WHITENESS EVALUATIONS ON TINTED AND FWA ADDED PAPERS

Burak Aksoy, Paul D. Fleming* and Margaret K. Joyce

Department of Paper Engineering, Chemical Engineering and Imaging

Center for Coating Development

Western Michigan University

Kalamazoo, MI 49008

* Corresponding author. Tel.: (269) 276 3511; fax: (269) 276 3501

E-mail address: dan.fleming@wmich.edu

ABSTRACT

Many whiteness formulas have been proposed over the years. Attempts have been made to standardize the calculation of whiteness, although colorimetry of fluorescent samples is still problematic. Most formulae used today assess relative whiteness. These formulae are generally meaningless when applied to colored samples. They are mostly unsuccessful in assessing tinted samples with chromaticities placed near the borders of “white” colors. Previously, we showed that large differences in CIE **w**hiteness can occur when the colors of papers are slightly altered from neutral white to varying “shades” of white. Observers assessed the whiteness of these tinted papers as similar in appearance to one another.

Here, different colorants were added to coating formulations and applied to a #1 publication grade base paper. Optical properties were measured and CIE, Hunter, Ganz and Fleming-Aksoy whiteness formulae were analyzed and compared.

INTRODUCTION

Whiteness is associated with a region in color space where objects are accepted as white inside the chromaticity diagram. Whites reside in an area near the top of CIE[1] and Hunter[2] color spaces. Although the white region appears fairly narrow, there are about 5,000 distinguishable white colors, and 30,000 so called "ish" whites, such as bluish white, yellowish white, greenish white etc. Therefore, there are apparent differences between different samples within the class described white. The term "white" used in the description of papers, is thus not an absolute term. Therefore, there are degrees of whiteness, and it is meaningful to claim that one paper is whiter than another[3].

Physically, a white surface reflects strongly throughout the visible spectrum. As this spectral reflectance becomes higher and more uniform, the surface appears whiter. In geometrical terms, a white surface reflects diffusely in all directions and, of course, white objects have high scattering coefficients and low absorption coefficients.

White objects always have high CIE tristumulus values[4], since they have high reflectance throughout the visible spectrum and the Z reflectance factor for the blue end of the spectrum has been given more attention and importance.

In principle, the degree of whiteness is measured by the degree of departure of the object from a perfect white. Evaluation of whiteness is commonly made by visual assessment and/or by instrumental measurements. Only the physical property, the spectral reflectance of a sample, can be measured. However, measured whiteness assessments gain validity only when combined with observer assessments. 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[5], Hunter[2], and Ganz[6,7] whitenesses are the most commonly used measurements by the paper industry.

CIE whiteness may give a different impression of the relative whiteness of two samples relative to what a human observer would conclude.[8,9] Secondly, measured spectral reflectance is not a standard fixed quantity. 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.

Whiteness of a material containing a FWA also depends strongly on the spectral properties of the illumination for both visual evaluations and instrumental measurements.[8,9] Some of the popular whiteness measures assign high whiteness values to colors of obviously high chroma, or saturation. This anomaly led us to propose a new whiteness formula that correlates better with observers' evaluations.[10]

TECHNICAL CONSIDERATIONS

CIE Whiteness

In 1981, CIE recommended an equation for whiteness, W, related to basic CIE tristumulus measurements and having the form:[1,11,12]

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

where x and y are the CIE chromaticity co-ordinates[4] and x_n and y_n are the co-ordinates for the perfect reflecting diffuser in the D_{65} illumination.

This equation is complemented by the tint value equations:

$$T = 1000(x_n - x) - 650(y_n - y), \quad \text{for a } 2^\circ \text{ observer} \quad (2a)$$

or

$$T = 900(x_n - x) - 650(y_n - y), \quad \text{for a } 10^\circ \text{ observer} \quad (2b)$$

These give tint-values in the red or green direction for the 1931[4] or 1964 CIE standard observer[13] respectively. A positive value of T indicates greenishness and a negative value indicates reddishness.

These equations are to be used only in a limited region. Criteria for whiteness are W must fall within the limits given by:

$$5Y - 280 > W_{CIE} > 40 \quad (3a)$$

and the tint value T shall fall within the limits given by:

$$3 > T > -3 \quad (3b)$$

The W formula describes an axis in the blue-yellow direction with a dominant wavelength of 466 nm in the CIE chromaticity diagram, and the criteria of later equations limit the extent to which a sample may enter the blue or yellow regions or stay towards the red or green and still be classified as white. According to this definition the perfect reflecting diffuser has a whiteness of 100 and a zero tint value.

One major disadvantage in CIE whiteness is that this system of equations does not clarify whether the whiteness has any component of blueness or yellowness. CIE recommends that the formulae should only be used for relative evaluations and are valid only for measurements with a single instrument at a given time and without reference to a white scale. Evaluations with the formulae are significantly improved if the sample illumination is stabilized and fitted as closely as possible to a desired illuminant. This also improves the matching of different measuring instruments for whiteness. The tint deviation or hue value can still not be adequately matched.[12]

Whiteness and tint formulae proposed by CIE are restricted to samples differing not too broadly in tint and fluorescence. The measurements have to be executed with the same instrument at about the same time. The formulae produce relative, not absolute, white assessments seemingly adequate for commercial uses in many cases. Again, the measuring instruments must have illumination resembling daylight.[7,14]

If the sample illumination is stabilized, assessments with the CIE formulas are significantly improved, and samples to be compared do not have to be measured at the same time. This also improves the matching of different measuring instruments for whiteness. The tint deviation or hue value can still not be adequately matched.[12,15]

The Ganz Whiteness Formula

The whiteness formulae that Ganz proposed is as follows:[6,7]

$$W = (D*Y) + (P*x) + (Q*y) + C \qquad (4)$$

Y, x, y are colorimetric variables,

D, P, Q and C are formula parameters.

Ganz provides that whiteness preferences must be precisely definable for a whiteness formula to be useful. The three-color attributes (hue, saturation and lightness) provide the information the best. Their influence on whiteness is given by Ganz formula as:

H=Hue: $\delta W/\delta H$ S=Saturation: $\delta W/\delta S$ Y=Lightness: $\delta W/\delta Y$

As seen above, these quotients are not formulas with fixed parameters. In fact, the parameters need to be calculated after the white preference has been fixed.[14]

$$D = \delta W/\delta Y \tag{5}$$

$$P = (-\delta W/\delta S)\ (\cos(\phi+\eta)/\cos\phi) \tag{6}$$

$$Q = (-\delta W/\delta S)\ (\sin(\phi+\eta)/\cos\phi) \tag{7}$$

$$C = \{-W_0\ (1-\delta W/\delta Y) - (px_1) - (Qy_1)\} \tag{8}$$

All calculations are made in radians, where η is the angle between a reference dominant wavelength (RWL) and the x-axis of the standard chromacity diagram. RWL represents an approximately neutral white, and can have the value λ_0= 470 nm, where

$$\eta = \mathrm{atan}(y_1 - y_0)/(x_1 - x_0) = 0.84084(D_{65}/10°) \tag{9}$$

x_1 and y_1 are the coordinates of the achromatic point; x_0 and y_0 designate the point of intersection of the RWL with the spectrum locus.

At $D_{65}/10°$ $x_1 = 0.3138$, $y_1 = 0.3310$, $x_D = 0.11518$, $y_D = 0.10904$

$$\delta W/\delta H = -\delta W/\delta S * \tan\phi = -1071.8$$

$$S = (\tan\psi(x_1 - x) - (y_1 - y)/(\tan\psi\cos\eta - \sin\eta) \tag{10}$$

Where $\psi = \phi + \eta + \pi/2 = 2.67343$.[7]

Any desired preference can be built with this formula. The following standard specifications have been found to be the good for constructing a theoretical whiteness formula through practical experience and accepted by the largest number of people:

a) Effect of lightness $\delta W/\delta Y$ = D= 1

b) ϕ that enters into the $\delta W/\delta H$, is preferably taken as 15° to achieve a neutral hue preference (radians: 0.26180)

c) $\delta W/\delta S = 4000$

d) W_0 is physically ideal white, and best taken as 100

P, Q and C formula parameters can be calculated from these inputs and constructed formula and its weighing factors, the three color attributes, hue, saturation and lightness are precisely defined within the whiteness results.[14]

Ganz and Griesser introduced a tint deviation formula as an additional factor to the in the calculation of whiteness to make instrumental whiteness assessments more accurate.

$$\text{Tint Deviation} = (m*x) + (n*y) + k \tag{11}$$

where x and y are colorimetric variables and m, n and k are the formula parameters that are specific to the measuring instrument.[14]

Tint deviation can also be correlated with the white scale as a reference. Whether or not a sample possesses the same hue as an equally white scale or whether it is greener or redder, and by how much can be found with this calculation. Of the three-color attributes, hue is the one most subjected to individual preference.[12]

Griesser [12] proposed in his earlier study that the CIE whiteness formula can be significantly improved if the sample illumination is stabilized and fitted as closely 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 are entirely different. This study aims to further explore whiteness formulas within their context and investigate the correlation between the formulas and perceived appearance. The construction and illumination source of the instruments were considered.

Hunter Whiteness

Hunter whiteness is given by [2]:

$$W_H = L - 3b, \tag{12}$$

where L and b are the Hunter values [2].

Individual preference for whites makes the optical evaluation of whiteness vary from one observer to another. Most of the whiteness formulas used today rate bluish whites higher than neutral whites in accordance with the judgment of most observers. Commonly, color of actual white can deviate from ideal white in two directions; toward yellow or green. Deviation from ideal white towards yellow is considered more serious for normal observers. Blue dyes or pigments are added to reduce yellowness while increasing grayness which benefits the Hunter whiteness whose formulation gives the blue component three times as much weight as the lightness component.[2] Therefore, whiteness values of significantly higher than 100 are possible.[2]

The application of CIE whiteness is restricted to specimens that are called white commercially and to W values greater than 40. On the other hand, equal differences in CIE whiteness do not always represent equal perceptual differences in whiteness.[2]

Hunter concludes that the best whiteness index will be based on an equation that locates the position of an ideal white, which is not the perfectly reflecting diffuser but at a "blue" white, and measures whiteness as the distance in color space from the sample to that ideal.[2]

Fleming-Aksoy Whiteness Formulas

Recently[10], we proposed two new whiteness formulas, based a combination of theoretical and empirical considerations. One formula, N_{FA}, corresponds to a maximum whiteness at the perfectly reflecting diffuser, i.e. zero chroma in the CIE[1] $L^*a^*b^*$ space (or Hunter[2,16,17] Lab space). The other formula, W_{FA}, is based on the assumption that observers prefer a more "blue" white, but only if it is not too blue. Thus, a local maximum in whiteness is expected. The coefficients in W_{FA} were determined from the CIE formula by requiring that the two formulas have the same value and derivatives with respect to a^* and b^* at zero chroma ($a^*=b^*=0$).

These formulae are given by:

$$N_{FA} = L^* \left({}^{1}/2\right)^{(C/C_0)^2} \tag{13}$$

and

$$W_{FA} = Y\left({}^{1}/2\right)^{[a^*(a^*-2a_1^*)+b^*(b^*-2b_1^*)]/C_2^2} \tag{14}$$

where

$C = (a^{*2}+b^{*2})^{1/2}$ is the chroma and C_0 and C_2 are characteristic chroma determined from the boundary region defined by inequalities 3.a_1^* and b_1^* are the coordinates for the local maximum whiteness at constant lightness Y (or L^*). They are determined by equating the corresponding derivatives of W_{FA} and W_{CIE} with respect to a_1^* and b_1^* to one another. The expressions are:

$$a_1^* = \alpha(Y_n/Y)^{4/3}C_2^2/(200\ln 2) \quad \text{and (15b)}$$

$$b_1^* = -\beta(Y_n/Y)^{4/3}C_2^2/(200 \ln 2) \tag{16c}$$

where

$\alpha = 3x_n(900y_n - 800z_n)/500$ and $\beta = 3z_n(800x_n + 1700y_n)/200$.

Basic Problems in Instrumental Whiteness Assessment

A physical property, reflectance, is not a standardized, absolute magnitude even if it is related to absolute whiteness. Different measurement devices and different illumination chambers lead to differences in results. The results are also influenced by the inclusion or exclusion of the gloss depending both on the measurement device and sample. Another factor is the surface structure of the measured sample that has influence on the results depending on the design of the instrument. Coated papers containing FWA are mainly influenced by the FWA type, age, illumination (lamp characteristics) and the design of the instrument.[14]

A full colorimetric scan needs to be performed to fully characterize whiteness because whiteness and hue values together provide a more complete assessment of whiteness. If there are significant differences in lightness, Y values should also be specified.[14] The degree of fluorescence is a function of the UV-content, the incident radiation must be carefully defined if the whiteness value is to be accurate.[3]

The intensity of fluorescence of FWA-added samples depends on the spectral power distribution of the illumination, especially in the UV region. Differences among visual assessments, measurements, and different measurement devices also arise from differences in of the spectral power distribution of the illumination.[7]

In the measurement of the optical properties of fluorescent materials, it is essential that the UV-content of the light source be defined, and that techniques are developed for calibrating or adjusting the level.[4]

In a given instrument, the degree of fluorescence developed and thus the reference factors evaluated refer to the actual light source in the instrument and to nothing else, where the "light source" refers not to the lamps with which the instrument is equipped, but to the light incident on the sample. The light source is defined in this sense that is thus influenced by the properties of the sphere lining, by any filters included, and indeed to some extent by the sample itself, as is discussed later.[3]

EXPERIMENTAL PROCEDURES

A coating suitable for a #1 publication paper grade was prepared according to the formulation outlined in Table 1. The coating consisted mostly of calcium carbonate and SBR latex, and contained smaller amounts of # 1 clay, calcined clay, TiO_2, and plastic pigment. For the coatings containing FWA, the TiO_2 was replaced with the same volume of $CaCO_3$, since TiO_2 adversely influences the FWA's UV absorbance and thus its whitening performance[18,19]. 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 addition levels.

Table 1. Coating Formulation Used in the Experiments

Coating Ingredient	Parts
$CaCO_3$	65
Clay#1	15
Calcined Clay	10
TiO_2	5
Plastic Pigment	5
SB Latex	14

In order to determine the appropriate dye addition levels needed to shift the shade of the papers around in the color space, preliminary studies were made where the dye levels added to the applied coatings were varied and measurements made on a GretagMacbeth spectrophotometer. The resulting blue and black dye addition levels selected for instrumental and observer evaluations were 0.025, 0.05, and 0.1 % in dry pigment weight. The selected final red dye addition levels were 0.0005, 0.001, 0.025 and 0.05 % in dry pigment weight.

The same methodology was followed for the selection of fluorescent brightening agent, FWA (Bayer- Blankophor UV liquid). The FWA addition levels selected ranged from .25 to 1 % FWA on weight of dry pigment. The selected FWA addition levels for instrumental and observer evaluations were 0.24, 0.49, and 0.97 % on dry pigment weight.

The tinted and FWA containing coatings were applied at 10 g/m^2 to a commercially produced base paper made from bleached Kraft and mechanical pulp (100 g/m^2 basis weight) using a CLC (Cylindrical Laboratory Coater).

The resulting coated papers were measured for their optical properties with a GretagMacbeth Spectrolino spectrophotometer. Calculated CIE[5], Hunter[2], Ganz[6,7] N_{FA}[10] (near neutral) and W_{FA}[10] (high luminance and medium saturation) whiteness values were compared. The CIEXYZ[4] and CIELab[1] color measurement systems for the spectrophotometer was used for this purpose. Coated papers were also evaluated for their optical appearance by 20 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, and black and 4 addition levels of red dyes. The last group consisted of the FWA treated coatings at 3 addition levels. Observers were asked to rank each sample group separately for their perceived whiteness in a 5000 °K light booth. Samples that appeared whitest within the same group were ranked as extraordinarily 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

Figure 1 shows the color spectra of coated # 1 publication grade paper, where blue, black and red dyes and FWA were added to the coating. The spectrophotometric curves were acquired using a GretagMacbeth Spectrolino Spectrophotometer.

Addition levels were 0.50 wt.% for blue and black (on dry pigment weight), 0.01% for red, and 0.486 pph (dry/dry) % for FWA. Figure 1 shows that the blue absorbs heavily in the middle of the spectrum from the green-yellow to yellow-orange region (540-620nm). The red dye absorbs mostly in the green region (490-570 nm). The the reflection spectrum for the black dye looks similar to the standard (coated and no dye added), but its curve falls in the lower reflectance percent scale. The FWA absorbs UV light as can easily be seen the figure. The reflectance values for the FWA are higher than any other dye and the standard in the blue region (420-460 nm) suggesting remitted UV light in the blue region by the FWA. Thus, it can be said by looking at its spectra from both of the figures that 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 Illuminate A light source used to illuminate the specimen in most spectrophotometers is unable to excite most of the FWA present in the coating layer, because of its very low intensity in the UV. This results in a small peak in the spectra at the 435 nm wavelength by the instrument and does not represent what would be observed by a viewer under daylight (D_{65}) conditions. As stated previously [8,9], a Xenon light source would be a better choice for measuring the effects of human observation of a FWA treated paper.

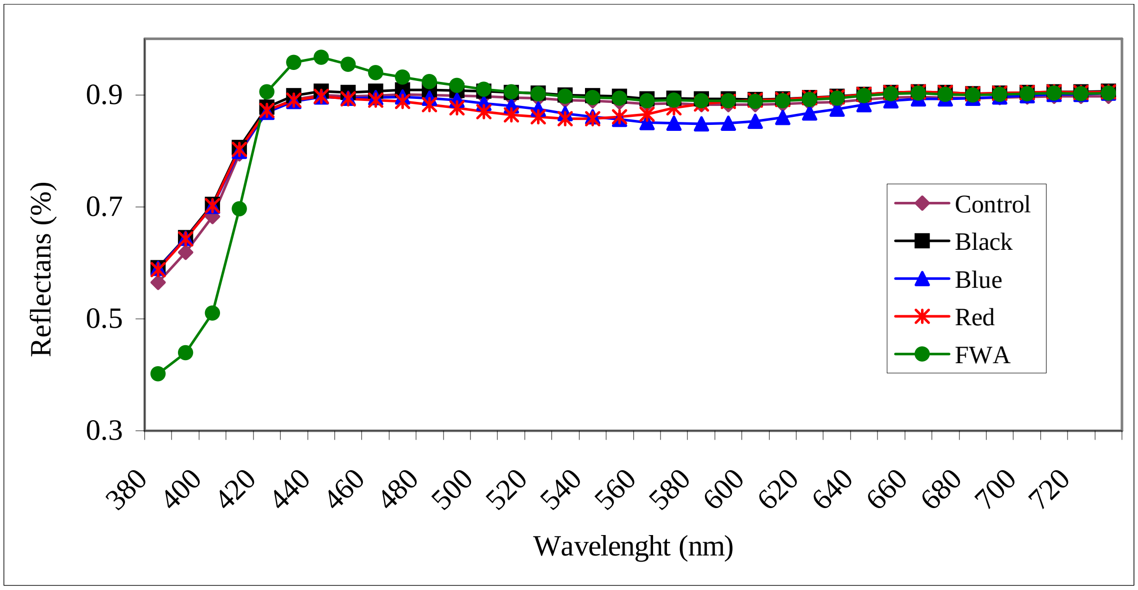

Figure 1. Color reflection spectra of coated paper, blue, black and red dyes and FWA.

Figure 2 was obtained through the statistical analyses of data collected from the rankings of 20 randomly selected observers who evaluated the optical appearance of each sample (how white they observed each sample from scale of 0-very white to 5-not very white). It was found that the samples appeared whiter to the observers up to where the maximum level of blue and black additions (0.1% on dry pigment weight) were made. At the maximum dye level, the coated samples appeared less white. This is due to the tint values being high at these levels of addition.

An increased appearance of whiteness is seen at the minimal addition level of red dye. This increase is a lot more significant than what was found for the other samples. As the addition level of red dye increased, the sample appeared less and less white to the observers.

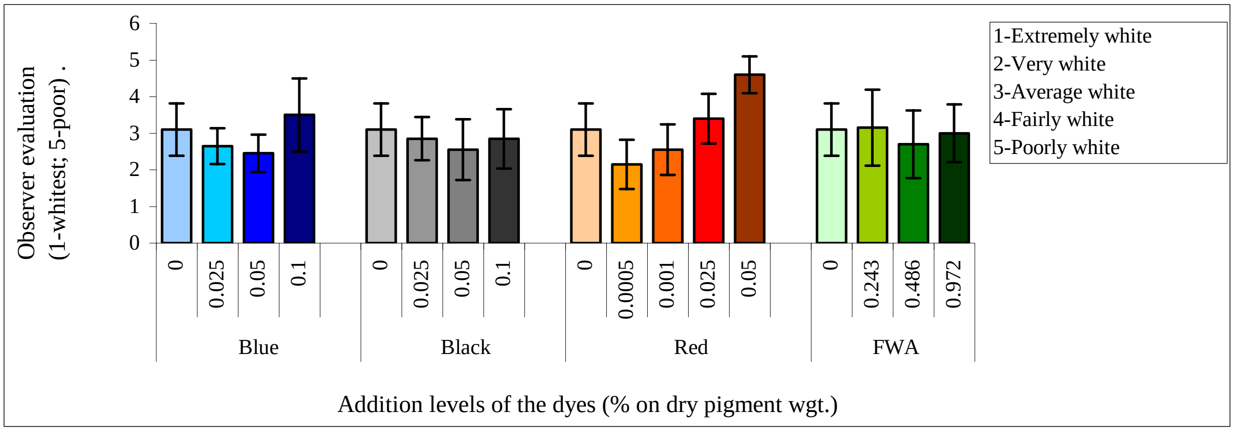

Figure 2. Observer evaluation of coated publication #1 grade papers at varying addition levels of blue, black and red dyes and FWA.

Figures 3 and 4 show the representative CIE, Hunter, Ganz, N_{FA} (near neutral) and W_{FA} (high luminance, medium saturation) whitenesses for blue, black and red tinted papers at D_{65}/10° and C/2°, respectively. All whiteness values but N_{FA} and W_{FA} at C/2° increase as the addition level of blue dye is increased. This increase is most pronounced for the Ganz whiteness. For the blue tinted samples at D_{65}/10°, the correlation coefficient for N_{FA} with the average rank data was -0.65. The corresponding correlation coefficients were 0.46 for Ganz, .44 for CIE and Hunter and .09 for W_{FA}. The corresponding rank correlations were –0.20 for W_{FA}, CIE, Ganz and Hunter, and 0.2 for N_{FA}. For C/2°, the corresponding correlation coefficients for average rank are -.12 for W_{FA}, .16 for N_{FA}, .44 for CIE and Hunter and .45 for Ganz and rank correlation coefficients are 0.40 for W_{FA}, -0.20 for CIE, Hunter and Ganz and -0.40 for N_{FA}. Only the coefficients for N_{FA} at D_{65}/10° and W_{FA} at C/2° have the correct sign. A negative sign for correlation with average rank is correct for a whiteness value (Higher whiteness means higher rank, which corresponds to a lower rank value). A positive sign for rank correlation is correct because both are based on rankings from 1 to n. The correlations are all poor because CIE, Hunter, and Ganz correspond to monotonically increasing whiteness values for increasing blue dye, while N_{FA} corresponds to monotonically decreasing whiteness. In contrast the observer data indicate a maximum whiteness for .05% blue dye (Figure 2). Of the whiteness formulas, only W_{FA} is capable of producing a local maximum in whiteness. However, the .05% blue dye corresponds to a b^* value of -1.7, while the maximum for W_{FA} at D_{65}/10°is closer to b^*=-5. For C/2°, the local maximum whiteness at .05% blue dye is correctly predicted by W_{FA}, but the whiteness value at .1% blue dye is higher than perceived by the observers. Thus, the overall correlation is still poor, although all of the others are even worse.

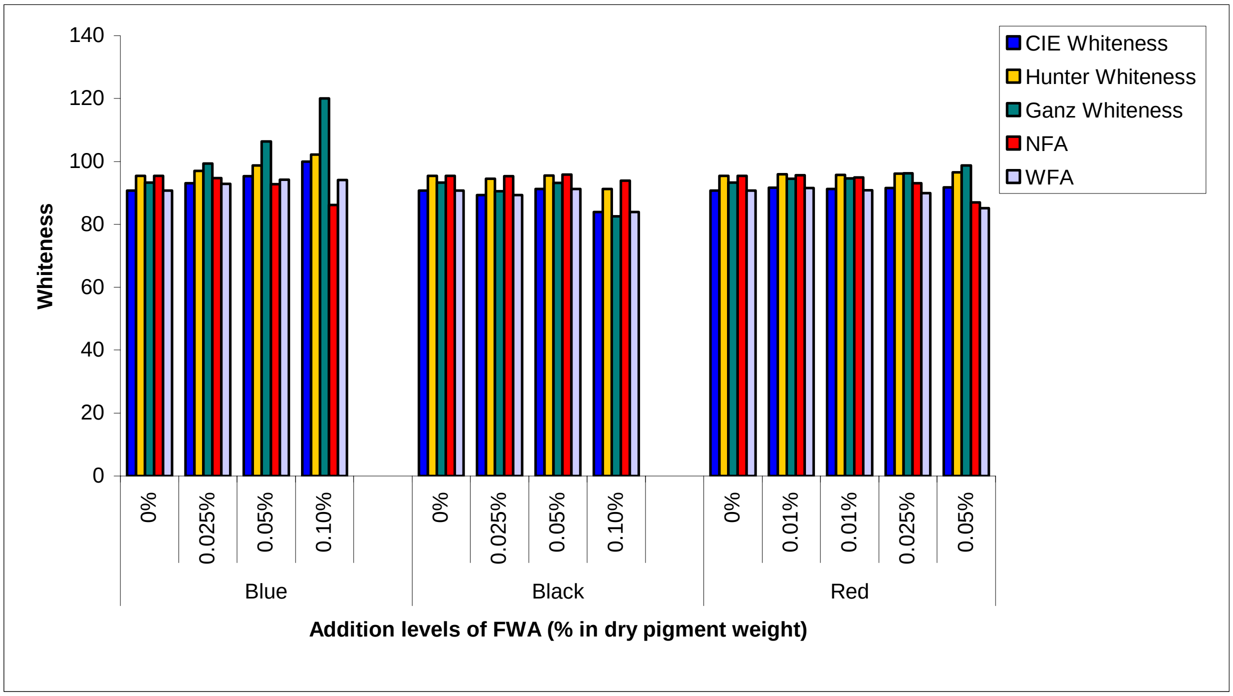

Figure 3. CIE, Hunter, Ganz, N_{FA} and W_{FA} whiteness values for blue, black, red dyed # 1 publication grade papers at D65/10°.

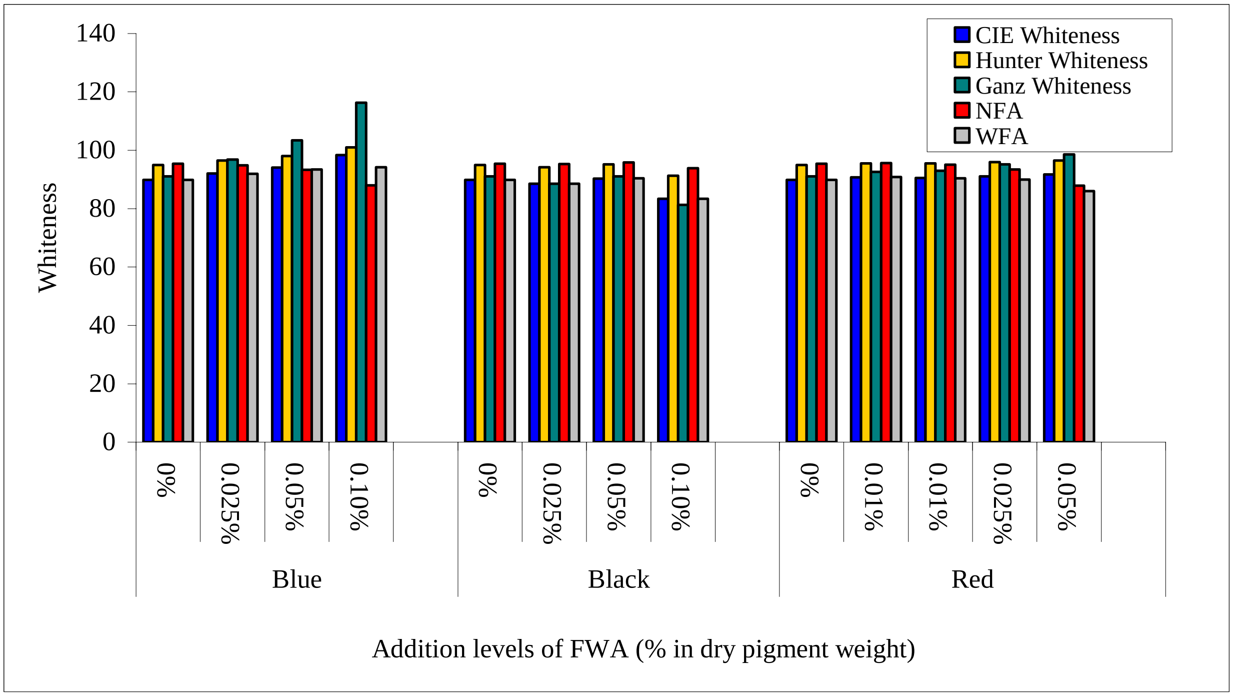

Figure 4. CIE, Hunter, Ganz and N_{FA} and W_{FA} whiteness values for blue, black, red dyed # 1 publication grade papers at C/2°.

All whiteness values changed only slightly after addition of the red dye. For D65/10°, W_{FA} and N_{FA} exhibited the best agreement with the observer assessments, each with a correlation coefficient of -0.94. The corresponding correlation coefficients for Ganz, Hunter and CIE were 0.85, 0.75 and 0.65 (with the wrong sign), respectively. Again, W_{FA} and N_{FA} produced the highest rank correlation each with 0.90. Rank correlations were -0.60 for CIE and Hunter and -0. 70 for Ganz. For C/2°, W_{FA} exhibited the best agreement with the observer assessments, with a correlation coefficient of -0.95, followed by N_{FA} with -0.93. The corresponding correlation coefficients for Ganz, Hunter and CIE were 0.85, 0.72 and 0.40 (again with the wrong sign), respectively. W_{FA} produced the highest rank correlation of a perfect 1.00, followed by N_{FA} with 0.90. Rank correlations were -0.30 for CIE, -0.60 for Hunter and -.70 for Ganz.

Whiteness values varied insignificantly with black dye addition in both figures. The corresponding correlation coefficients and ranking correlations for black dye added samples were fairly small for all whiteness formulas. For D_{65}/10°, the correlation coefficients were -0.25 for N_{FA}, -0.12 for W_{FA} and CIE, and -0.11 and -0.06 for Hunter and Ganz, respectively. Ranking correlations were 0.40 for W_{FA}, N_{FA}, CIE and Hunter, and -0.20 for Ganz. For C/2°, the correlation coefficients were -.26 for N_{FA}, and -0.12, -.011, -0.10, -0.05 for W_{FA} CIE, Hunter, Ganz, and respectively. Ranking correlations were 0.40 for W_{FA}, N_{FA}, CIE and Hunter, and -0.20 for Ganz. It should be noted that the compared mean ranks from observer evaluations and whiteness values were in a very narrow region. The correlations for C/2° are totally consistent with those of the D_{65}/10° data.

The correlation coefficients for the red dye tinted samples were comparatively high, while variations of these test samples were lower. The main reason would be that observers give similar weights and exhibit similar preferences and responses towards test samples that are slightly tinted with red dye. All calculated correlation coefficients for black and blue added test samples were fairly small. One reason could be due to the fact that the reliability of the observers is variable, so it is hard to know the correct weighting. A higher number of observers would have reduced the variability and/or increased the correlation coefficients and ranking correlations. Additional test samples in each group would need to be constructed to reduce variation and probably increase the correlation coefficients and ranking correlations. However, N_{FA} gives the highest correlation coefficients in each test sample group except for the red tinted samples, where the highest correlation coefficients belong to W_{FA}. It appears overall that the N_{FA} and W_{FA} exhibited a better correlation with observer evaluations over the CIE, Hunter, and Ganz whiteness formulas. In particular, the overall average ranking correlation coefficients were -0.72 for N_{FA}, -0.27 for W_{FA} and 0.01, 0.04 and 0.10 for CIE, Hunter and Ganz, respectively for D_{65}/10° evaluations and -0.73 for N_{FA}, -0.34 for W_{FA} and -0.03, 0.00 and 0.05 for CIE, Hunter and Ganz, respectively for C/2° evaluations. The overall rank correlations were 0.54 for W_{FA}, 0.34 for W_{FA}, 0.00 for CIE and Hunter and -0.16 for Ganz for D_{65}/10° evaluations and 0.69 for W_{FA}, 0.23 for N_{FA} and -0.03, 0.00 and 0.05 for CIE, Hunter and Ganz, respectively.

The CIE tint values for each dye, at each addition level, were calculated and are shown in Figures 5 and 6 for a D65/10° and C/2°, respectively. All dyes, at all addition levels, were within the inequality region for whiteness as specified by CIE with the exception of highest addition level red dye (0.5% in dry pigment weight). The Ganz tint deviation values correlate well with the CIE tint values for all edition levels except for the highest level of red dye addition (0.05% in dry pigment weight).

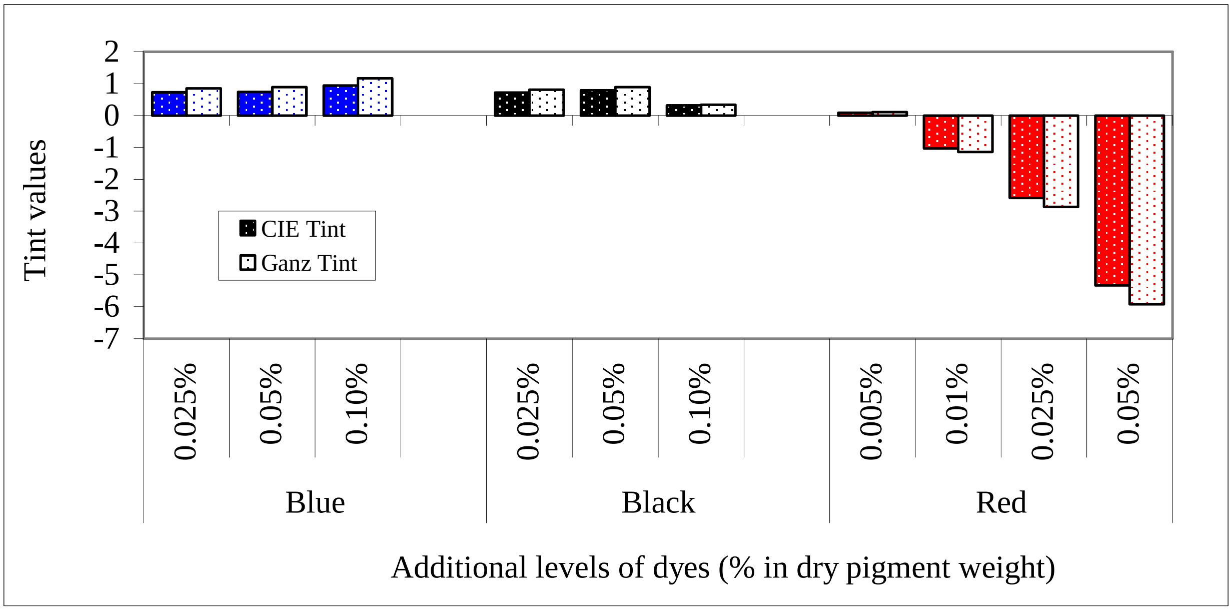

Figure 5. CIE and Ganz Tint values for blue, black, red dyed #1 publication grade papers at D65/10°.

It should be noted that the metrics are different for the CIE and Ganz tint values; the threshold for distinguishing different whiteness is defined by the Ganz scale as being about 5 points, while for CIE whiteness it is about 2.3 to 2.4 points. The threshold for distinguishing different tints lies at 0.5 points.

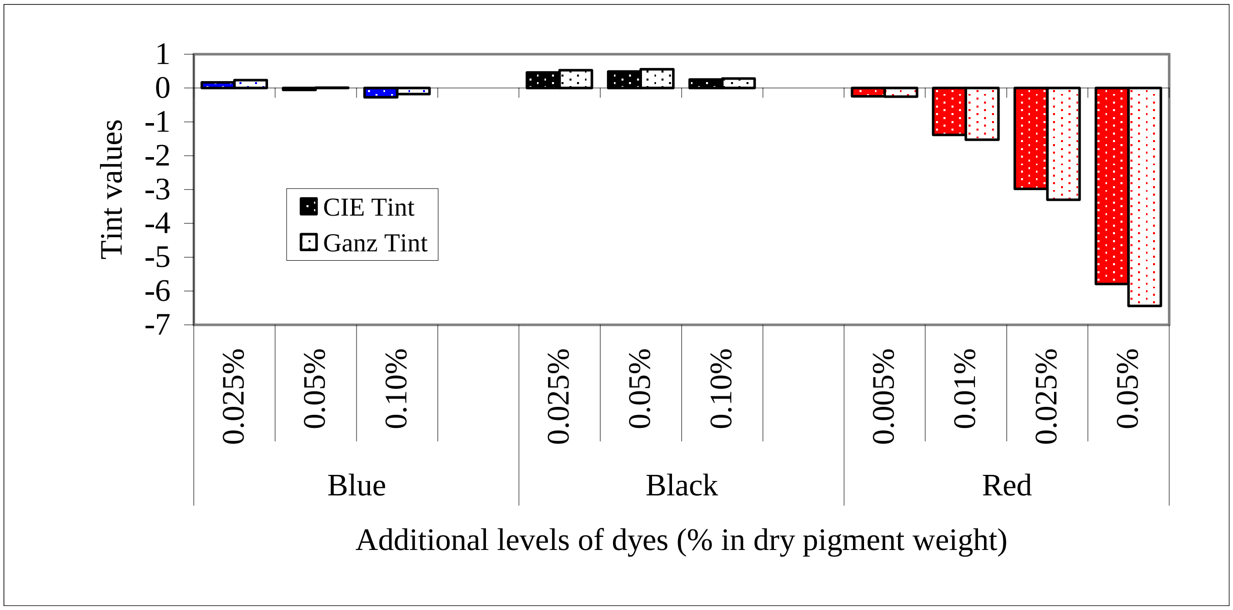

Figure 6. CIE and Ganz Tint values for blue, black, red dyed #1 publication grade papers at C/2°.

The CIE and Hunter L values for the three dyes and FWA added samples are given in Figures 7 and 8 for D65/10° and C/2°, respectively. The L values decreased significantly with the addition of blue and black dye. This decrease is more pronounced with blue dye relative to black.

CIE and Hunter a, b values for the three dyes and FWA samples are shown in Figures 9 and 10 for D65/10° and C/2°, respectively. The “a” values of the red tinted samples exhibit a significant increase as expected. This increase is less pronounced for the other samples. The b values of the blue and red tinted samples show a significant decrease with dye addition.

The b values for FWA samples decreased significantly at low addition levels and then appeared to reach an asymptotic value. Such effects are well known for FWA addition[20], where no benefit is obtained beyond some addition level. Both the “a” and “b” values were near 0 for the black dyed samples.

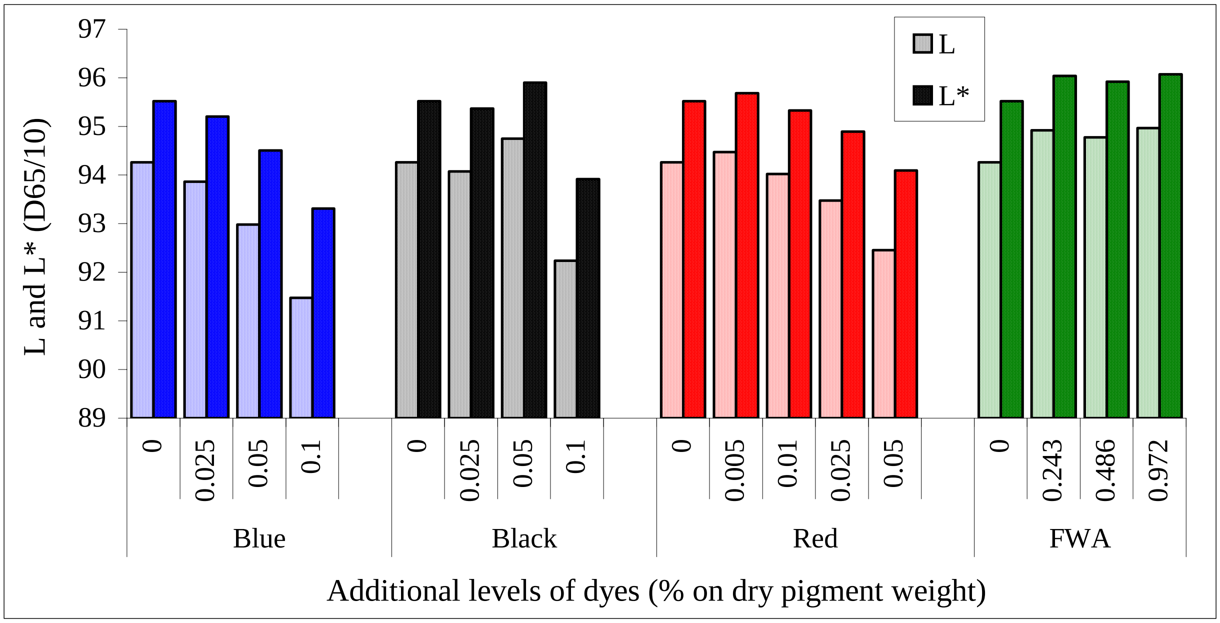

Figure 7. CIE and Hunter L values for blue, black and red dyed #1 publication grade papers at D65/10°**.**

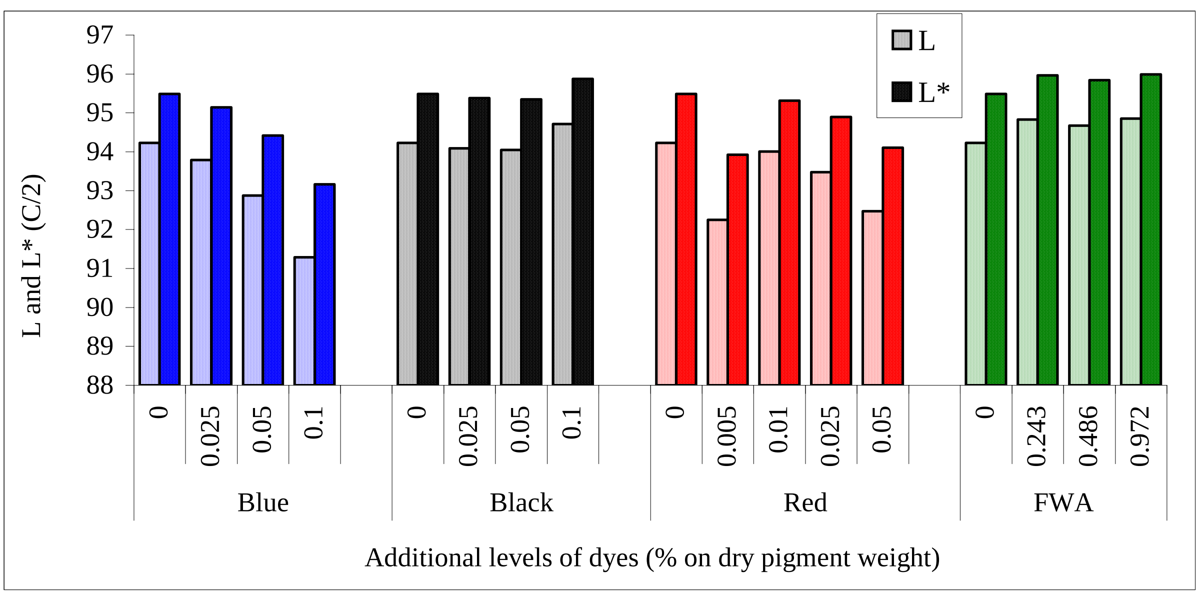

Figure 8. CIE and Hunter L values for blue, black and red dyed #1 publication grade papers at C/2°.

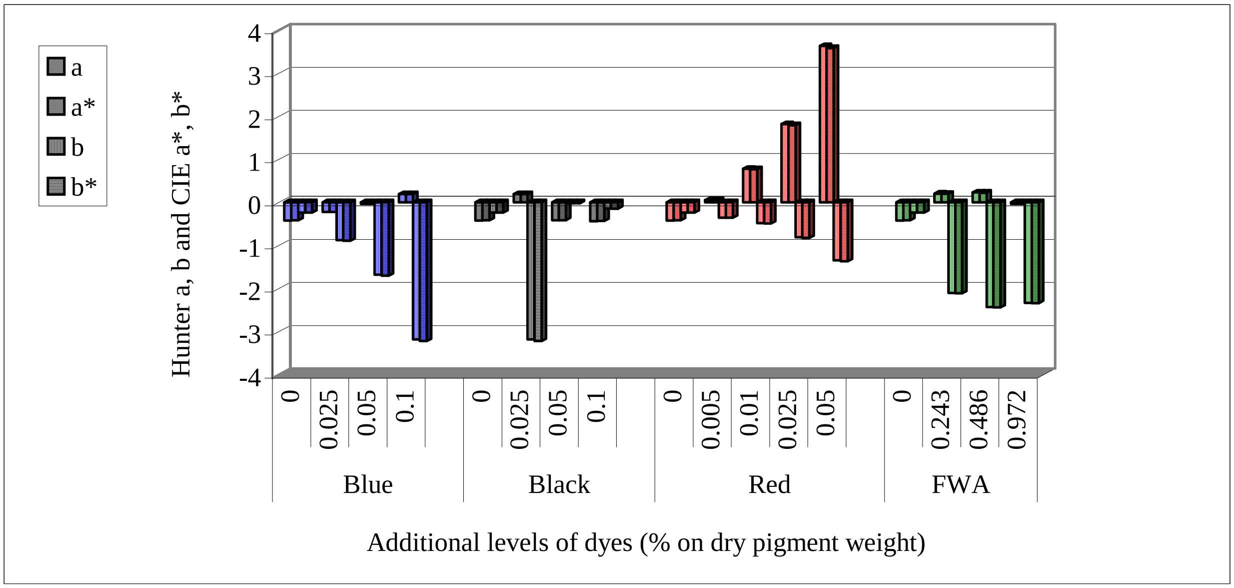

Figure 9. CIE and Hunter a and b values for blue, black and red dyed #1 publication grade papers at D65/10°.

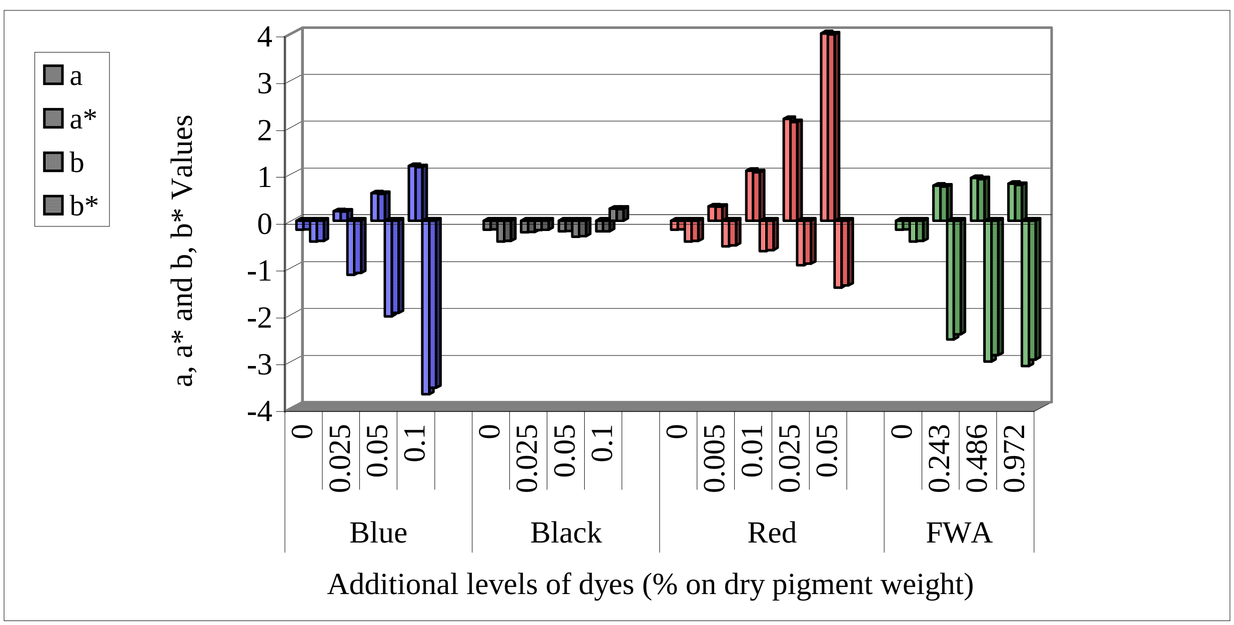

Figure 10. CIE and Hunter a and b values for blue, black and red dyed #1 publication grade papers at C/2°.

Figures 11 and 12 show CIE, Hunter, Ganz N_{FA} and W_{FA} whiteness values of the papers containing FWA at D65, 10° and C, 2°, respectively. The figures show all the whiteness values, except N_{FA}, to be higher for the uncoated base sheet than for the coated sheets with no FWA addition. This indicates that the coating layer is reducing the contribution of the base paper to the optical properties of the coated paper. This could be important because it indicates that adding an FWA into the base sheet prior to coating may not provide the desired optical effect. As the FWA addition level increased, the Ganz, CIE Hunter and WFA whiteness values increased. This increase was more pronounced for the Ganz values. The N_{FA} whiteness was found to be fairly insensitive to FWA addition. This is probably because the FWA adds to the blue component of the color space. Both the CIE and Hunter whiteness formulas give a higher weighting to the blue component than the lightness (L, L*) component. In fact, the Hunter whiteness formulation gives the blue component three times as much weight as the lightness component. On the other hand, the N_{FA} is designed to detect changes in the neutral whiteness and the formula does not choose any color component over any other as a preference color component.

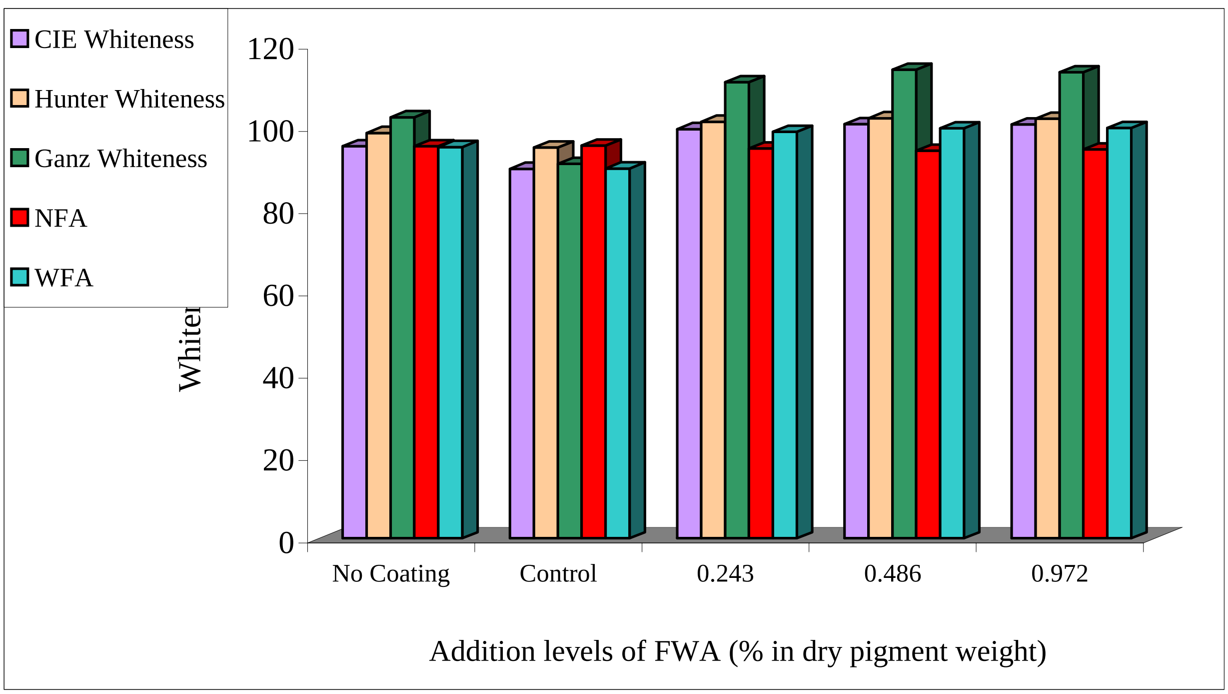

Figure 11. CIE, Hunter, Ganz, N_{FA} and W_{FA} whiteness values of FWA #1 publication grade papers at D_{65}/10°.

The correlation coefficients for the average rank data were 0.80 for N_{FA}, -0.57 for W_{FA}, -0.58 for CIE, -.59 for Hunter and -0.60 for Ganz for D_{65}/10°. The corresponding rank correlations were -0.80 for N_{FA}, 0.60 for W_{FA} and 0.80 for Ganz, CIE and Hunter. The correlation coefficients for the average rank data were 0.81 for N_{FA}, -0.60 for W_{FA}, -0.62 for CIE, -.63 for Hunter and Ganz for C2°. The corresponding rank correlations were -0.80 for N_{FA}, 0.60 for W_{FA}, Ganz, CIE and Hunter.

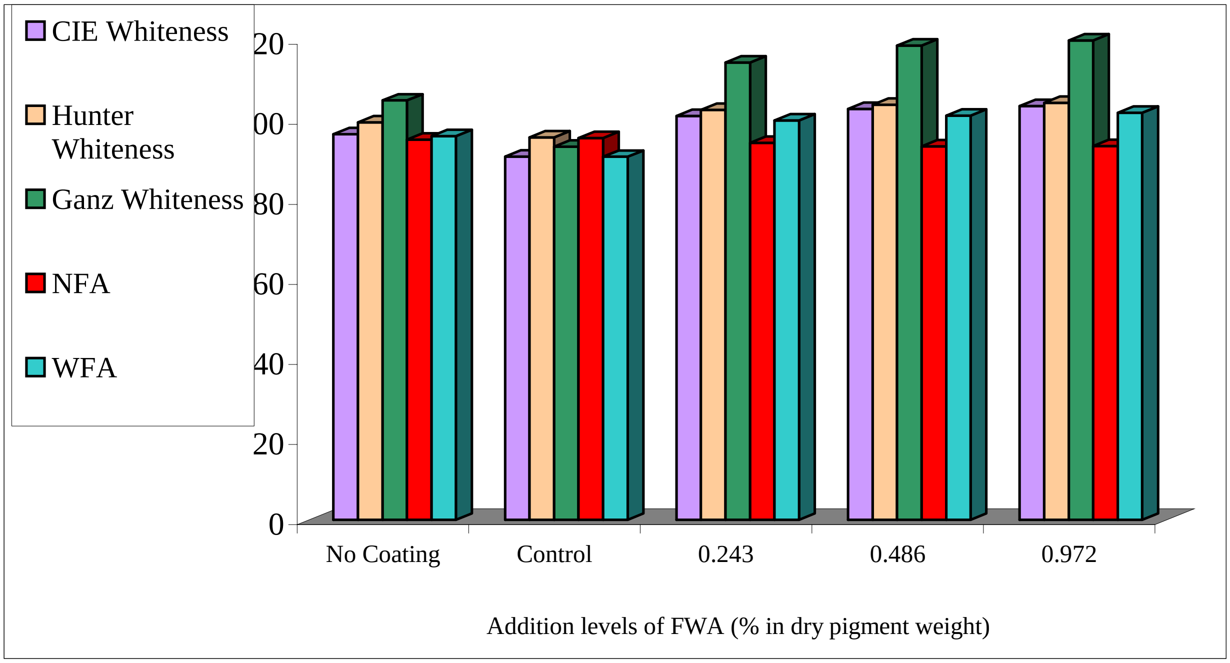

Figure 12. CIE, Hunter, Ganz, N_{FA} and W_{FA} whiteness values of FWA #1 publication grade papers at C/2°.

The tint values for FWA dyed samples were all well within the inequality region. The lowest tint value calculated was 0.014 for the 0.24 % FWA sample while the largest tint value calculated was 0.603 for the control sample (no FWA added).

Figures 13 and 14 show the FWA influence measured with the GretagMacbeth Spectrophotometer for D_{65}/10° and C/2°, respectively. Measurements were made with and without a UV-filter and the differences in the calculated whiteness values are given as the fluorescent effect. The quenching effect of the coating is again seen. As the FWA the addition level increased, the fluorescent effect increased. The increase is significantly higher for the Ganz whiteness than for the CIE, Hunter and N_{FA} whitenesses. The W_{FA} whiteness remained near constant regardless of how much FWA was added.

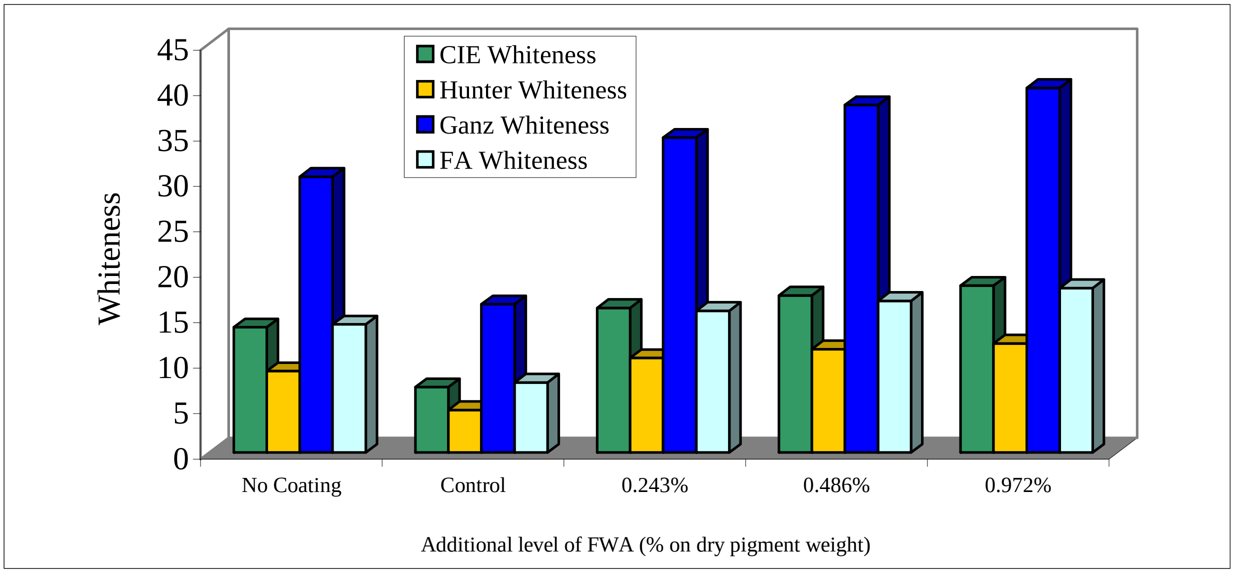

Figure 13. Fluorescent effect at D_{65}/10°.

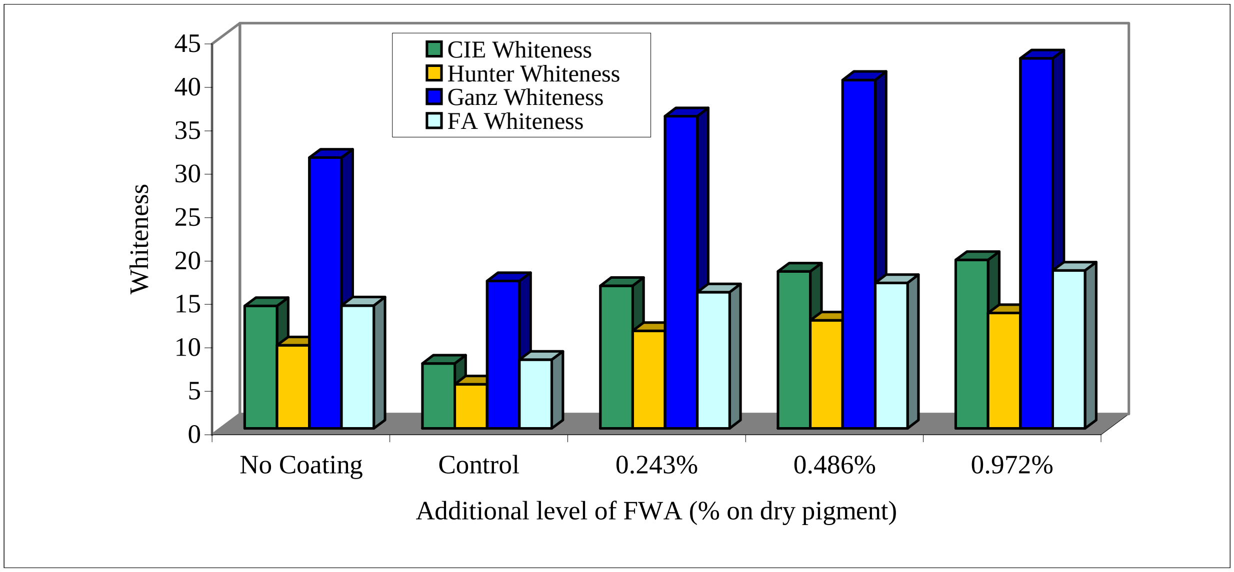

Figure 14. Fluorescent effect at C/2°.

CONCLUSIONS

The N_{FA} and W_{FA} whiteness values exhibited the best correlation with observer assessments overall. All other whiteness values increased more as the addition level of blue dye increased even though samples appeared less white to the observers at the maximum blue addition level. In addition, L, and L* values exhibited a sharp decrease while b and b* values showed a significant increase towards blue as the blue dye addition levels increased. The N_{FA} whiteness correlated very poorly with the observer assessments for the FWA treated samples. WFA and the other whiteness formulas correlated better with the FWA data. The correlation between the observer assessments and all the whiteness formulas studied correlated well for red tinted samples. The change in whiteness values were much less for the red and black tinted papers in comparison to large changes seen in L, L*, a, b and a*, b* values. The correlation coefficients and ranking correlations were found to be fairly low for the black dyed samples for each of the whiteness formulas studied. The correlation coefficients of the N_{FA} was slightly higher than that of the CIE, Hunter and Ganz whiteness formulas for the black dye samples.

The fluorescent effect of the uncoated paper was quenched after coating the sheet. This raises the question as to whether adding an FWA prior to coating provides any real advantage to the final desired optical properties of the paper. The N_{FA} whiteness formula did not detect any changes in whiteness as the addition level of FWA increased. This is probably due to the added blue shade to the surface of the measured samples with the usage of FWAs. The W_{FA}, CIE, Hunter and Ganz whiteness values increased as the addition level of FWA increased.

REFERENCES

1. *CIE, Recommendations on Uniform Color Spaces, Color-Difference Equations, Psychometric Color Terms, Supplement No. 2 of CIE Publication No. 15* (E-1.3.1) 1971, Bureau Ventral de la CIE, Paris 1978.
2. Hunter R.S., Harold R.W., "The Measurement of Appearance", (John Wiley & Sons, 1987).
3. W. H. Banks (Editor), "Advances in Printing Science and Technology", Proceedings of the 20th Research Conference of the International Association of Research Institutes for the Graphic Arts Industry, (Academic, Moscow, USSR, September 1989), pp. 191-217
4. *CIE Proceedings 1931*, Cambridge University Press, Cambridge, 1932.
5. CIE 15.2 – 1986, *Colorimetry*, Second Edition, 1986, Corrected Reprint 1996.
6. Ernst Ganz, "Photometric Specification and Colorimetric Evaluation", Applied Optics, **15**:9, 2039-2058, (September 1976).
7. Ernst Ganz, "Whiteness Formulas: A Selection", Applied Optics, **18**:7, pp. 1073-1078, (April 1979).
8. Burak Aksoy, Margaret K. Joyce and Paul 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).
9. Burak Aksoy, Margaret K. Joyce and Paul D. Fleming, "Exploring Myths of Measured and Perceived Whiteness", submitted to Applied Optics.
10. Burak Aksoy, Paul D. Fleming and Margaret K. Joyce, "A New Measure of Whiteness that Correlates with Perceived Color Appearance", submitted to Applied Optics.
11. Roy S. Berns, *Principles of Color Technology*, (John Wiley & Sons, 2000).
12. Rolf Griesser, "CIE Whiteness and Tint: Possible Improvements" Appita Journal, v. **49**, no. 2, 105-112 (March 1996).

13. CIE Proceedings 1963, “Supplemental Standard Colorimetric Observer”, (Vienna Session), Vol. B., (Committee Report E-1.4.1), (Academic, Bureau Central de la CIE, Paris, 1963), pp 209-220.

14. 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).

15. Rolf Griesser, “Whiteness not Brightness: A new way of measuring and controlling production of paper”, Appita J., v. **46**, no. 6, 439-445 (November 1993).

16. Hunter, R. S., “Photoelectric color-difference meter”, *J. Opt. Soc. Am*. **38**, 597, (1948).

17. R.S. Hunter, “Measurements of the Appearance of Paper”, *TAPPI*, **45**, 203A (1962).

18. Technidyne Corporation, Measurement and Control of Optical Properties of Paper, 1996.

19. Roltsch, C.C., Lloyd, T.A., “The Efficient Use of Fluorescent Whitening Agents in the Paper Industry”, (Academic, 1987 TAPPI Papermakers Conference, TAPPI Press, Atlanta), pp. 87-98.

20. Claudio Puebla, “Whiteness Assessment: A Primer”, Downloadable from http://mitglied.lycos.de/whiteness/.

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