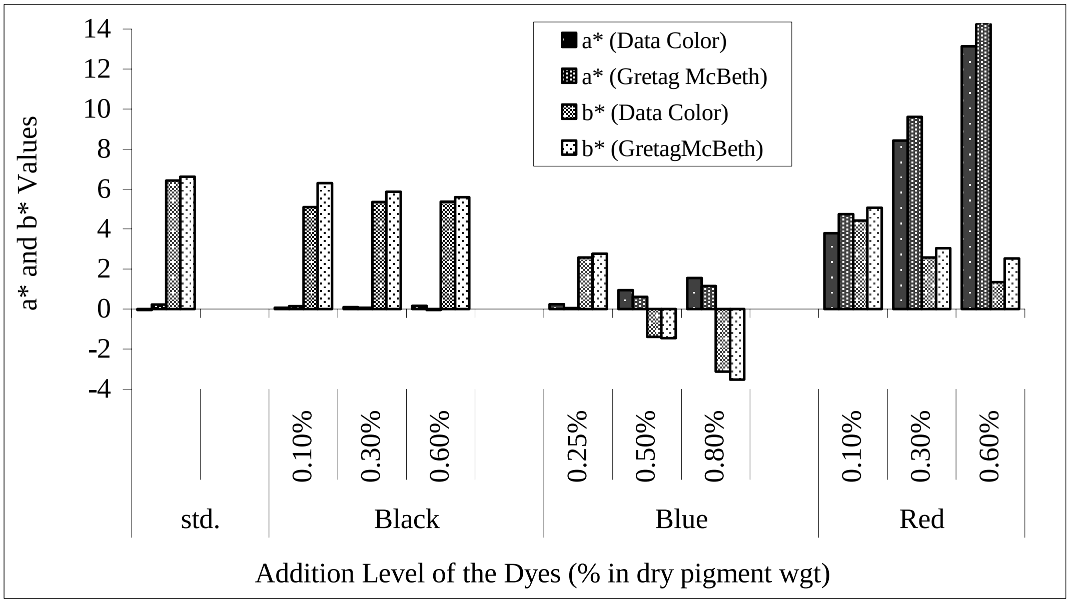

Figure 14.b: Measured a* and b* Values Acquired by datacolor Spectraflash and GretagMacbeth Spectrophotometers.

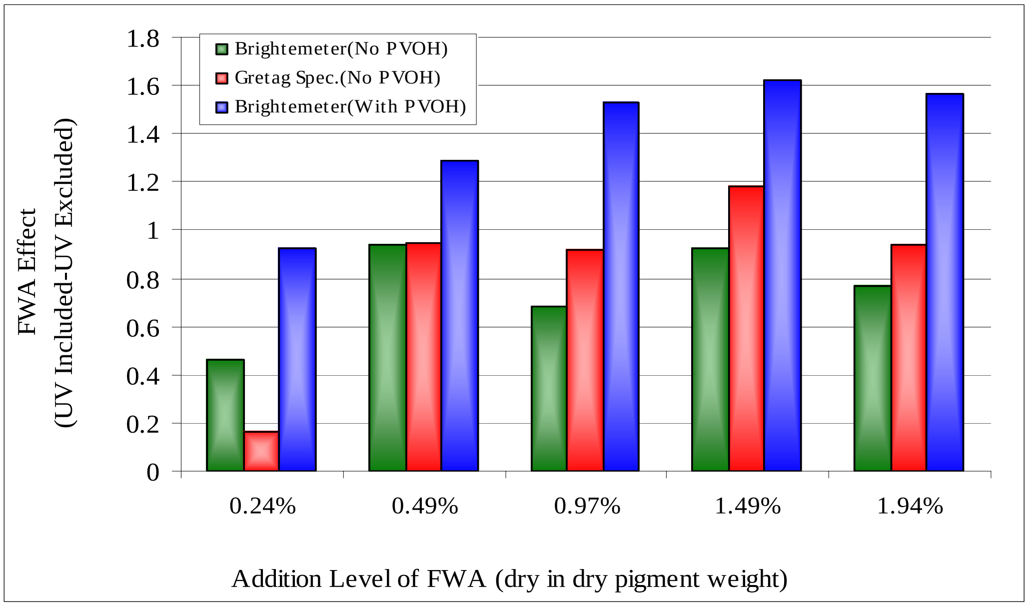

Figure 15: FWA effect on TAPPI Brightness and the corresponding reflectance values for GretagMacbeth Spectrophotometer (R@ 460 nm).

The a* values, shown in Figure 16b, are slightly decreased by the addition of FWA. The b* values are systematically lower without the UV filter versus measurements with the UV filter. These reductions are, however, less than would be expected for observations under daylight conditions, again because of the lack of UV strength in the light source. The perception of whiteness of the coated sheets is masked because of the yellow tint (relatively high b* value) of the basesheet (mixture of Kraft and groundwood pulp). The b* values for all of these cases are more than twice that of the proposed SWOP guidelines [8] for the #5 LWC grade. We see that there is a systematic reduction in the b* value with addition of FWA up to about 1%.

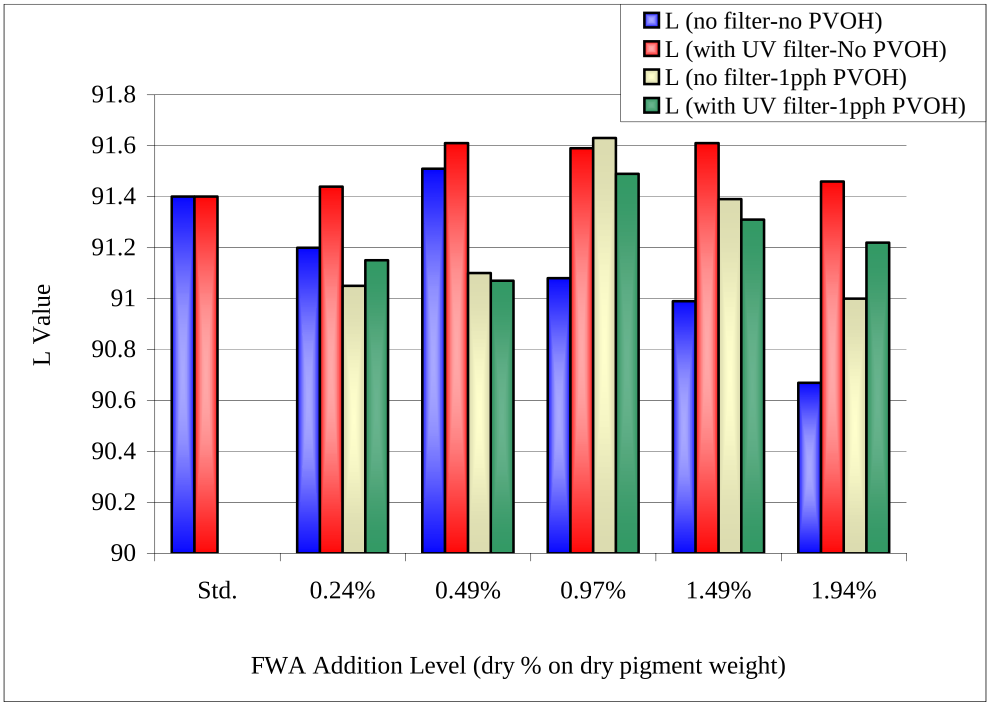

Figure 16a: FWA effect on CIE L values for the GretagMacbeth Spectrolino Spectrophotometer.

Above about 1% FWA, the b* increases to being larger than the base case, with no FWA. Thus, there is no benefit, and in fact there is a detriment, of FWA above about 1% on a dry basis. This result, along with the associated slight shift of a* towards the green, are consistent with well known “greening” effects [10]. In all cases, however, the beneficial effects of the FWA and subsequent effects of greening are masked by the weakness of the light source in the UV and the yellowness of the base sheet.

CIE, Hunter and Ganz whiteness values were also calculated for the paper samples for which the FWA was added at varying levels with and without 1 pph PVOH. However, the calculated whiteness values were generally inconclusive, in that no clear trends were seen such as those found for the brightness measurements. Numerical results of whiteness are not given for this reason.

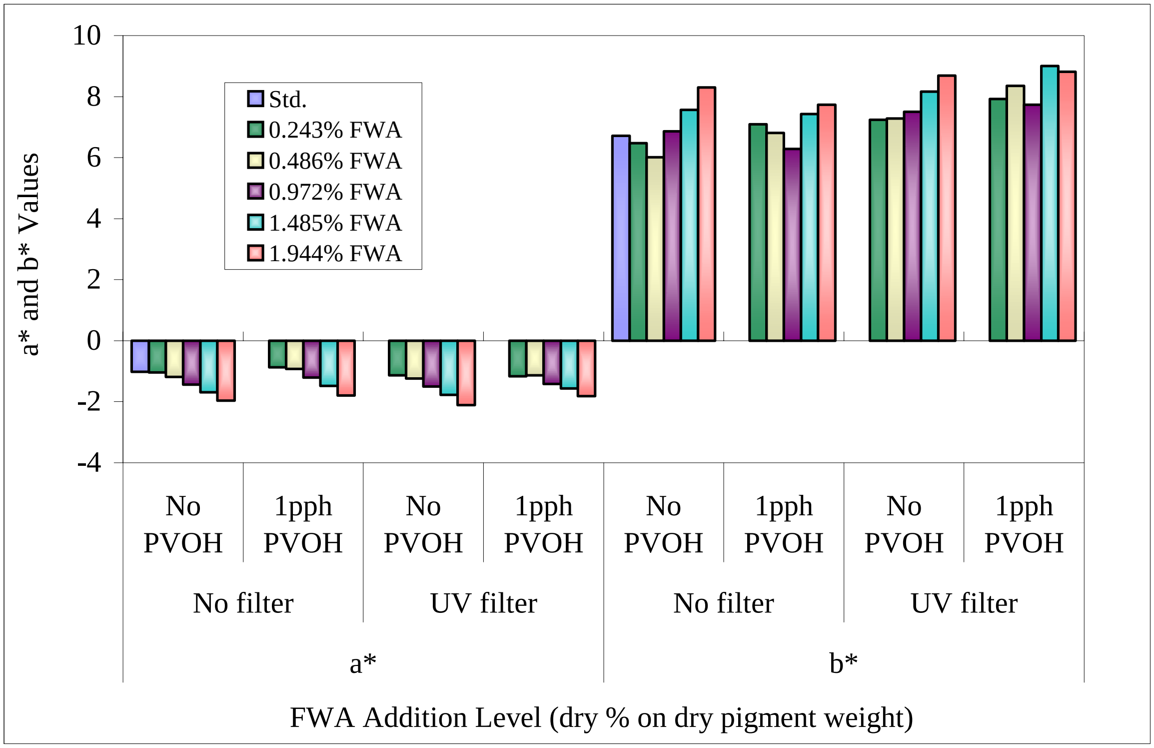

Figure 16b: FWA effect on CIE a*b* values for GretagMacbeth Spectrolino Spectrophotometer.

Figure 17 shows the statistical analyses of observer evaluation for samples with varying levels of FWA added with and without PVOH. Again, all observations were made in a D_{50} light booth. The scale of 5 implies extraordinary whiteness, and 1 implies not observed whiteness at all for the whiteness evaluations. Similarly, scale of 5 implies extraordinary green tint on the paper surface while 1 implies no green tint observed at all. As can be seen from the figure, the observed whiteness is consistent with the colorimetry, in the sense that the perceived whiteness drops after about 1% FWA dry to dry. There is little evidence of the greening in the observer data.

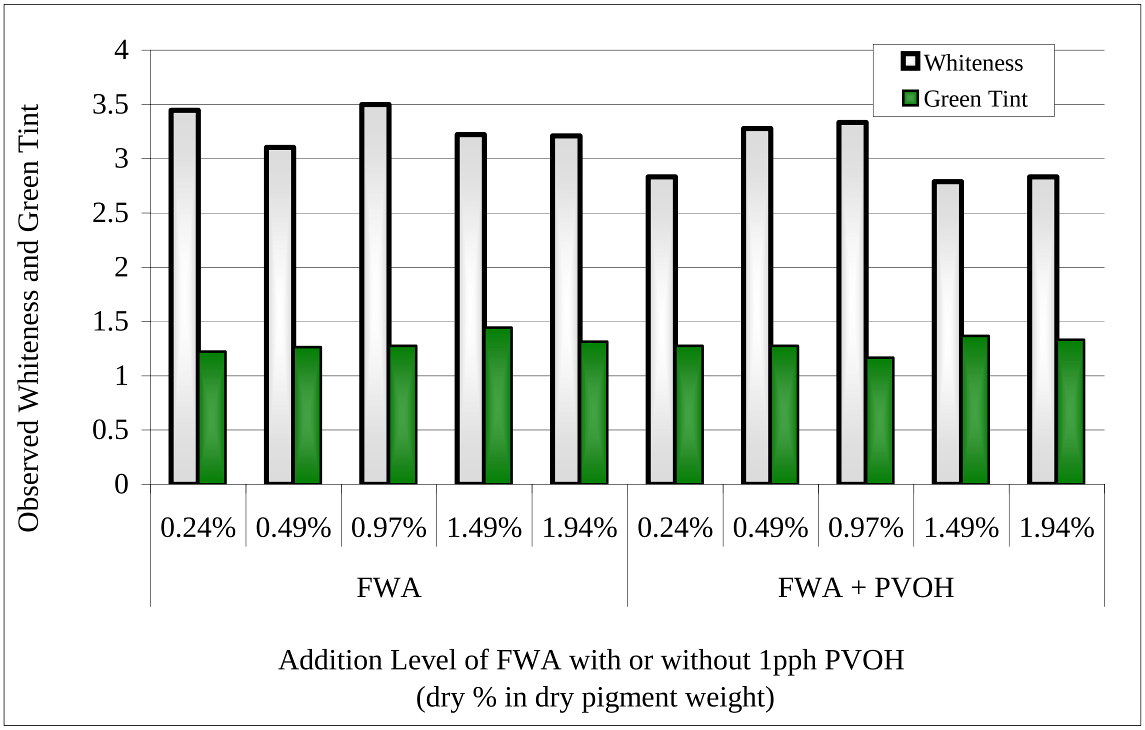

Figure 17: Observer Evaluation of Coated Light Weight Papers at Varying Addition Levels of FWA.

Effect of Coat Weight

In addition to dye levels, the influence of coat weight was also investigated for each of the three dyes and FWA. Coated samples were tested for their optical properties at four coat weight levels. They are 6 g/m^2, 8 g/m^2, 10 g/m^2, and 12 g/m^2. Addition levels of dyes are chosen as 0.1 % for black and red dye, 0.25% for blue dye, and .486 % in dry pigment weight of FWA. Figure 18 shows the representative TAPPI brightness values for non-dyed (standard) blue, black and red dyes and FWA at different coat weights measured by Micro S4-M, and CIE, Ganz and Hunter Whitenesses from the Data Color Spectrophotometer. All calculated whiteness values seem to exhibit an increasing trend as the coat weight is increased for each color and standard. This increase looks to be steeper for Ganz whiteness. On the other hand, TAPPI brightness seems to be only slightly influenced with the increased coat weight. Changes in TAPPI brightness are insignificant in most cases.

The Micro S4-M and the GretagMacbeth Spectrolino spectrophotometer were used to acquire the data shown in Figure 19. Again, all the whiteness values exhibited a very similar distribution with the GretagMacbeth Spectrophotometer. Ganz whiteness values seem to give the largest values, indicating that it is more influenced by the changes in the tristimulus values when samples with blue dye are measured with both spectrophotometers.

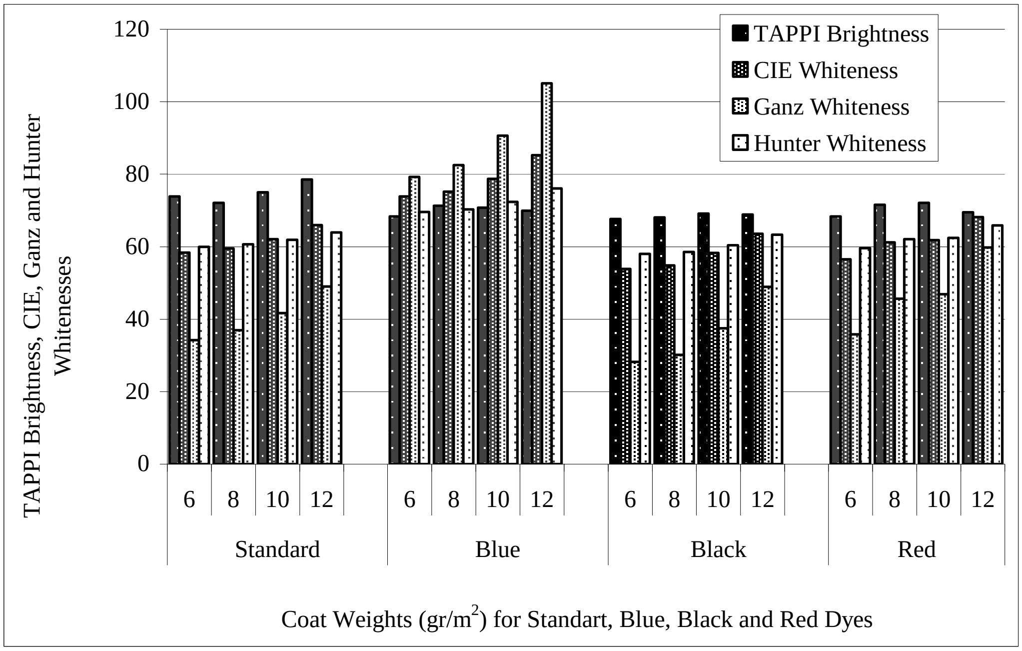

Figure 18: Coat Weight Effect for Standard Coated Papers, Blue, Black, Red Dye on TAPPI Brightness and CIE, Ganz and Hunter Whiteness Values Measured by the datacolor Spectraflash Spectrophotometer.

Figure 20 shows the influence of coat weight on TAPPI brightness for the coated paper samples containing FWA. As explained previously tests were made including and excluding the UV light source during the measurements. The measured reflectance difference at 457 nm for the two light wavelength range is interpreted as the fluorescent effect for the Micro S4-M. The FWA effect is found to vary from .6 % to 1.46% and steadily increased with increasing coat weight.

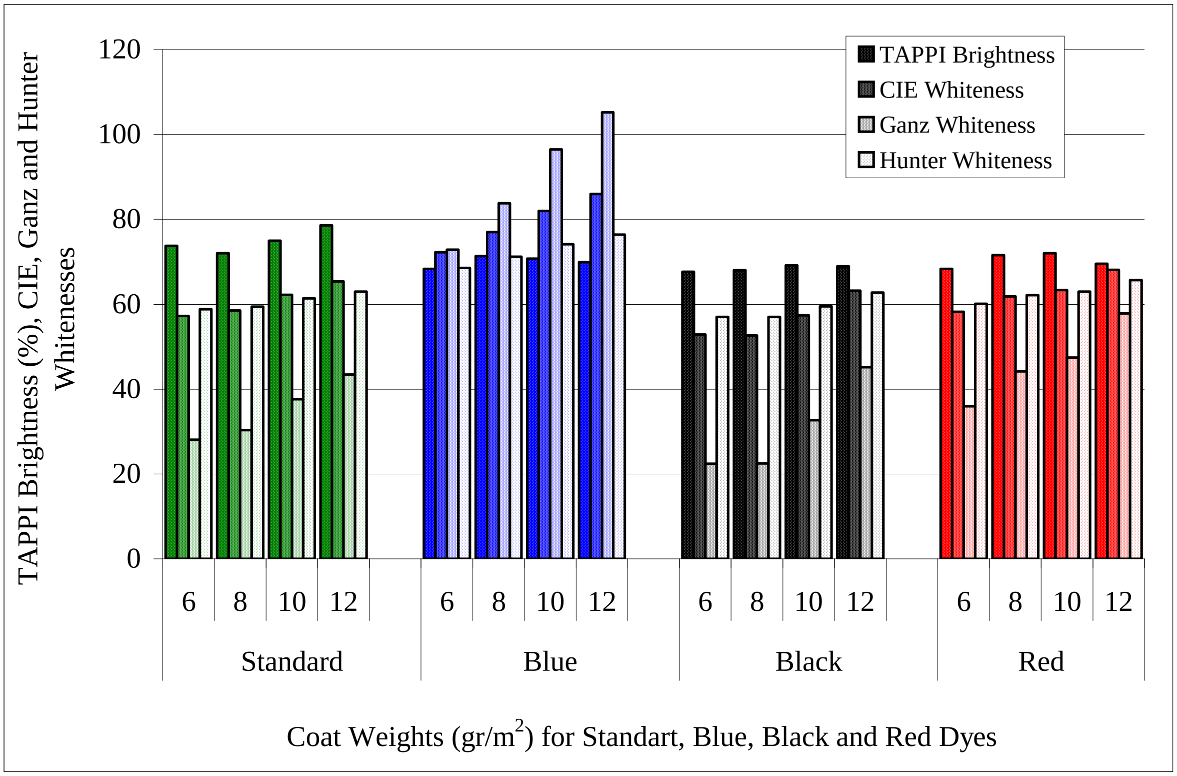

Figure 19: Coat Weight Effect for Standard Coated Papers, Blue, Black, Red Dye on TAPPI Brightness and CIE, Ganz and Hunter Whiteness Values Measured by the GretagMacbeth Spectrophotometer.

The GretagMacbeth Spectrophotometer was used to investigate the effect of coat weight on CIE, Ganz and Hunter whitenesses for coated sample papers containing FWA. Measurements were made with and without the UV-filter and the difference in the calculated whiteness values are taken as the fluorescent effect. As explained above, the Illuminant A light source used to illuminate the specimen in this instrument is unable to excite most of the FWA present in the coating layer, since illuminant A contains very low UV intensity. Therefore, the calculated FWA effect would be much lower than that which would be observed by a viewer under daylight conditions. Under this condition, the CIE whiteness values and corresponding fluorescent effects are shown in Figure 21. The fluorescent effect ranged from 1.87 to 7.67 in CIE whiteness with increasing trend as the coat weight increased until 10 g/m^2. There is a slight, but probably insignificant, decrease at 12-g/m^2-coat weight. Increasing the fluorescent effect with increasing coat weight may indicate that the FWA could migrate into the base sheet at lower coat weights, thus loosing its whitening efficiency.

Figure 22 represents the coat weight effect on Ganz whiteness of coated paper samples containing FWA. The fluorescent effect and Ganz whiteness again increase with increasing coat weight until 10 g/m^2. Although the Ganz whiteness values are numerically lower than those of CIE whiteness, the fluorescent effect in Ganz whiteness is significantly higher (from 5.28 to 16.64).

Figure 23 shows the coat weight effect on Hunter whiteness of coated paper samples containing FWA. This trend is again similar to the previous whiteness and fluorescent effect trends, that is, both whiteness and fluorescent effect increases with increasing coat weight until about 10 g/m^2.

Considering figures 18-21, it may be suggested that FWA migration into the base sheet could occur at low coat weights. Thus, the FWA amount available for the existing UV portion of the light at the surface of the paper may be significantly reduced. This occurrence could significantly reduce the efficiency of FWA. Therefore, applying FWA at higher coat weights could improve its efficiency since there would be less and less FWA migrated into the base sheet as the coat weight is increased. This again imposes another problem. It is not practical economically to apply higher coat weights on to LWC grade papers, so that FWA could work efficiently and adequately. Reaching the desired optical properties with papers containing large amounts of lignin, LWC grade papers, therefore, could be fairly challenging at low coat weights.

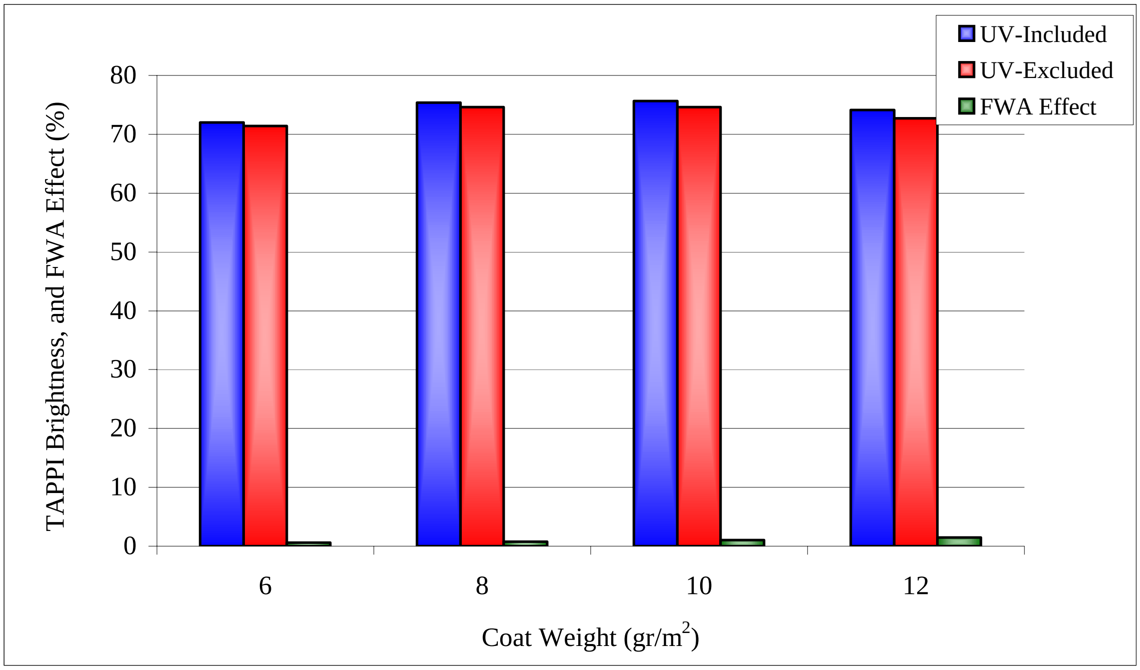

Figure 20: Coat Weight Effect for FWA on TAPPI Brightness.

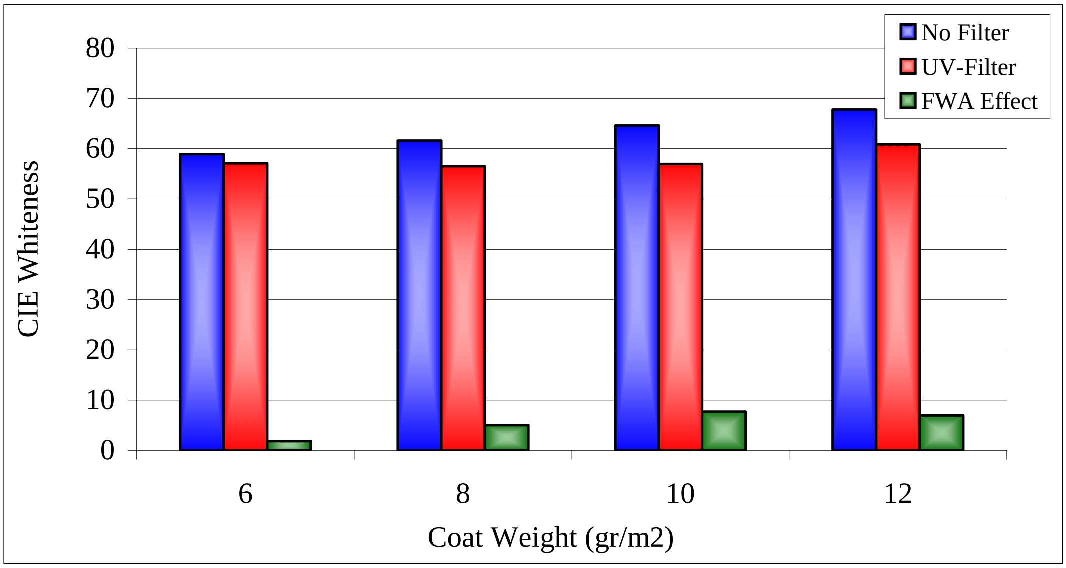

Figure 21: Coat Weight Effect on CIE whiteness of Coated FWA Containing Paper.

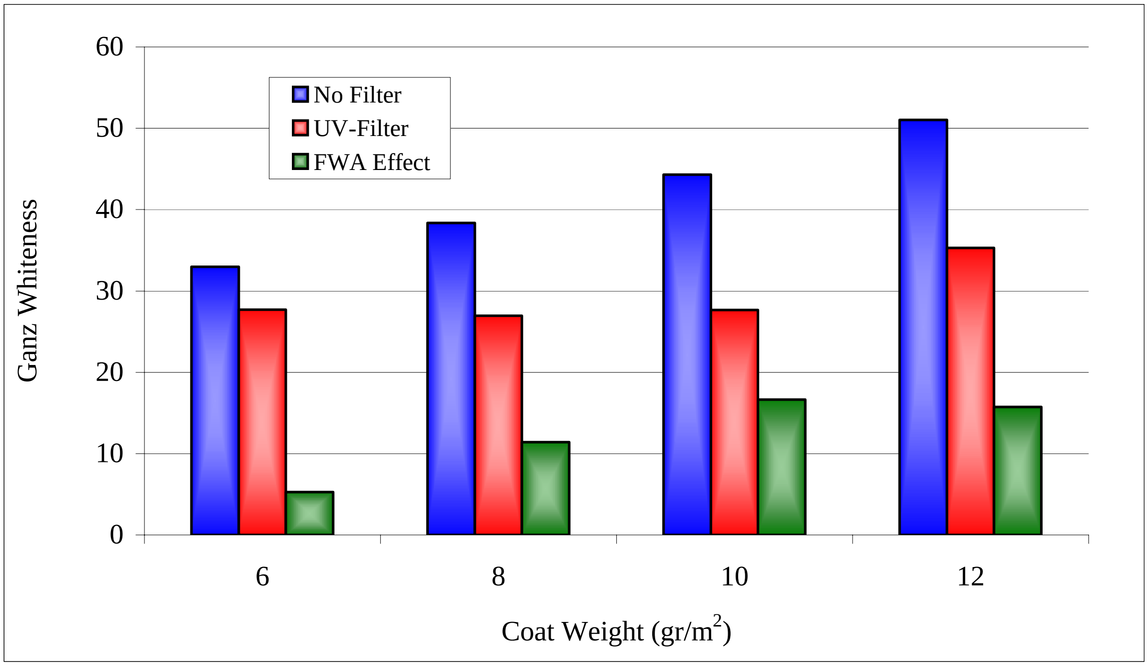

Figure 22: Coat Weight Effect on Ganz Whiteness of Coated FWA Containing Papers.

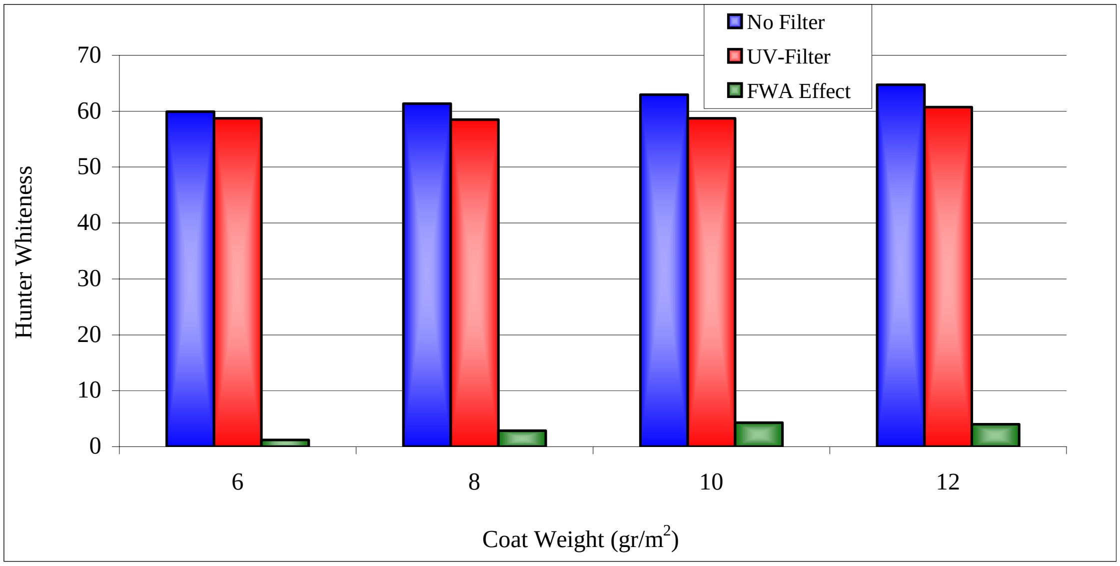

Figure 23: Coat Weight Effect on Hunter Whiteness of Coated FWA Containing Papers.

Conclusions

It was found that in some cases, calculated CIE, Hunter, and Ganz whiteness values increased with increased amount of colors in the coating layer, although papers appeared darker or redder to the observers. Brightness measurements, observer evaluations and calculated L*, a*, and b* values were mostly in consensus with each other, and these measures were generally found to be independent of the instrument used. In addition, it was found that relatively small deviations in measured CIE tristimulus functions X, Y, and Z caused significant changes in the calculated CIE and Ganz whiteness values.

The two spectrophotometers used in the experiment provided similar data. General agreement from one spectrophotometer to another was very good. On the other hand, calculated whiteness values mostly did not agree with the observer evaluations, brightness measurements and calculated L*, a* and b* values. This suggests that CIE, Ganz and Hunter whiteness values, as measures of perceived whiteness, are only mythical. FWA added coated papers were also tested for colorimetric properties of perceived whiteness and "greenness". No evidence of significant “greening” was seen by the observers, even at high levels of FWA. There was slight colorimetric evidence of greening, but it was at the borderline of delectability, consistent with the observer results.

References

1. Bristow, J. A., *Advances in Printing Science & Technology*, W. H. Banks, Ed., **20**: 193, John Wiley and Sons Ltd (23 August, 1990).
2. Tlach, H., *16th ABTCP Conference*, Sao Paulo, November 1983, p.1251.
3. *Measurement and Control of the Optical Properties of Paper*, 2nd ed., Technidyne Corporation, New Albany, Indiana, 1996, pp. 7.5–7.6.
4. CIE 15.2 – 1986, *Colorimetry*, Second Edition, 1986, Corrected Reprint 1996.
5. TAPPI T452 Standard Test.
6. Podhajny, Richard M., “What can cause yellowing in printed package materials?”, *Paper, Film & Foil Converter*; March 01, 1999;

7. SWOP, *SWOP for the New Millennium, Specifications for Web Offset Publications*, Published by SWOP Incorporated, NY, 9th edition, 2001.
8. P. D. Fleming and Mike Evans, "Color Measurement Issues and Proposed SWOP Guidelines for LWC #5", Printing & Converting Common Interest Group Luncheon Presentation, *TAPPI Spring Technical Conf. & Trade Fair*, Chicago, May 12-15, 2003.
9. Hunter, R.S., Harold, R.W., *The Measurement of Appearance*, John Wiley & Sons, 1987.
10. Claudio Puebla, “Whiteness Assessment: A Primer”, Downloadable from http://mitglied.lycos.de/whiteness/.
11. Roltsch, C.C.; Lloyd, T.A., *1987 TAPPI Papermakers Conference*, TAPPI Press, Atlanta, p87.
12. Parkes, D., *TAPPI Dyes, Fillers, & Pigments Short Course*, Atlanta, TAPPI Press, April 25-27, 1990, p.139.
13. Krantz, D. H., “Color Measurement and color theory: I Representation theorem for Grassman Structures”, J. Math. Psychol. 12, 283-303 (1975); “Color Measurement and color theory: II Opponent-colors theory, J. Math. Psychol. 12, 304-327 (1975).
14. Griesser, R., 1995 TAPPI Dyes, Fillers, & Pigments Short Course, Chicago, April 1995, p.331.
15. Bala, R., “What is the Chrominance of “Gray”?”, *Proceedings of the 9th Color Imaging Conference*, Sponsored by IS&T and SID, Scottsdale AZ, Nov. 6-9, 2001, p102.
16. Bureau, W.H., *Graphic Arts Monthly*, **47**8: 80-82 (August 1975).
17. Aksoy, B., Fleming, P. D. and Joyce, M. K., “A New Measure of Whiteness that Correlates with Perceived Color Appearance”, submitted to *Applied Optics*.
18. Rolf Griesser, “Whiteness not Brightness: A new way of measuring and controlling production of paper”, *Appita J.*, v. **46**, no. 6, Nov. 1993, 439-445.
19. Anderson, K.A., *PIMA*, May 1998, p.14.
20. Griesser, R, “CIE whiteness and Tint: Possible Improvements”, Appita J., vol.49, no.2, March 1996, p. 105-112.

21. Roltsch, C.C., Lloyd, T.A. “The Efficient Use of Fluorescent Whitening Agents in the Paper Industry”, 1987 TAPPI Papermakers Conference, TAPPI Press, Atlanta, p. 87.
22. R.S. Hunter, “Measurements of the Appearance of Paper”, *TAPPI J.*, **45**, 203A (1962)
23. Ganz E, "Whiteness: photometric specification and colorimetric evaluation", *Appl. Opt.* 15 2039-2058 1976
24. Ganz E., "Whiteness formulas: a selection", *Appl. Opt.* 18. 1073-1978 1979
25. *CIE Proceedings 1931*, Cambridge University Press, Cambridge, 1932.
26. *CIE, Recommendations on Uniform Color Spaces, Color-Difference Equations, Psychometric Color Terms, Supplement No. 2 of CIE Publ. No. 15* (E-1.3.1) 1971, Bureau Ventral de la CIE, Paris 1978.
27. Burak Aksoy, Margaret K. Joyce and P. D. Fleming, “Comparative Study of Brightness/Whiteness Using Various Analytical Methods on Coated Papers Containing Colorants”, TAPPI Spring Technical Conf. & Trade Fair, (Academic, Chicago, May 12-15, 2003).
28. Ganz E. and Griesser, R, “Whiteness: assessment of tint”, *Appl. Opt.* **20**, 1395 (1981).

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Figure 20: Coat Weight Effect for FWA on TAPPI Brightness.

Figure 21: Coat Weight Effect on CIE whiteness of Coated FWA Containing Paper.

Figure 22: Coat Weight Effect on Ganz Whiteness of Coated FWA Containing Papers.

Figure 23: Coat Weight Effect on Hunter Whiteness of Coated FWA Containing Papers.

APPENDIX A

Coating Material Information

Delaminated Clay (Huber-Hydraprint)

Calcined Clay (Engelhard-Ansilex)

TiO_2 (Millenium- Tiona AT-1)

Plastic Pigment (Dow Chem.- 756A)

SB Latex (Omnova-Genflo 5170)

AZC (MEI-Bacote 6200)

Calcium Stearate (Geo Specialty -Nopcote DC-100)