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**EFFECT OF COATING ADDITIVES ON THE RHEOLOGICAL AND OPTICAL
PROPERTIES OF COATED PAPERS**

by

Burak Aksoy

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Paper Engineering, Chemical Engineering, and Imaging

ADVISOR: DR. MARGARET K. JOYCE

Western Michigan University
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Burak Aksoy

*To my dear wife Mediha,
and to my wonderful daughter Janset.*

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I. INTRODUCTION

Additives play an important role in the runnability and end-use performance of paper coatings (1) and are extensively used to achieve desired properties in the final coatings. Some of the more commonly used coating additives include dispersants, pH control agents, foam control agents, water retention and rheology modifiers, dyes and fluorescent whitening agents (FWAs), lubricants, insolubilizers, and biocides (1). The name of the additive usually describes the role it plays within the coating formulation. Of the additives just listed, insolubilizers (1,2) and fluorescent whitening agents (1,3) have been gaining a special importance and widespread usage due to the increase in demand for higher quality graphic papers and packaging.

Although there are many different types of insolubilizers, they all have the same function to add water resistance. Zirconium compounds are the newest generation of insolubilizers being used by the paper industry (1,2,4,5).

Ammonium zirconium carbonate (AZC), and potassium zirconium carbonate (KZC) insolubilizers have gained commercial acceptance over the past years because they offer various advantages over traditional glyoxal and formaldehyde-insolubilizers (1,2,4,5). First, they work well in anionic coatings and have a broad pH tolerance, since they are anionic in nature. Secondly, they do not require a long cure time. Curing starts upon drying and high temperatures are not required. Finally, they provide excellent water resistance and improve the printing characteristics by reducing print mottle (1,3,4).

However, one drawback to their use is their tendency to increase a coating's viscosity at low shear rates. This may cause some processing problems in agitation, pumping and application. In this study, the rheologies of zirconium containing insolubilizers were investigated in silica containing coatings. Silica coatings were selected because of their inherent problem of having high low shear viscosities at low solids even without the addition of crosslinker. Silica pigments are largely used in ink jet coating media for their high surface area and microporous structure (6-10). Crosslinkers are added to these coatings to improve the bleed and water resistance of the coating. Any additional increase in viscosity due to crosslinker addition is not desirable.

Fluorescent Whitening Agents (FWA) are used extensively in the paper industry to enhance the appearance and optical performance of coated and uncoated papers (1,3). Other than the physical properties of a paper, appearance is especially important to the printer (11). By increasing the whiteness of paper, printers can produce "snappier images" due to the higher print contrast between the paper and the ink. For this reason, practically all offset grades and, most gravure grades contain FWAs (12). Tissue papers and products in contact with food also contain FWAs. Besides adding FWAs, papermakers may also improve whiteness by bleaching the pulp (13,14), adding white filler pigments into the paper (15), and coating the paper with high brightness pigments (16). However, bleaching and filler addition weaken the strength of the paper (13-15) and the amount of whiteness that can be achieved by coating is limited (16). Thus, high whiteness can be achieved only with the proper use of FWAs (12). Accurately and precisely measuring the whiteness of coatings containing FWAs presents significant challenges (17-19). In this study, the challenges and problems associated with today's

commercially accepted whiteness measurement methods for FWA containing papers were investigated in detail. An effort was made to develop a whiteness measurement method that correlates well with the perceived appearance of paper.

II. LITERATURE REVIEW

Zirconium Containing Insolubilizers

Zirconium based insolubilizers are primarily used as crosslinkers to improve the water resistance of papers, especially for offset grades (20). They can also be used as rheology modifiers in most coating formulations (20). Rheology modification is believed to be caused by the reactivity between free zirconium and coating binder. It has been suggested that zirconium forms hydroxyl linkages with the hydroxyl and carboxyl groups present on a binder (20). Zirconium can form cationic, anionic, or neutral polymeric complexes in the presence of some ligands such as hydroxyl, phosphate, carbonate, sulfate, and nitrate ions. Zirconium in these complexes is found in the form of hydroxy-bridged polymers (20). Hydrogen bonds will break at high shear rates but will rapidly reform allowing good flow properties to the coating formulation. The ability of zirconium compounds to react with natural binders such as starches and proteins to produce irreversible gels has been known and used in several applications (20).

Zirconium complexes used as insolubilizers for paper/paperboard coatings are extremely sensitive to pH and temperature changes, which can initiate rapid polymerization, hydrolyses and the precipitation of hydrous zirconia (21,22). These premature reactions can be observed by an increase in coating viscosity or hazy solutions. Therefore, it is important to adjust the coating formulation's pH as close to the zirconium

species used in the formulation, and the zirconium solutions should be applied at the concentration received. The affinity of zirconium for oxygenated paper coating components does not show any preference for specific components and will interact with any chemical that has the proper reactive sites. Thus, zirconium addition sequencing gains importance. The addition first or mid way into the formulation may result in the premature bonding to undesired sites leading to less available reactive zirconium for crosslinking the binder which may result in a weakened coating in the final state. It is therefore best that the zirconium salt be added into the coating formulation last to avoid these undesired interactions (21,22).

McAlpine (23) studied the rheology of AZC containing coating formulations and used Brookfield RVT and Ferranti-Shirley viscometers at speeds up to 1000 rpm ($10^4/s$). The coating colors showed thixotropic-pseudoplastic flow behavior with a yield value increasing with AZC addition. It was concluded that AZC produces a weak gel structure through hydrogen bonding interactions with the starch causing increases in viscosity at low shear rates. At moderate shear rates, the viscosity increase was minimal. The viscosity increase at low shear rates in the coating colors containing starch was higher at a pH value of 5.0; than at higher pH values. The experiment also exhibited increases in viscosity due to either ammonium ion or the polyanionic zirconium carbonate affecting the clay suspension. On the other hand, viscosity increase over time was believed to be caused by slow hydrolyses of the AZC in both the clay dispersions and starch solutions. AZC was found to have little effect on the viscosity of synthetic binders immediately after addition. However, the increase in viscosity of the emulsion was substantial over time, especially at pH 6.0. In all formulations tartrate ions were found to be important for

the viscosity stability. Tartrate ions, which are used as an AZC stabilizer, also act as a secondary dispersant in the slurry, solution or coating formulation. No adverse effects of AZC on the optical paper properties were found.

Ryu, Gilbert and Khan studied the coating rheology, and printing qualities of silica/PVOH ink-jet formulations containing AZC, zirconium acetate (ZAA), and poly-DADMAC (2). They reported an increase in steady shear viscosity and yield stress with the addition of all 3 additives, AZC having the lowest affect, with poly-DADMAC having the highest affect, ZAA in the middle. They concluded that this was the result of the cationic structure of poly-DADMAC and ZAA causing them more affinity to react with either the oxygen of the surface siloxane or the silanol groups in the silica network to enhance material viscosity more readily than AZC. Because AZC is anionic in nature, it does not interact as much with the silica/PVOH structure as the cationic poly-DADMAC or neutral ZAA. If the increase in viscosity is significant, there could be a need to lower the solids content of the formulation, leading to on-machine runnability problems. They also found a significant increase in the elastic modulus of the ink-jet coatings when the 3 additives were added. An increase in elastic modulus for this coating formulation is not desired since this may cause coating application problems like scratches, skips and stalagmite formation. The elastic modulus of every coating tested was higher than the viscous modulus, suggesting gel-like behavior of the silica/PVOH coating. The gel-like behavior was more pronounced when the 3 additives were present, poly-DADMAC giving the highest. They also investigated the effect of additive addition level on ink-jet rheology, and concluded that the initial addition level (0.2 parts in dry pigments) increased the elastic modulus drastically, while this increase was constant, but

at a slower rate for poly-DADMAC. On the other hand, there was a slight increase in elastic modulus with increasing amounts of AZC, and ZAA in the formulation, after an initial drastic increase when first added.

Fluorescent Whiteness Agents, Whiteness and Whiteness Measurements

FWA's absorb invisible UV-light in the range of 300-400 nm and emit it in the bluish range of 430-470 nm. The result is that the surface reflects more visible light than it receives. The FWA applied surface appears whiter to the eyes because the reflected bluish light compensates for the original yellow. In other words, FWAs correct the blue deficiency in the light reflected from paper and increases the overall intensity. There have been numerous attempts to measure the contribution of FWA's to the whiteness of papers. No single approach or whiteness formula has been completely adequate to measure the whiteness effect of FWA's to paper for reasons that will be explained below (24-26).

First, there have been disagreements on what perfect white is and which directions of departure from it should be preferred or avoided (17-19). In addition, use of fluorescent whitening agents to improve whiteness of objects adds to the confusion. Whiteness of a material with a fluorescent whitening agent strongly depends on the spectral properties of the illumination for both visual evaluations and instrumental measurements. For these reasons, no single formula has been widely accepted for whiteness (12).

Secondly, 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 (27,28). Whiteness depends on observers and observer references (29). Visual assessment is impaired by individual preference. Instrumental whiteness assessment will be absolute only if the uncertainties of measurement and of evaluation are overcome (30). The concept also depends on the assessment methods applied such as, ranking, pair comparison, scaling differences, and ratio scaling for a particular observer. Many varying conditions such as the level and spectral power distribution of sample irradiation, the color of the surrounding whites, and the desired appearance of various products will also have a direct impact on the whiteness perceived (29). The intensity of fluorescence of FWA depends on the spectral power distribution of the illumination, especially in the UV region. Differences among visual assessments, measurements and different measurement devices also result from differences in spectral power distribution of the illumination (30). On the other hand, the general agreement is that samples are considered less white or darker if they are yellower and darker (29).

According to Ernst Ganz three uncharacteristic observations are made if samples are compared where they differ only moderately in whiteness (30):

1. Different observers may give different weights to lightness and blueness. A sample can be ranked for its whiteness although a difference in lightness and/or blueness may be clearly perceived.
2. Some observers prefer whites with a greenish while some prefer reddish tint. This causes contradictory evaluations of whitenesses where there is a hue difference in a given sample. At the same time, samples with an intermediate bluish or neutral tint are assessed more consistently.

3. There is general agreement among observers for hue differences, which is assessed independent of the perceived difference in whiteness.

Another problem in whiteness assessment is that 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 more or less differences in results. The results are also influenced by the inclusion or exclusion of the gloss depending both on the measurement device and sample (30). Another factor is the surface structure of the measured sample that has influence on the results depending on the design of the instrument. FWA containing samples are mainly influenced by the FWA type, age, illumination (lamp characteristics) and the design of the instrument (31). The intensity of fluorescent 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 the spectral power distribution of the illumination (30).

For the reasons explained above, the following precautions should be taken for a more reliable instrumental measurement: Full colorimetric information needs to be collected. Whiteness and hue values together provide a more complete assessment for whiteness. If there are significant differences in lightness, Y values should also be specified (31). The degree of fluorescence is a function of the UV-content of the incident radiation and must be carefully defined if the whiteness value is to be accurate (32). 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 (33).

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, thus influenced by the properties of the sphere lining, by any filters included and indeed to some extent by the sample itself (32).

It is important to note that whiteness must be defined based on perceptual evaluations and psychometric techniques before instrumentally measuring whiteness. In reality, the observer evaluates the appearance of an object. Therefore, an objective measure cannot be built until the subjective reality has been analyzed (32).

Instrumental measurement of whiteness simulating a psychometric scale is accompanied by an additional term that indicates to what extent and in what direction the appearance of the sample deviates from the maximum whiteness (32).

Whiteness Formulas

Over the years, many studies have been carried out and many formulae proposed (17). It has been realized through the studies that whiteness is entirely based on experience on the reflection of light of all wavelengths and that no measurement with a single filter in any particular region of the spectrum can ever be sufficient as a whiteness measurement. The visual experience of whiteness is done through color assessments and the instrumental measurement of whiteness is based on color measurement (17).

The main effort in developing whiteness formulas has been to develop a conversion of these three values into a three-dimensional co-ordinate system similar to the three-dimensional color values developed by non-instrumental psychometric studies (17). The X, Y, Z tristimulus values (33) are related to the measured reflectance values through amber, green and blue filters, respectively, R_x , R_y , and R_z by the equations (17,19,34,35).

$$X=0.78319R_x + 0.19753R_z \quad (1a)$$

$$Y= R_y \quad (1b)$$

$$Z=1.823R_z \quad (1c)$$

In whiteness measurements, the problem is to develop a single formula that gives an appropriate weighing to the tristimulus values. Many formulas have been developed, most of them have attempted to add the X, Y, Z tristimulus values in different algebraic proportions in order to achieve a weighting towards the blue region corresponding to subjective experience (19). Another problem is that the perfect reflecting diffuser is not perfectly white. The human eyes, in combination with the brain, classify a white that is slightly bluer than an object that reflects perfectly over the whole visual range (17,36,37).

Selection of a single whiteness formula would not be sufficient, since the perception of the appearance of an object varies from one individual to another. In addition, there is no general agreement in the evaluation of whiteness (30).

The CIE tristimulus system and CIE chromaticity diagram are not based on steps of equal visual perception. In other words, equal distances on the diagram do not correspond to equal visual differences, because equal chromaticity values can have

arbitrary intensities. However, whiteness evaluations made at uniform chromaticity spacing are less problematic, because only a small part of the color space is taken by white colors. There, chromaticity spacing correlates well with human perception (30).

Since it is not possible for a producer to fabricate a stable source that has the relative power distribution of D_{65} (CIE daylight illuminant at 6500 °K) with adequate accuracy, there have been methods developed to convert to illuminant D_{65} through the use of the spectral radiance factors that are measured with a source of different but known relative spectral power distribution.

An approximation to a stable relative spectral power distribution was attained by a device for controlling the relative UV contents of the sample irradiation for use by spectrophotometers. The excitation of the fluorescence of a stable white reference sample is attenuated sufficiently to keep the tristimulus values of this sample constant with an adjustable UV filter (30).

Attempts have been made to standardize the calculation of whiteness, although colorimetry of fluorescent samples is still problematic. Most formulae used today assess a sample relatively as to whiter, lighter and bluer. When these formulas are applied to colored samples they are generally meaningless. On the other hand, they satisfactorily characterize the appearance of commercial whiteness. They are mostly unsuccessful in assessing tinted samples with chromaticities placed on the borders of white colors (38,39). However, there are formulas developed for dealing with such cases. They produce ellipses that are equivalent lines that should be centered on the unknown preferred white in the chromaticity chart. This point is not reached under normal viewing

conditions, because of lower UV content of the illumination source in comparison to daylight limiting the excitation of fluorescent (32).

Any whiteness formula defines surfaces of constant whiteness in color space and is based on a luminous reflectance Y and on transformed chromaticity coordinates, such as colorimetric saturation (30).

Whiteness determined by colorimetric measurements through a whiteness formula is not an exact quantity. Its value depends on the spectrophotometer used, properties of the whiteness formula used and illumination state. Therefore, differences in whiteness values are considered significant only if the same instrument is used for the measurements (32).

While whiteness is a qualifying assessment, tint deviation is a descriptive assessment and thus not a simple quality judgment. Tint deviation describes the hue of the sample in comparison with the equally white step of the white scale to which the formula parameters relate. Therefore, tint deviation is mainly a descriptive assessment and does not entail quality judgment. It directly depends on the tint of the white scale being used as reference (31).

The tint is assessed visually and chosen by colorimetric means, because the whiteness value does not characterize a white all alone. The influence of the relative UV content in the measurement on the evaluation of tint is negligible.

In 1981, CIE (Commission Internationale de l'Eclairage) recommended an equation for whiteness, W , related to basic CIE tristimulus measurements and having the form (17, 40,41);

$$W = Y + 800(x_n - x) + 1700(y_n - y) \quad (2)$$

Where x and y are the CIE chromaticity co-ordinates (33) and x_n and y_n are the chromaticity co-ordinates for the perfect reflecting diffuser in the D_{65} illumination.

This equation is complemented by the equation:

$$T(\text{tint}) = 1000(x_n - x) - 650(y_n - y), \quad \text{for a } 2^\circ \text{ observer} \quad (3a)$$

or

$$T(\text{tint}) = 900(x_n - x) - 650(y_n - y), \quad \text{for a } 10^\circ \text{ observer} \quad (3b)$$

These give tint-values in the red or green direction for the 1931(33) or 1964 CIE standard observer (42), respectively. A positive value of T indicates greenishness and a negative value indicates reddishness.

These equations can be used only in a limited region. Criteria for whiteness are that the value of W fall within the limits given by (40,41):

$$5Y - 280 > W > 40 \quad (4a)$$

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

$$3 > T > -3 \quad (4b)$$

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 bluishness or yellowishness.

The application of CIE whiteness is restricted to specimens that are called white commercially and W values are greater than 40. On the other hand, equal differences in CIE whiteness do not always represent equal perceptual differences in whiteness (43).

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 (30, 44).

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 close 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 (40).

If the sample illumination is stabilized, assessments with the CIE formula 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 (31, 40).

The Ganz Whiteness Formula

The whiteness formulae that Ganz proposed is as follows (29,30):

$$W = (D \cdot Y) + (P \cdot x) + (Q \cdot y) + C \quad (5)$$

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 this the best.

Any desired preference can be built. The following standard specifications have been found to be useful for constructing a theoretical whiteness formula, through practical experience and accepted by a large number of people (29,30). They are:

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 (31).

Ganz and Griesser introduced tint deviation formula as an additional factor to the calculation of whiteness to make instrumental whiteness assessments more accurate (45).

$$\text{Tint Deviation} = (m \cdot x) + (n \cdot y) + k \quad (6)$$

x and y are colorimetric variables

m , n and k are the formula parameters and they are specific to the measuring instrument (31).

Tint deviation can also be correlated with the white scale as reference. Whether or not a sample possesses the same hue as an equally white scale or whether it is greener or redder, and if it is, by how much can be found by calculation (27). One of the three-color attributes, hue, is the one that is most subjected to individual preference (40).

Hunter Whiteness

$$W = L - 3b \quad (7)$$

Individual preference for whites makes optical evaluation of whiteness variable 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. They are toward yellow and toward 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. As a result it is possible to obtain whiteness values of significantly higher than 100 (43). The Hunter whiteness formulation gives the blue component three times as much weight as the lightness component (43).

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 an imaginary blue-white and measures whiteness as the distance in color space from the sample to that ideal (43).

III. STATEMENT OF THE PROBLEMS AND OBJECTIVES

In this study, two problems involving paper coating additives, Zirconium insolubilizers and fluorescent whitening agents were investigated. Zirconium insolubilizers were studied for their rheological influence on silica containing ink-jet coatings, while Fluorescent whitening a

gents were studied for their optical influences especially on whiteness on a variety of coated paper grades.

Zirconium insolubilizers containing coating formulations have special rheological problems that cause problems and defects during the coating's application; some problems are shear blocking during the screening process and film split patterning in the size press (20-23).

There have been many whiteness formulas 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 a sample relatively as to whiter, lighter and bluer. When these formulae are applied to colored samples, they are generally meaningless. While they satisfactorily characterize the appearance of commercial whiteness, they are mostly unsuccessful in assessing tinted samples with chromaticities placed on the borders of white colors (38,39).

The objectives of this dissertation are as follows:

- a) to determine the effect of zirconium-containing insolubilizers on rheology of ink-jet paper coatings,
- b) to establish a methodology to determine the optimum addition level of zirconium containing insolubilizers from the rheological perspective, and,
- c) to be able to predict, from rheological data, possible coating application problems when zirconium containing additives are used.
- d) to investigate widely accepted and commercially used CIE, Hunter and Ganz whiteness formulas and TAPPI brightness for tinted and FWA added paper samples.
- e) to investigate measurement instrument influence on whiteness formulas.
- f) to investigate base paper influence on tinted and FWA added paper samples.
- g) to establish correlation between several whiteness formulas and perceived appearance through observer evaluations on tinted and FWA added papers.
- h) to develop a whiteness formula that correlates well with perceived appearance through observer evaluations for neutral white as well as tinted and FWA added papers.
- i) to compare the newly developed whiteness formulas to CIE, Hunter and Ganz Whiteness formulas by investigating their correlation with perceived appearance through observer evaluations.

IV. EFFECT OF ZIRCONIUM INSOLUBILIZERS ON SILICA COATING RHEOLOGY

Abstract

Zirconium species are used in inkjet coatings to improve the waterfastness of the coating and print quality by reducing the ink spread and excessive ink migration into the coated layer. We investigated the effect of two anionic zirconium complexes, ammonium zirconium carbonate (AZC) and potassium zirconium carbonate (KZC), on the rheology of a gel-silica/PVOH inkjet coating. Both zirconium species had an influence on the rheological properties of the coating and its components. The interactions between the zirconium salts and the coating were found to be weak and lessened as the shear rate increased. The viscous modulus was higher than the elastic modulus indicating more fluid like behavior.

Introduction

The ink jet market is fast growing because ink jet printing can provide special consumer needs such as high image quality and photographic quality at relatively low cost (1). The printing technology as well as the specialized ink (2-5) and the substrate (6-9) are all necessary for this high quality printing. The inks used contain relatively high amounts of water (1), approaching 65% to 90%. Water based inks are inexpensive, and, more importantly, do not plug the print head (1). Water containing inks require substrates that have a high and open surface porosity so that the ink can be held on the surface and

dry quickly due to fast absorption right beneath the substrate (6). These requirements are met with special coated papers (6-14). A typical inkjet coating formulation includes silica-based pigments, polyvinyl alcohol binders, and additives. Silica-based pigments are unique in structure and provide the paper substrate an open, porous structure (10-15). Polyvinyl alcohol is a strong enough binder to hold silica pigments with high surface area on the substrate, providing the best ink holdout along with silica-based pigments (15). Additives are also used to improve print quality and water fastness (16). Among the additives, ammonium zirconium carbonate is widely used (16-19). Unfortunately, these coating formulations have special rheological problems (17) that cause problems and defects during the coating's application; some problems are shear blocking during the screening process and film splitting at the exit nip of the size press. Studies are continuing to explore the rheology of silica/polyvinyl alcohol-containing ink jet coatings, and significant progress has been achieved in regards to silica and polyvinyl alcohol coatings (20,21).

KZC usage is expanding and currently its application is preferred to AZC in most mills due to its odorless structure. However, there is limited research available, if any, on its detailed rheology especially in ink-jet coatings. This study investigates the rheology effect of KZC along with AZC on silica containing ink-jet coating formulations.

Literature Review

Zirconium compounds are frequently used as additives or insolubilizers in coating formulations. They are used in inkjet formulations to improve dot resolution and water fastness. The improvement results from the association interactions between the additive

and the ink. As a result, a bleed-free, water resistant colorant forms without too much absorption into the substrate (17).

Ammonium zirconium carbonate (AZC) and potassium zirconium carbonate (KZC) insolubilizers are commonly used in paper and paperboard coatings because they offer various advantages over other commercial insolubilizers. First, they give good results in anionic coatings and have a broad tolerance to pH changes since they are anionic in nature. Second, they do not require a long cure time. Curing starts and is completed very quickly when the coating formulation applied on the substrate surface starts drying; it does not require a high temperature. Third, they provide excellent water resistance to paper coating binders, improve printability of the paper, and reduce print mottle (16,18,19).

Zirconium is a widely distributed element and is ranked 18th in abundance in the earth crust (22). It is in Group IV in the Periodic Table. It has a valence of 4, a small ionic radius, and a high coordination number. Because of the high charge to ionic radius ratio, the aqueous chemistry of zirconium is characterized by hydrolysis and the presence of anionic species. Zirconium can form cationic, anionic, or neutral polymeric complexes in the presence of some ligands such as hydroxyl, phosphate, carbonate, sulfate, and nitrate ions. Zirconium in these complexes is found in the form of hydroxy-bridged polymers (23). The chemical structure of AZC's is shown in Figure 1.

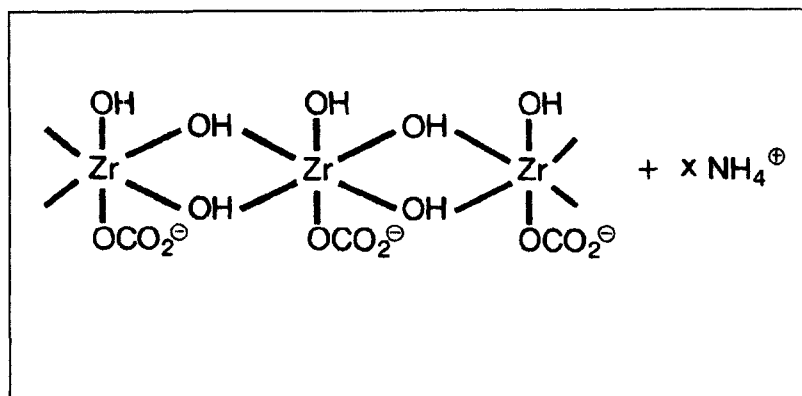


Figure 1. Chemical Structure of Ammonium Zirconium Carbonate.

Source: Floyd, W.C., Boss, S.F., Paper Coating Additives, TAPPI PRESS, Atlanta, 1995.

Zirconium complexes contain oxygenated sites, and this enables them to react with oxygen-containing organic polymers as well as carboxylated latexes (24). Zirconium complexes can crosslink with organic polymers containing carboxyl and/or hydroxyl groups (24,25). These crosslinking reactions are what permit the polymers to form water resistant structures and insolubilize in water. When added to paper coating formulations, zirconium complexes crosslink with paper coating binders containing either carboxyl or hydroxyl groups. The result is modified coating rheology, and a water resistant coating film on the substrate after drying (24). The reaction mechanism of AZC with hydroxyl groups and carboxyl groups are shown in Figure 2 and Figure 3, respectively. Bonds formed between carboxyl groups on organic polymers, such as carboxyl- methylcellulose, and zirconium ions, are strong and durable. However, reaction conditions should be controlled to achieve optimum efficiency and to avoid precipitation and gelatin. On the other hand, bonds formed between organic polymers with hydroxyl groups, such as starches, polyvinyl alcohol, and cellulose derivatives and zirconium ions

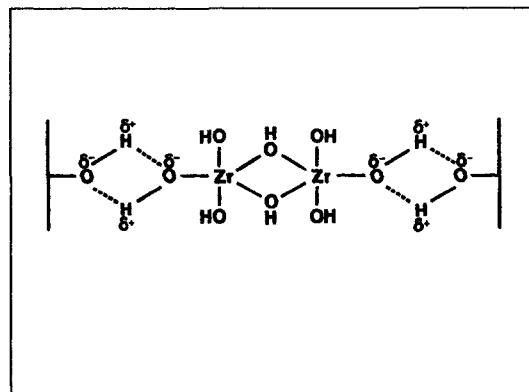
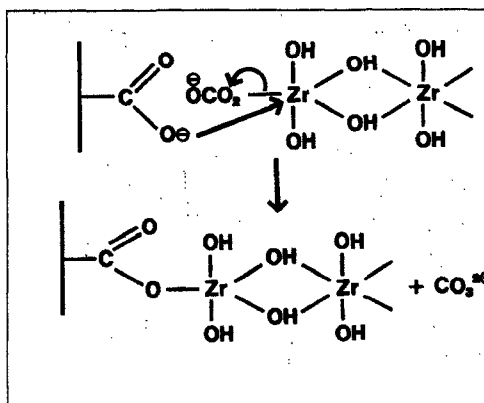


Figure 2. Carboxylic Bonding Mechanism. Figure 3. Hydrogen Bonding Mechanism.

Source: Esa Lehtinen, Pigment Coating and Surface Sizing of Paper, Fapet Oy, Finland 2000.

are through a hydrogen bonding mechanism (23). This type of interaction may result from very weak to fairly strong bonding depending on the polymer solution of zirconium species. Thus, the choice of zirconium species depends on the coating system (23). Zirconium compounds exist in aqueous and solvent solutions as polymeric species, and polymerization is through hydrogen bonding at oxygen sites on the zirconium. The chain length of zirconium species can be varied by altering temperature, pH, or chelating agent; all of these can have a significant effect on the crosslinking reaction (26).

Zirconium complexes used as insolubilizers for paper/paperboard coating pigments are extremely sensitive to pH and temperature changes (27). Dilution initiates rapid polymerization, hydrolysis, and the precipitation of hydrous zirconia. These unwanted reactions can be observed as increased viscosity or hazy solutions. Therefore, it is important to adjust the coating formulation's pH as close as possible to the zirconium species used in the formulation. Also, the affinity of zirconium for oxygenated paper coating components does not show any preference for specific components and will

interact with any chemical that has the proper reactive sites. Therefore, the order of zirconium addition into paper coatings is important. If it is added first or midway into the preparation of a formulation, premature bonding may result at undesired sites, leading to less available reactive zirconium. It is better to add the zirconium salts to the coating formulation last to avoid these undesired interactions (27).

AZC is the most widely used insolubilizer in paper coatings because of its versatility (16,28). It works best under alkaline conditions and is very compatible with alkaline coating pigments, such as CaCO_3 and satin white commonly used in the paper industry, while other commercial insolubilizers such as glyoxal and aldehydes require acidic conditions to produce catalytic condensation reactions with coating binders. AZC is an alkaline salt of zirconium and is used as an aqueous solution. There are ammonium cations, anionic hydroxy-bridged zirconium polymers that contain carbonate in the zirconium solution. Excess carbonate ions in the solution are also present to improve the stability of the solution; the concentration of carbonate ions can be varied to modify the molecular size distribution and properties of the AZC solution. Carbonate ions are very sensitive and unstable to dilution, pH changes, and temperature changes. They require an alkaline environment and are stable at a pH of 9-10. If the solution is excessively diluted, the pH changes, or the temperature changes, then carbonated hydrous zirconia may form that appears as a gelatinous solid. Stability of the solution can be improved by the addition of tartrate ions that act as chelating ligands (16,28).

If AZC decomposes in the presence of organic binders, reactions occur between the reactive sites on the zirconium and the functional groups on the binders (16). As water evaporates from the AZC solution, CO_2 from CaCO_3 and ammonia are released

from the solution; the resultant chemical is an insoluble, carbonated hydrous zirconia of variable composition. This is dependent on the drying conditions. If this occurs, reactive sites form on the zirconium that can enter into crosslinking reactions with the functional groups of the paper coating binders; the result is crosslinked binders that are insoluble in water (16).

AZC in solution generally does not react with functional groups of coating binders because of its preference for carbonate ions in the solution (23). However, any condition that causes AZC to decompose may result in interactions of zirconium with the coating components in the formulation mostly due to hydrolyses of oxygenated zirconium species. Those interactions are mostly weak and are due to hydrogen bonding generated on zirconium by hydrolyses. This, of course, influences the rheology of the coating formulation; the rapidity of the reaction may produce structural changes in the coating. At low shear rates, a viscosity increase may be observed. But, these interactions are weak and easily broken at higher shear rates (23).

The crosslinking reaction of AZC with coating binders upon drying are dependent on the functional groups in the binder, the conformation of the polymer chains, and the rate of decomposition of the AZC (23).

The chemistry and reaction mechanisms of KZC with coating binders and coating components are very similar to that of AZC. The ammonium cations are replaced by potassium cations in the zirconium complexes to produce ammonium-free, odorless insolubilizers.

Ryu et al. (17) studied AZC, zirconium ammonium acetate (ZAA), and poly-DADMAC in a typical silica/PVOH inkjet formulation, investigating their effect on

coating rheology and print quality. They reported steady shear viscosity and yield stress increase with the addition of all 3 additives; AZC had the smallest effect, while poly-DADMAC had the highest affect. They concluded that this is the result of the cationic structure of poly-DADMAC and ZAA. This causes functional groups of each additive to react with either the oxygen of the surface siloxane or the silanol groups in the silica network to enhance viscosity more readily than AZC. AZC is anionic in nature, and therefore does not interact as much with the silica/PVOH structure as the cationic poly-DADMAC or neutral ZAA. If the increase in viscosity is significant, there could be a need to lower the solids content of the formulation, leading to coating quality problems and higher drying costs. They also found a significant increase in the elastic modulus of the inkjet coatings where the 3 additives are added into the coating formulation. An increase in the elastic modulus for a coating formulation is not desired since that may cause coating application problems like scratches, skips, and stalagmite formation. The elastic modulus of each coating was higher than the viscous modulus, suggesting gel-like behavior of silica/PVOH sample. Gel-like behavior is more pronounced with all 3 additives, poly-DADMAC giving the highest gellation. They also investigated the effect of additive addition level on the rheology of the inkjet coating and concluded that the initial addition level (0.2 parts on dry pigment) increased the elastic modulus drastically, while this increase was constant, but at a lower rate for poly-DADMAC. On the other hand, there was a slight increase in elastic modulus of the coatings for increasing addition amounts of AZC and ZAA in the formulation, after a drastic increase in their initial addition level.

The objectives of this study were:

- a. to determine the effect of zirconium-containing insolubilizers on rheology of inkjet paper coatings,
- b) to establish a methodology to determine the optimum addition level of zirconium containing insolubilizers from the rheological perspective, and,
- c) to determine if the type of zirconium complex influences the rheological behavior of a silca-based inkjet coating formulation.

Experimental Design

Coating Preparation

A 30 % by weight, highly hydrolyzed, low molecular weight, cold-water soluble polyvinyl alcohol solution (Airvol-203S) was prepared by adding dry PVOH into 40- 45 °C distilled water under agitation. Mixing was continued for one hour. The speed of the mixer was adjusted to maintain a slight vortex without incorporating air. There were no defoamers or antifoams used during the preparation because of their possible effect on the rheology of the PVOH; still an excessive amount of foam was present in the solution. To eliminate the foam from the solution, the PVOH solution was kept overnight and the foam accumulated on the top of the solution was collected and discarded the next day. The resultant solution was clear and foam-free. AZC (Bacote 6200) and KZC (Zirmel M) were added into smaller batches of PVOH solution at six different addition levels under low agitation. The pH of the solution was maintained at 6.0 after the preparation of the solution. Addition levels of these cationic additives ranged from 5 to 10 % of dry binder

weight, with a 1 % difference at each level. Before the addition of AZC and KZC, the pH of the solution was maintained in a slightly acidic side, since any adverse effect of the insolubilizer on the binder or strong interactions between the additive and PVOH would be observed most dramatically at alkaline conditions. The highest practical solids content was 30% for this particular PVOH, and the same concentration of solution was prepared for coating make up as well.

The gelled silica pigment was dispersed into 25 °C distilled water with a high-speed disperser. Dispersing under high shear rate was continued for 40 minutes. The solids content of the silica gel pigment slurry (Grace, SyloGel P612) was 25 %, which is about the critical solids content for this particular pigment. AZC and KZC were added into small batches of the gelled silica slurries at six different addition levels under agitation. The pH of the slurry was not adjusted prior to crosslinker addition. The addition levels of AZC and KZC were determined on the basis of dry binder content in a typical inkjet formulation and ranged from 5 to 10 %, at 1 % increments.

One inkjet coating formulation was prepared by mixing 40 parts PVOH into 100 parts gelled silica under agitation, and AZC and KZC were added in the above amounts in small batches.

Characterization of Rheological Properties

The viscosity and viscoelastic parameters of the coating were characterized by a Brookfield RVT viscometer (#3 spindle, 20 rpm) and a Rheometrics dynamic stress (controlled-stress) rheometer (DSR5000), respectively.

To distinguish the effect of the cationic additives on the PVOH and the silica, rheological studies were also performed on them separately. Prior to Brookfield and Rheometrics measurements, all samples were left under agitation. Agitation prevented the silica pigment from settling out; the same shear protocol was used with the PVOH solutions, ink jet coatings, and silica slurries.

Steady and dynamic oscillatory rheology measurements were performed using a Rheometrics dynamic stress rheometer (DSR5000). Double couette geometry was used for the measurement of silica, PVOH, and the coatings, because the double wall couette geometry enabled the lowest shear rates along with the most sensitive measurements. Although the addition levels of AZC and KZC from 5 to 10 %, at 1 % increments, were prepared and rheological tests performed on each, the results for only 5%, 8% and 10 % addition levels are reported to eliminate redundancy.

Initial tests were performed to determine the strain percents of each sample before performing the dynamic stress sweeps. All the samples were pre-sheared at 10% strain with creep tests for 90 seconds. Then, all the samples were tested with the same pre-shear history. While a 5-minute test delay was used for the PVOH and the coating for loading history following the preshearing, a delay time was not used for the silica suspension because of the rapid settling of particles in the slurry. Following the pre-shearing and test delays as described, steady-shear experiments were performed to determine shear rate dependent viscosity and oscillatory measurements to determine the microstructure of the tested samples.

Results and Discussion

Polyvinyl Alcohol

Figure 4 shows representative Brookfield viscosity curves as a function of insolubilizer type (AZC or KZC), and additive addition level for a 30% PVOH solution. While the Brookfield viscosity did not significantly change and remained constant for all addition levels of KZC, it significantly increased (~15%) with increasing addition levels of AZC. Figure 5 shows representative steady shear curves for PVOH solutions containing different addition levels of AZC and KZC insolubilizers. The steady shear viscosity curves exhibited a slight increase as the addition level of AZC increased. As the addition levels of KZC increase from 5% to 10 % on dry binder weight, the increase in steady shear viscosity is steeper and more apparent than that of AZC addition. At the lowest addition level of KZC (5% in dry binder weight) and for all AZC addition levels, the low steady shear viscosity for PVOH remained essentially constant with increasing stress. In other words, the drops in steady shear viscosity with shear stress for the given additives and their addition levels were fairly small. At the highest KZC addition level (10% on dry binder weight), steady shear viscosity is initially considerably higher. As the applied shear stress increases, the decrease in viscosity is considerable for this solution. There seems to be a yield stress behavior for the PVOH +10 % KZC solution at about 0.2 dyne/cm² suggesting a structure breakdown of the solution at the given stress value. This behavior may be true for all other solutions in the stress range between 0.1 dyne/cm² and 0.2 dyne/cm².

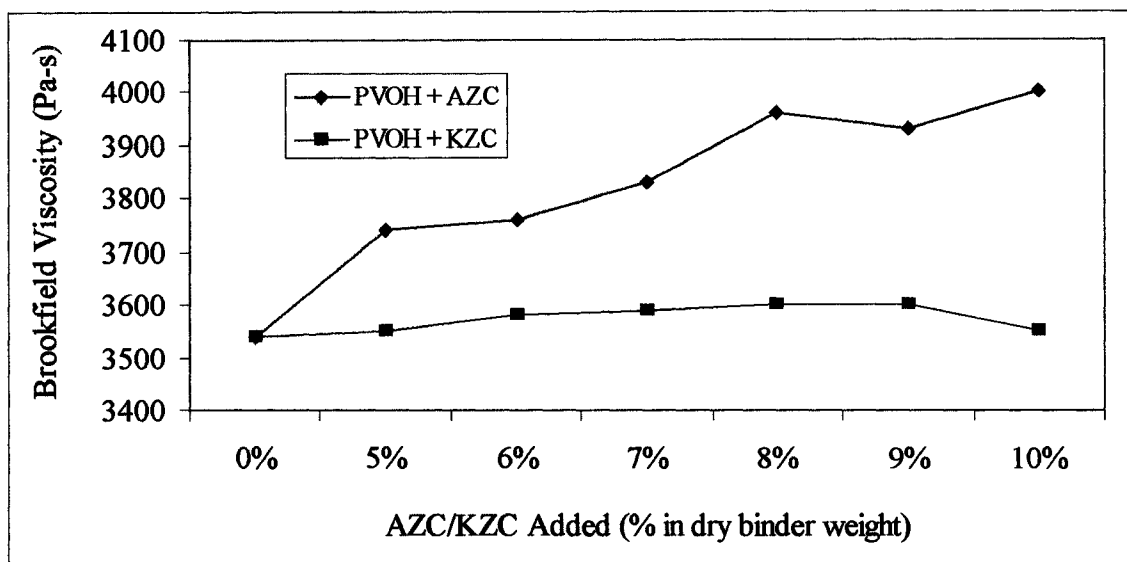


Figure 4. Brookfield Viscosity of PVOH at Different Addition Levels of AZC & KZC.

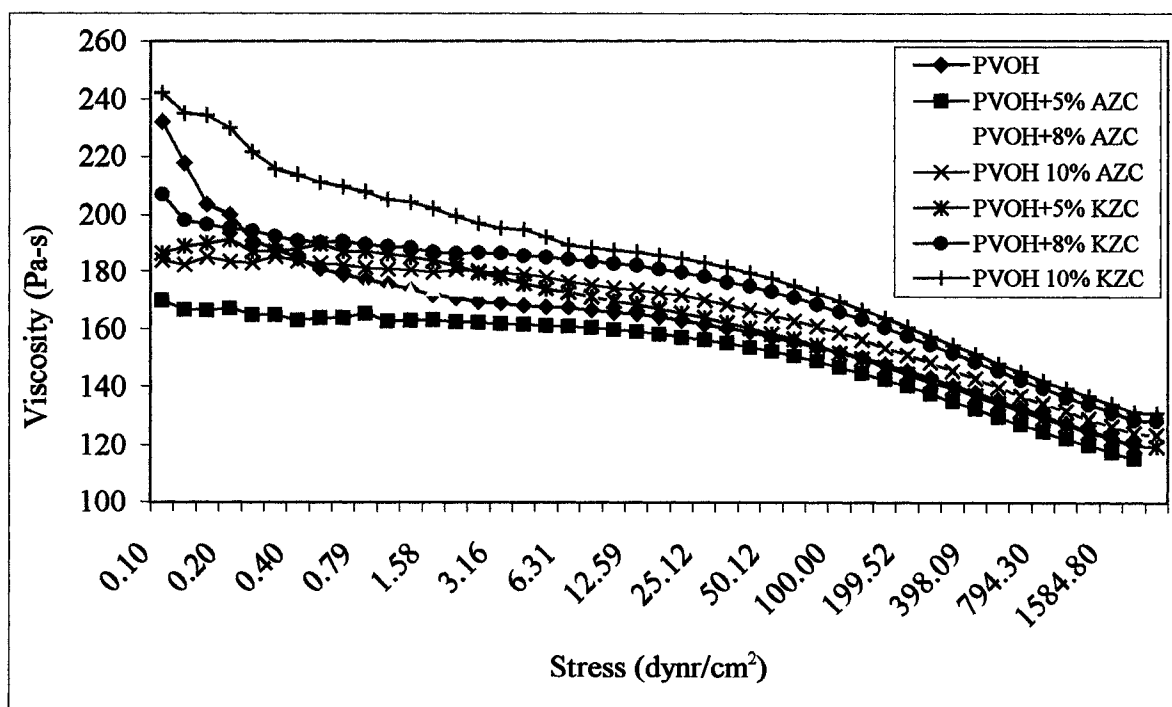


Figure 5. Steady Shear Viscosity of PVOH as a Function of Shear Stress at Different Addition Levels of AZC & KZC.

All the viscosity curves at low shear rates indicate pseudoplastic flow of the PVOH regardless of the additive type and the addition level of the additive.

Critical stress (yield stress) values, where a viscosity curve exhibits a sharp change with increasing shear rate and/or shear stress, were not completely apparent at addition levels below 10%, indicating additive type and addition level did not influence the structure of the PVOH solution significantly at these addition levels.

Figure 6 and Figure 7 show the viscous and elastic modulus of PVOH solutions at different addition levels of AZC and KZC as a function of shear stress where frequency is constant at 1/s. The viscous modulus was 100x higher than the elastic modulus, suggesting a fluid like behavior. Further tests as a function of frequency were not needed for this reason. Because the samples exhibited a fluid like behavior, the structure recovery from the elastic component of the material could not be observed for these samples. Both elastic and viscous moduli of the samples were constant and not influenced by the insolubilizer type or addition amount.

The change in viscous modulus as the addition level of the added insolubilizers increased exists but can be considered insignificant. Changes in the elastic modulus of the PVOH + AZC/KZC solutions also exists and can again be considered as insignificant since the elastic modulus values over the measured region are small and already indicate a fairly weak solid like structure. Therefore, it can be concluded that the lowest and the highest addition levels of AZC and KZC did not have a significant effect on the solution structure. This indicates that neither the AZC nor KZC interacted strongly with the PVOH solution to cause structural changes. This is desired in solution prior to coating application. If there were strong interactions in solution between the pronounced coating

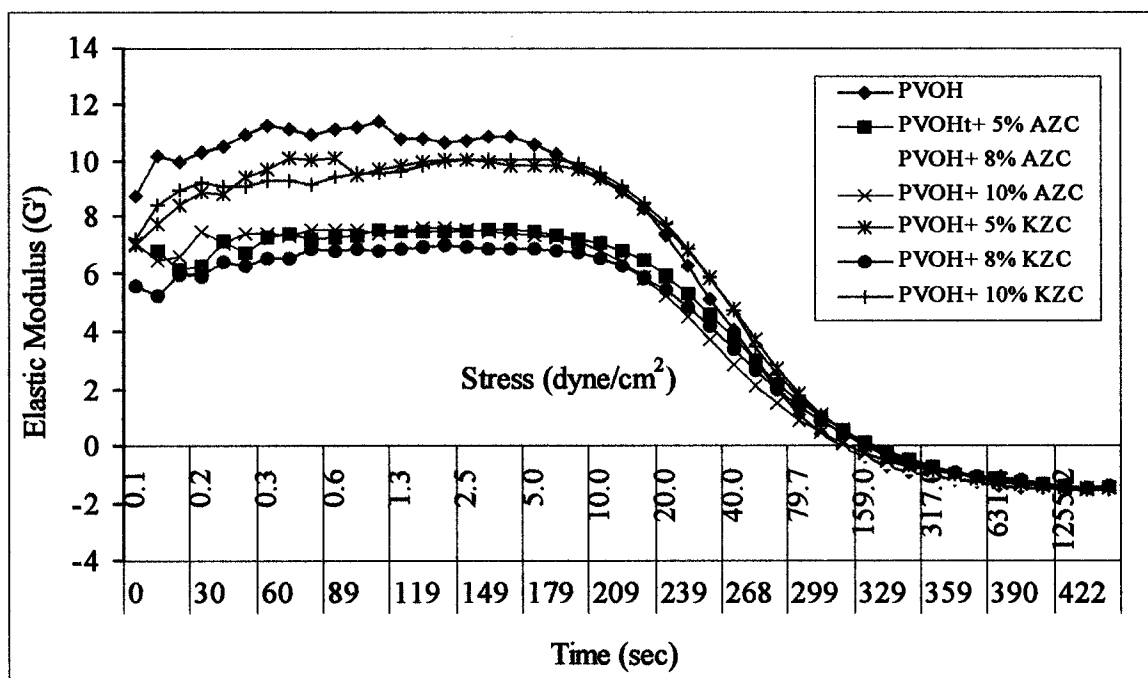


Figure 6. The Elastic Modulus of PVOH at Different Addition Levels of AZC & KZC.

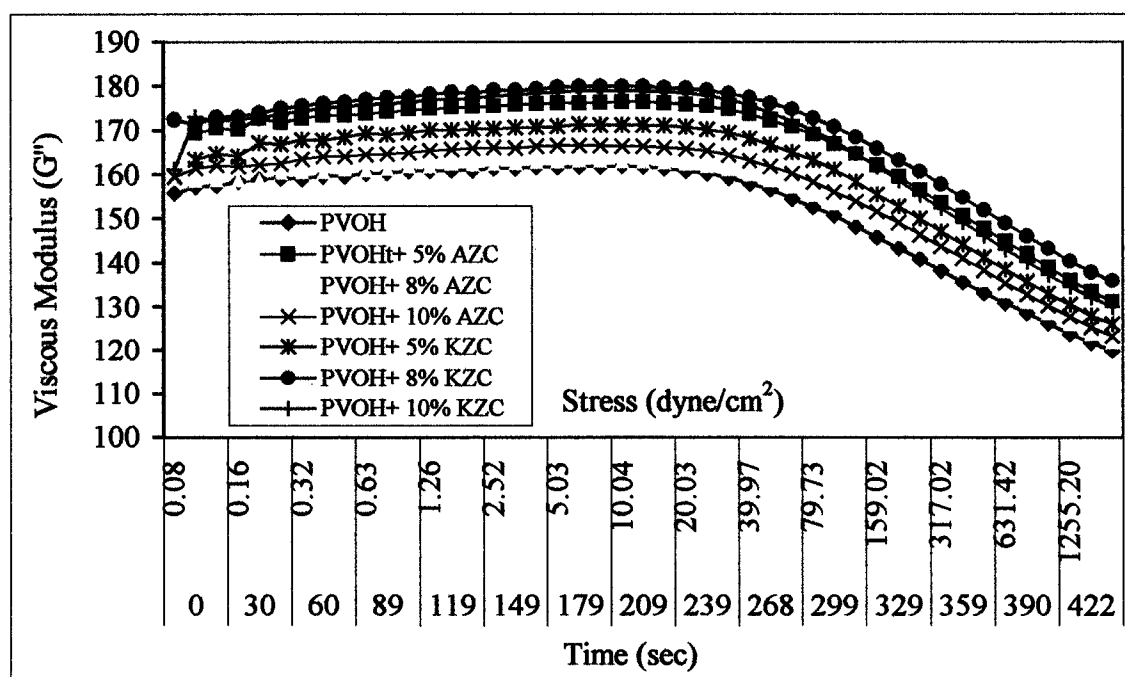


Figure 7. Viscous Modulus of PVOH at Different Addition Levels of AZC & KZC.

components and the zirconium species, any structural change in coatings would affect the coating application negatively, possibly causing scratches, skips, etc., during application. The desired interaction between zirconium species and the coating binders should start after the coating application when drying starts.

The addition of both AZC and KZC somewhat contribute to the viscous and elastic modulus of a PVOH solution. At the highest addition of KZC, the effect is more pronounced. This is probably due to the weak interaction between the zirconium species and the hydroxyl functional groups on the PVOH binder.

Silica

The Brookfield viscosity of the silica suspensions decreased at the lowest addition levels of AZC and KZC; increasing addition levels did not have any significant effect on Brookfield viscosity (Figure 8). The silica suspension (Figure 9) started with a higher viscosity at low shear stress values, and then at the higher values silica with AZC and KZC caught up with the silica without additives. It should be noted that this difference in viscosity between the silica slurry with no additives and the silica slurry with AZC/KZC additives is very small (from 1 to 4 Pa-s) and can be considered as insignificant. However, the different steady shear response curves observed for the silica with and without zirconium species suggests an interaction between oxygen sites of the zirconium and the silanol and/or siloxane groups on the silica. Zirconium species might have acted as dispersants for silica and might have had a stabilizing effect by reducing the charge interaction between silica particles or agglomerates by bonding their reactive oxygenated sites if the two viscosity curves given are interpreted together.

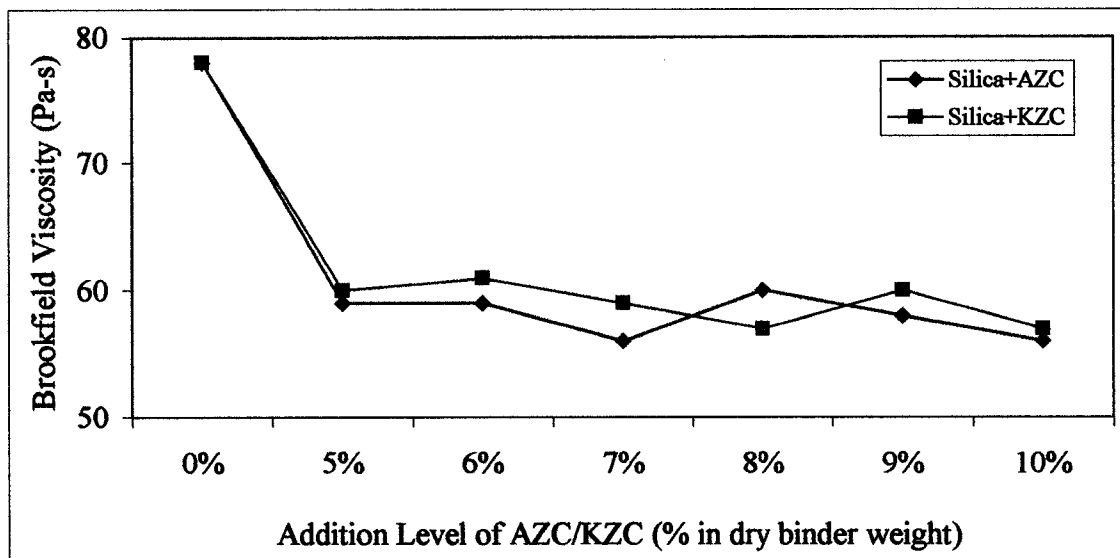


Figure 8. Brookfield Viscosity (20 rpm) of Silica at Different Addition Levels of AZC & KZC.

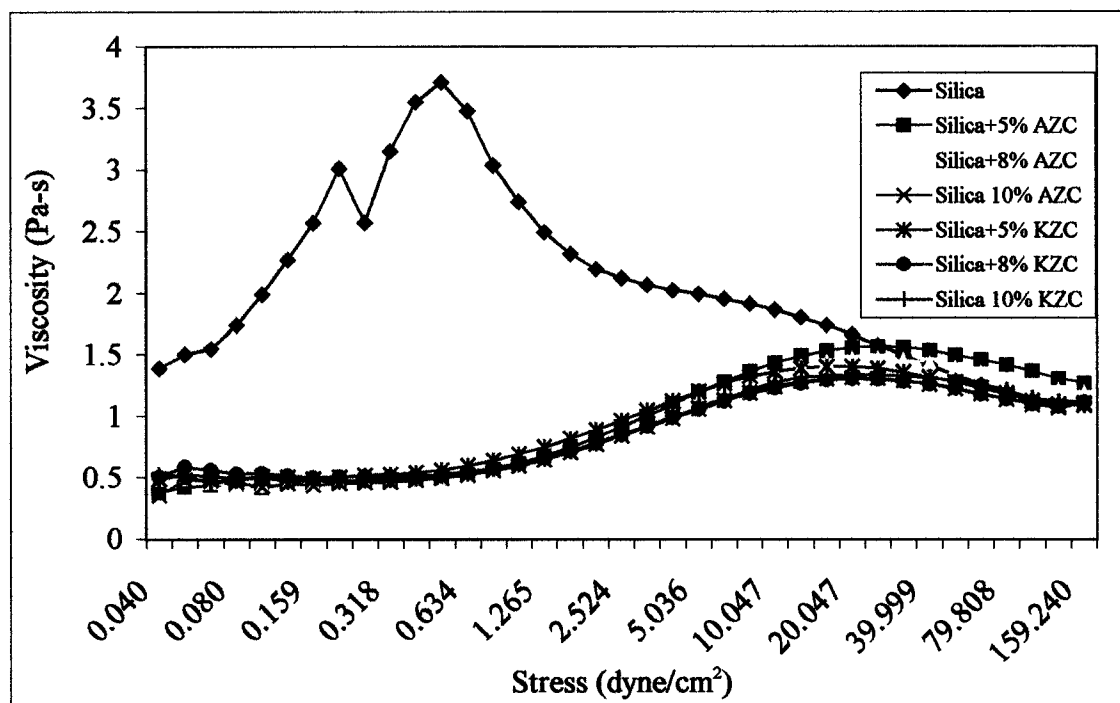


Figure 9. Steady Shear Viscosity of Silica at Different Addition Levels of AZC & KZC.

Dynamic stress sweep tests for silica suspensions with and without the two-zirconium species at different addition levels at constant frequency (1/s) were run. Since the silica slurries were low concentration suspensions, negligible elastic values were obtained. Also, no apparent linear region was found in the viscous modulus curves (Figure 10).

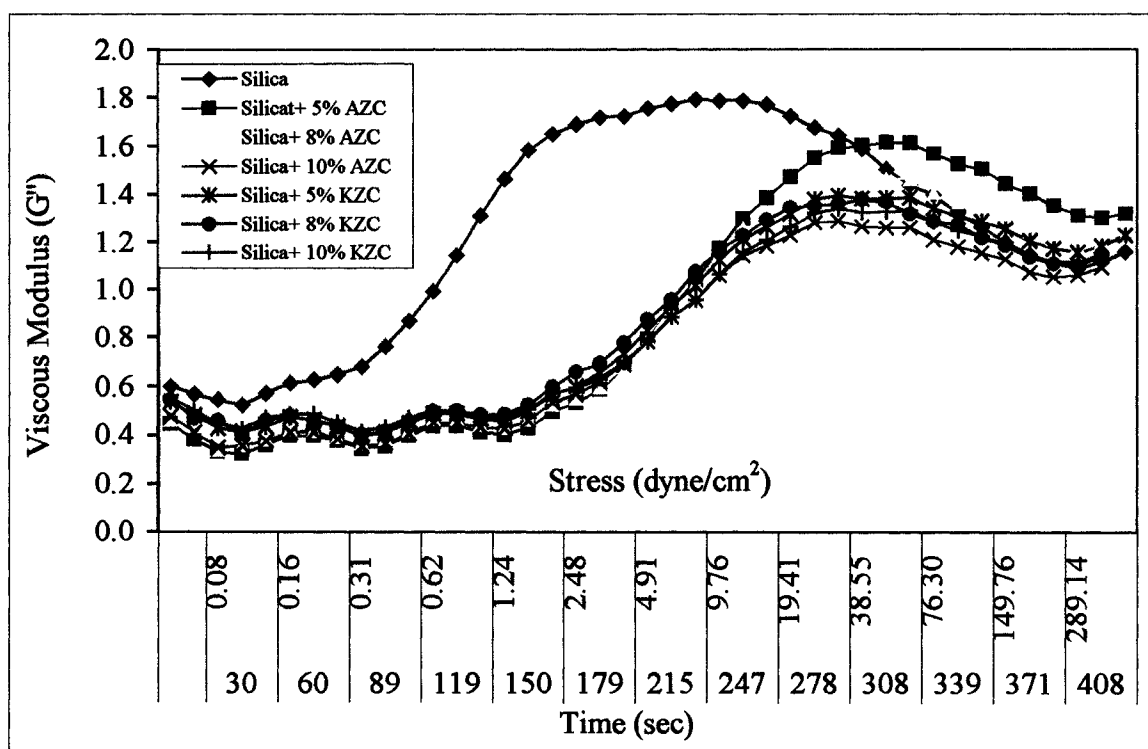


Figure 10. Viscous Modulus of the Silica at Different Addition Levels of AZC & KZC.

Inkjet Coating

As shown in Figure 11, the Brookfield viscosity of the inkjet coating formulation exhibited a significant increase with the addition of both AZC and KZC. The viscosity

was also dependent on the addition level of the zirconium species in the coating formulation.

The Brookfield viscosity of the inkjet coating was slightly influenced by KZC addition; increasing addition levels of KZC increased the viscosity. The low shear, steady viscosity curves for the inkjet coatings are shown in Figure 12. An increase in viscosity was observed at low shear rates for the inkjet formulations containing AZC or KZC. At higher shear stress values ($2\text{--}3\text{ dyne/cm}^2$) the viscosity of the inkjet coatings with AZC, and KZC approached the viscosity of the inkjet coating formulation without additives. This indicates that both AZC and KZC interact weakly with the oxygen sites (hydroxyl groups) of PVOH and/or silanol and/or siloxane groups of silica pigments that are easily broken down with increasing shear rates (stresses).

Dynamic stress sweep tests to determine viscous and elastic moduli of the inkjet coatings with and without zirconium species as a function of shear stress at constant frequency ($1/\text{s}$) were also made. The elastic modulus values of all coatings were fairly low, and no linear region was obtained. Plots in the elastic modulus–shear stress exhibited a typical dilution polymeric solution behavior (10). This is interesting because the solids content of the coating formulation prepared was 23%, which is not considered as a dilute solution for inkjet coatings due to the high surface area and internal pore structure of the gelled silica. Viscous modulus curves barely exhibited a linear region, but still were significantly higher than the elastic modulus, indicating a liquid-like behavior.

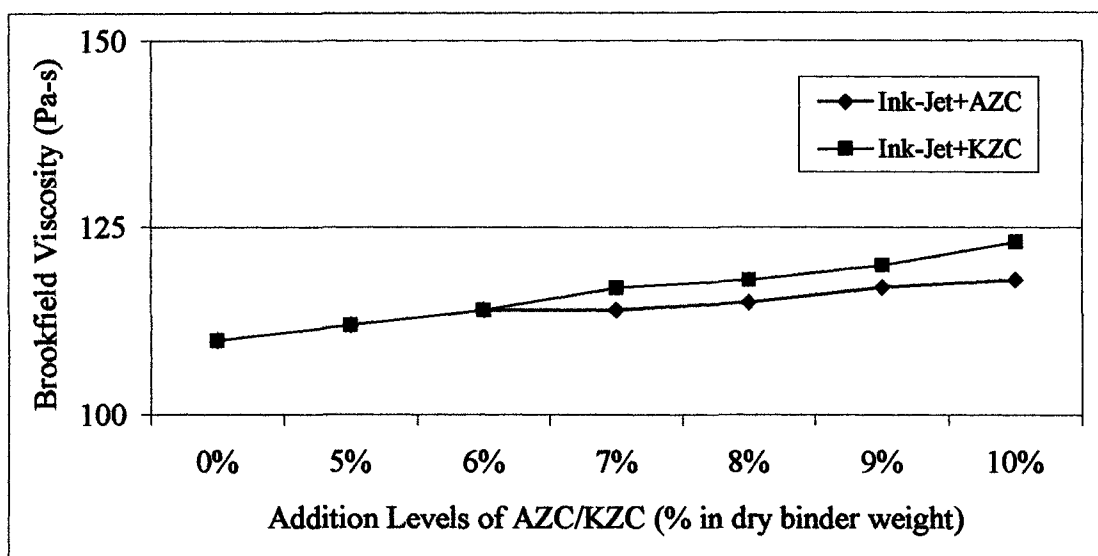


Figure 11. Brookfield Viscosity of Inkjet Coating at Different Addition Levels of AZC & KZC.

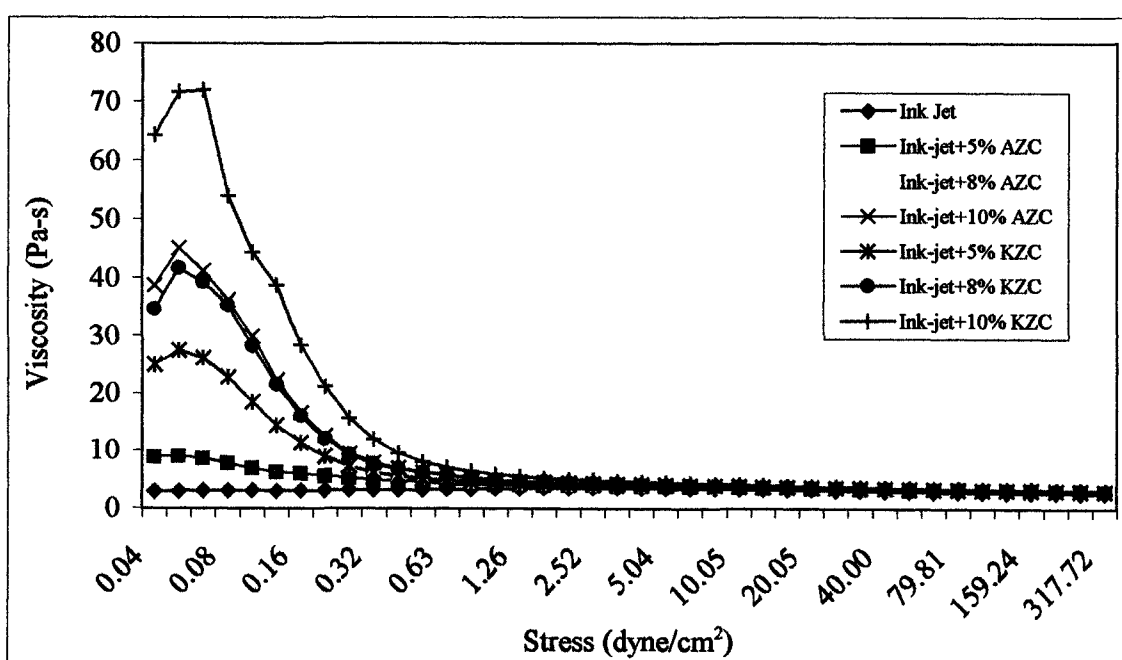


Figure 12. Steady Shear Viscosity as a Function of Shear Stress for Inkjet Coating at Different Addition Levels of AZC & KZC.

Zirconium added into the coating formulation, together with the addition level, had an influence on the viscous modulus of the coating formulation. Viscous modulus values were higher for the coating formulations where KZC is used, and increasing. Both AZC and KZC addition levels increased the viscous modulus (Figure 13).

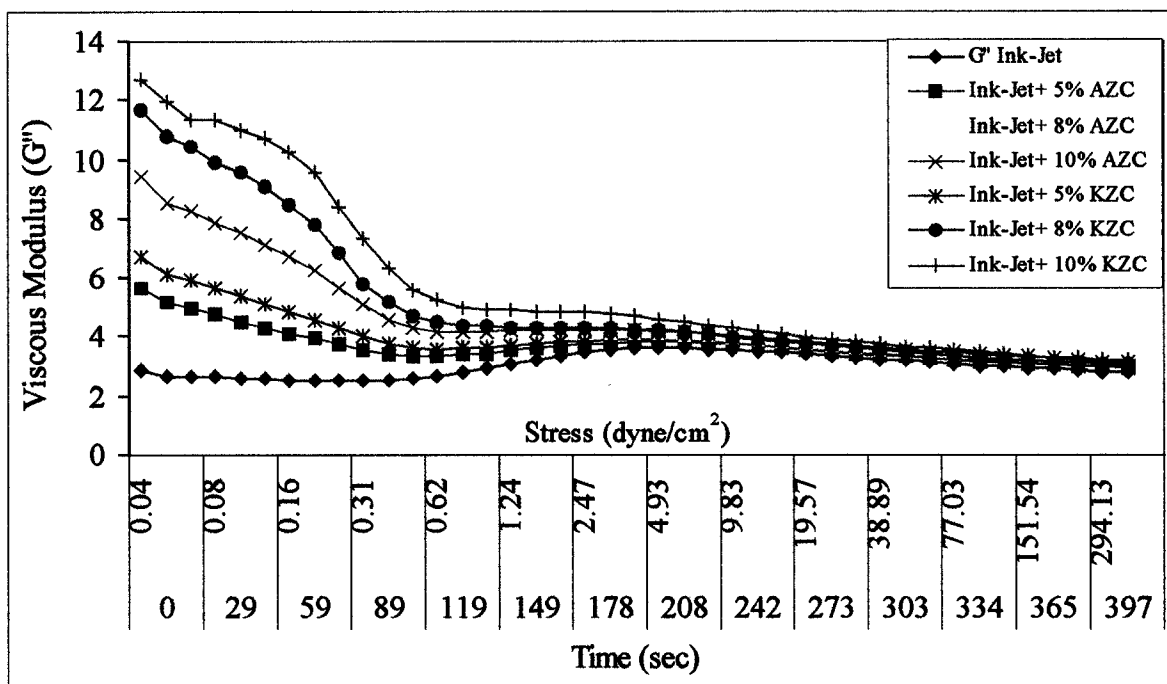


Figure 13. Viscous Modulus of the Inkjet Coating at Different Addition Levels of AZC & KZC

Conclusions

Anionic zirconium species of AZC and KZC added to inkjet coatings had some influence on the rheology of the coating formulation, KZC giving a little higher viscosity. Both zirconium species interacted with the silica and the PVOH in suspension, solution, and coating. However, these interactions were weak and easily broken down at higher shear rates. Both AZC and KZC increased the viscosity of the PVOH while increasing the viscosity of the silica pigments. Both AZC and KZC probably worked as secondary dispersants with the silica pigments with charge repulsion between pigments preventing agglomeration. Since the viscous modulus was much larger than the elastic modulus and exhibited more fluid-like behavior, no problems in high-speed paper coating applications are expected. Addition levels of the AZC and KZC were not found to greatly influence the rheology of the final coating composition and coating components. Thus, from a rheological viewpoint, there is no limitation on the amount of anionic zirconium species that can be used in inkjet coating formulations, within the range of experimented addition levels (from 5% to 10% in dry binder weight).

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V. EXPLORING MYTHS OF MEASURED AND PERCEIVED WHITENESS

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, using colorimeters, spectrophotometers and brightness meters. 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.

It was found that, in some cases, calculated CIE whiteness values increased with increasing amount of colorant in the coating layer, although the papers appeared darker or redder to the observers. Small deviations in measured CIE tristimulus functions X, Y, and Z, often caused significant changes in calculated CIE, and Ganz whiteness values. Hunter whiteness values also followed the same trend as CIE and Ganz whiteness, although Hunter whiteness is less sensitive to small changes in the tristimulus values. The results show the deficiencies in the current measurement techniques for the assessment of

brightness and whiteness of wood containing papers and coatings containing optical brightening agents.

Introduction

Other than the 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. 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) (6) standard adopted

for this grade (7). 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 (8). The object appears white if it totally reflects the light, and scatters diffusively at all wavelengths of the visible spectrum (8,9). The object appears colored if some wavelengths of the light are reflected, while the others are absorbed (8). It is black if the object absorbs all the wavelengths of the light in the visible spectrum (1,10). 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 (2,8,11). In general, all objects absorb illuminating light energy to some degree. The color white, as with any color, can be interpreted in a three-dimensional color space (12). For example, it can be described by hue, saturation and lightness (10). 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 (9,13,14). 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 (9,10,14).

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 (3,9,15). 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 (13). Thus, brightness is not a

complete description of the visual appearance of the paper (15). 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 (16).

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 (10). Assessment by the TAPPI method generally functions very well only if the reflectance properties of the papers to be compared are similar (13).

Whiteness Evaluation

Whiteness can be evaluated both visually and instrumentally⁽¹⁰⁾. 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 (3,11). 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 (10). 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 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 (7,17).

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 is that it has a relatively uniform, high-energy emission (1,18).

Griesser, R. (19) 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, essentially it was aimed to further explore whiteness formulas within their context, investigate the correlation between the formulas and perceived appearance and 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.

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

For the coatings containing FWA, the TiO₂ was replaced with the same volume of plastic pigment, since TiO₂ adversely influences a 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.

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 Spectrolino 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/m² to a commercially produced base paper made from bleached Kraft and mechanical pulp (35 g/m² 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 a datacolor Spectraflash and GretagMacbeth Spectrolino spectrophotometers and a Micro S4-M brightimeter. Calculated CIE (4), Hunter (8,21) and Ganz (22,23) whiteness values and measured TAPPI brightness (5) values were compared. The CIEXYZ (24) and CIELab (25) 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

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.

As can be seen from both Figures, the blue absorbs heavily in the middle of the spectrum from the 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. The 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 surmised from both Figures that the FWA works, as expected for this particular paper and coating system. However, the peak in the spectra observed with the FWA is smaller than expected and shows one of the problems of using the current

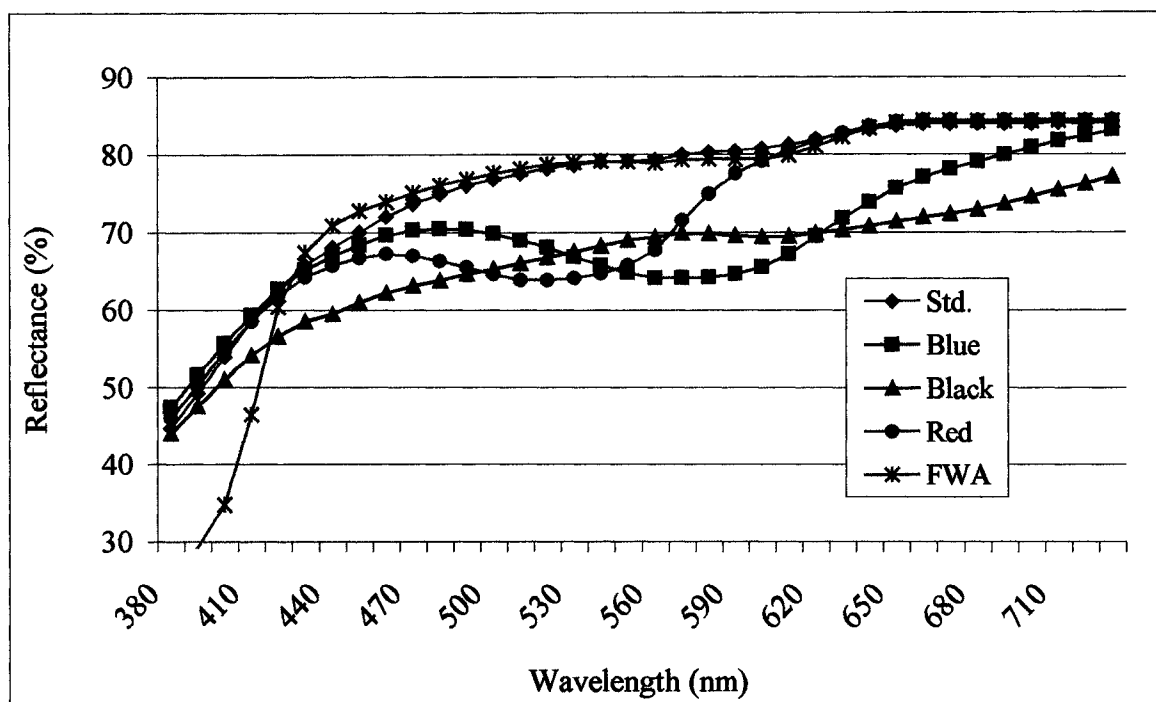


Figure 1. Color Spectra of Coated Paper, Blue, Black and Red Dyes and FWA Acquired from the datacolor Spectraflash Spectrophotometer.

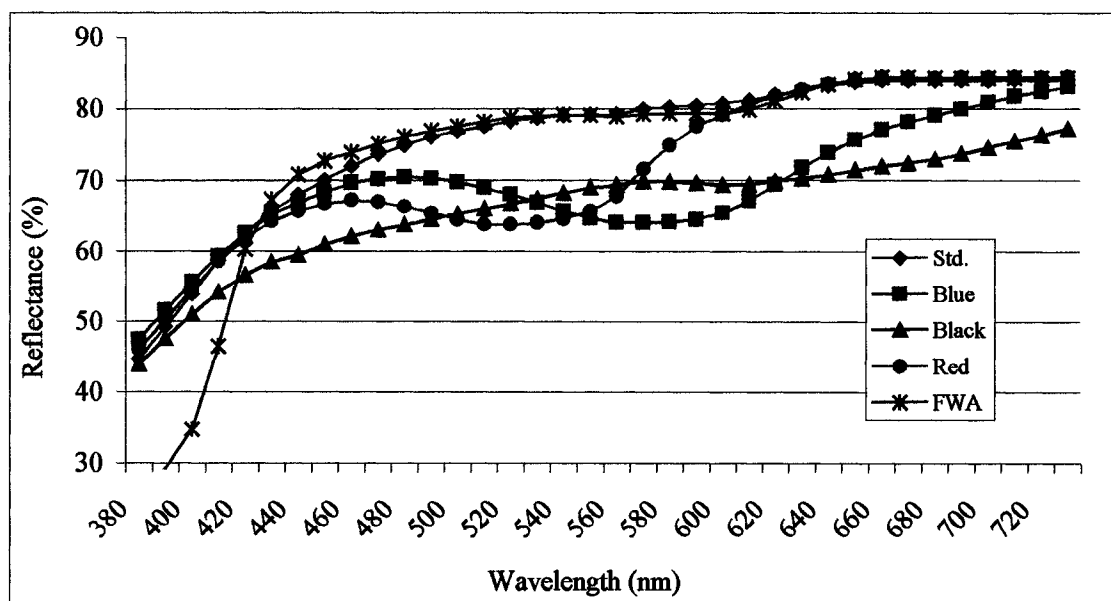


Figure 2. Color Spectra of Coated Paper, Blue, Black and Red Dyes and FWA Acquired from the GretagMacbeth Spectrolino Spectrophotometer.

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. This results in the observation of only a small peak in the spectra at the 425 nm wavelength by the instrument, which 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 a FWA whitened paper.

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 D₅₀ 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 4 shows the representative CIE whiteness and tristimulus values for the blue dye contribution.

The CIE whiteness (3) is given by

$$W = Y + 800(x_n - x) + 1700(y_n - y), \quad (1)$$

where

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

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

$x_n = 0.3138$, and $y_n = 0.3310$ for D₆₅/10°.

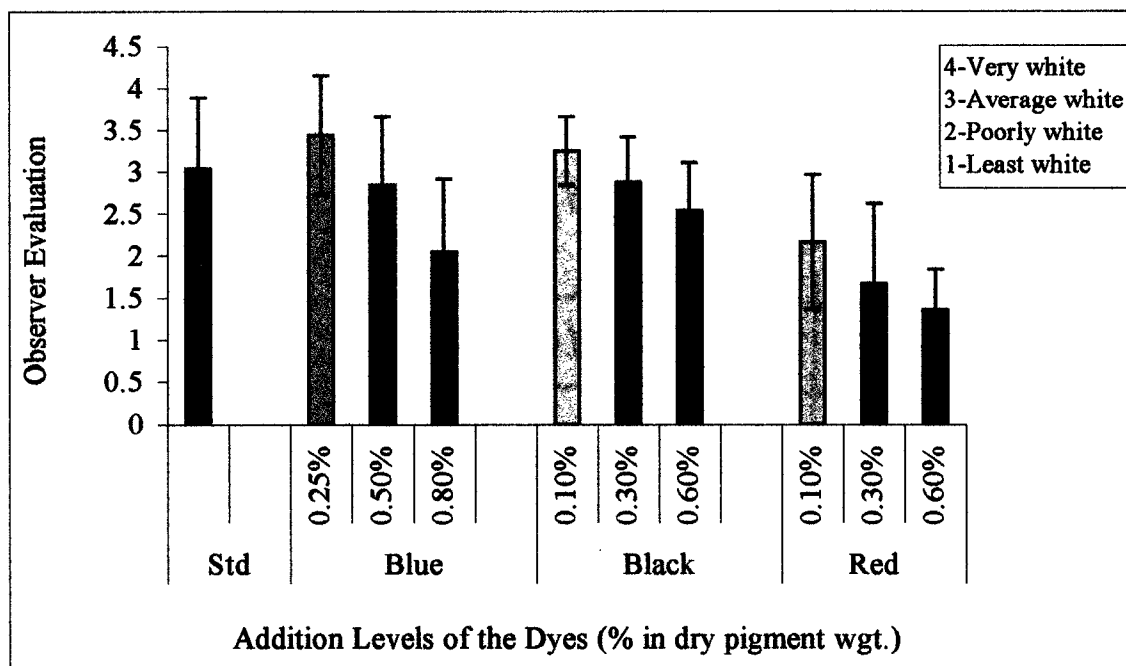


Figure 3. Observer Evaluation of Coated Lightweight Papers at Varying Addition Levels of Blue, Black, and Red Dyes.

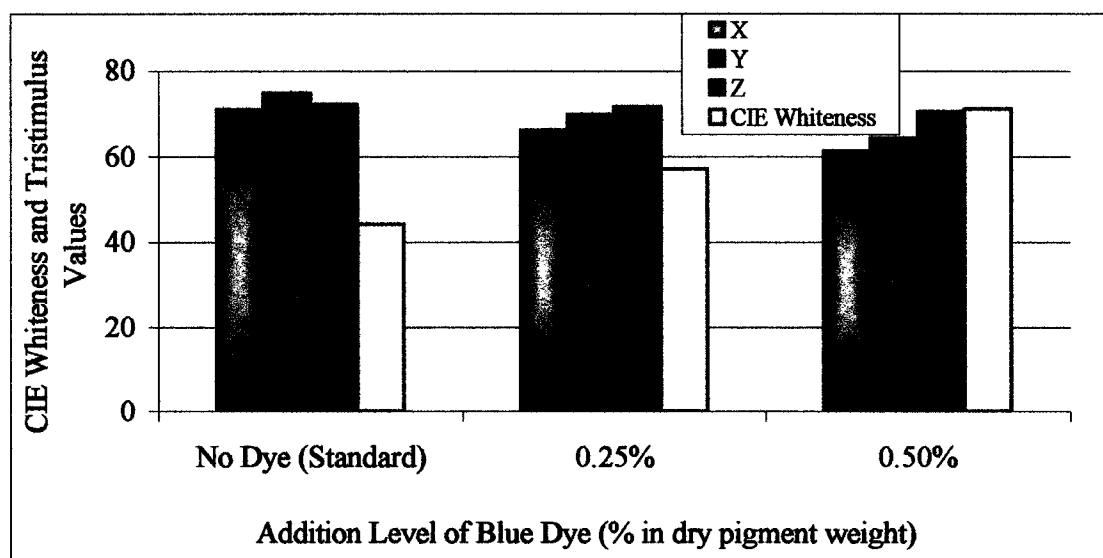


Figure 4. CIE Whiteness for Blue Dye Addition Tristimulus Values on CIE Whiteness Measured with datacolor Spectraflash Spectrophotometer.

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

$$5Y-280 > W > 40 \quad (2a)$$

and the tint relation for 10° observer

$$3 > 900(x_n - x) - 650(y_n - y) > -3 \quad (2b)$$

As can be seen easily and distinctively from the Figure, CIE whiteness values calculated from measurements made by the datacolor Spectraflash spectrophotometer, 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 the calculated tint values were slightly outside the given borders (2b), the CIE whiteness results are still reported because the appearance of these 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 Spectrolino spectrophotometer, as a function of added blue dye is shown in Figure 5. The calculated values were similar to the

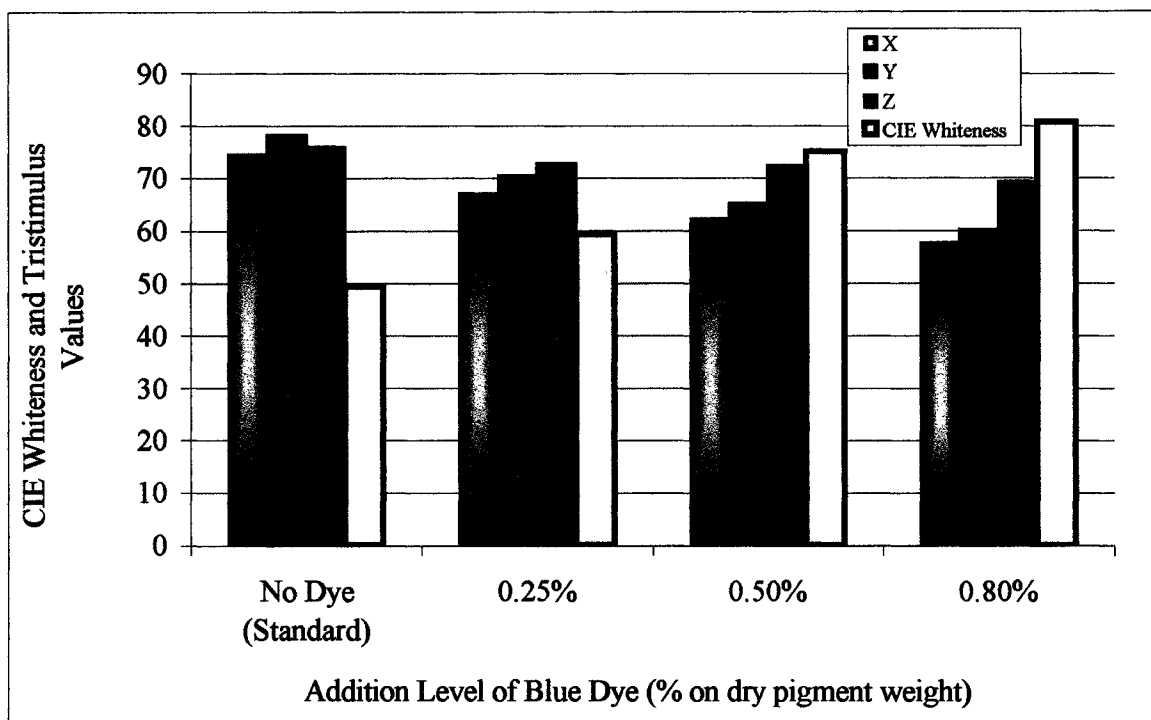


Figure 5. CIE Whiteness for Blue and Influence of Tristimulus Values on CIE Whiteness with the GretagMacbeth Spectrolino Spectrophotometer.

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 values are all within the applicable range of the inequality (2) for the GretagMacbeth measurements.

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 GretagMacbeth Spectrolino 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 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 Spectrolino 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.

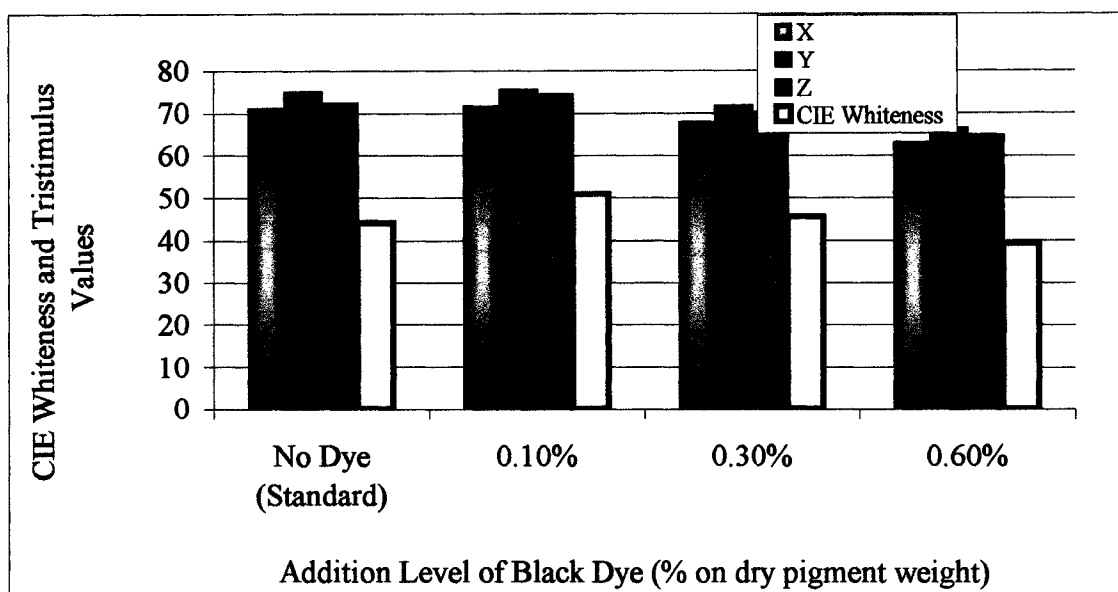


Figure 6. CIE Whiteness for Black and Tristimulus Effect on CIE Whiteness with the datacolor Spectraflash Spectrophotometer.

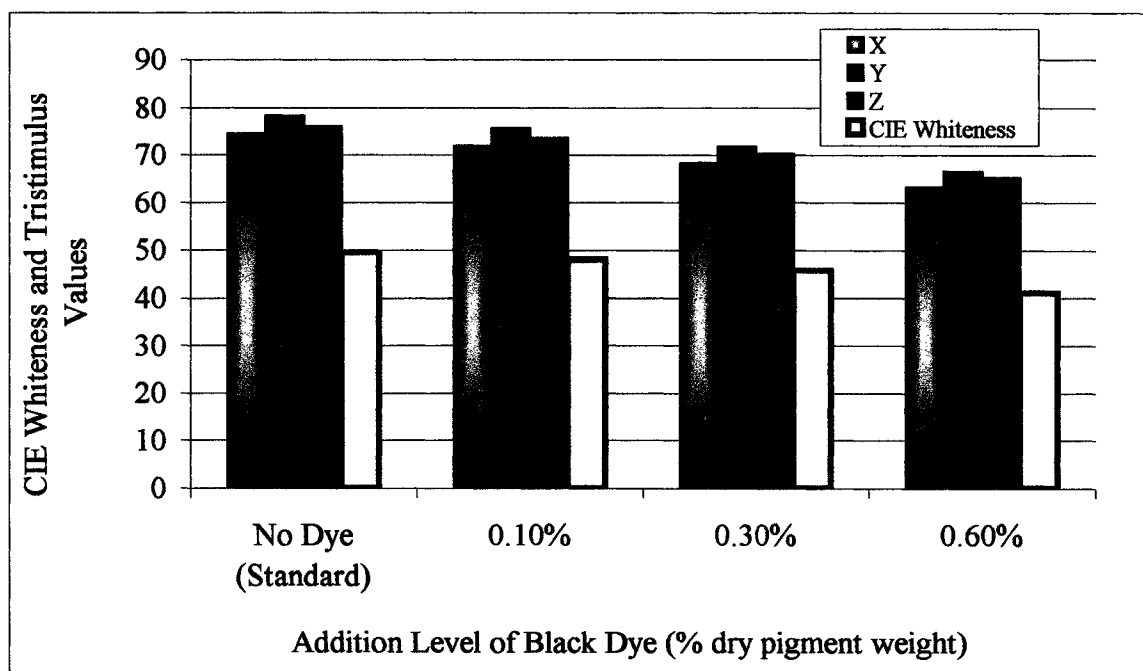


Figure 7. CIE Whiteness for Black Dye and Tristimulus Effect on CIE Whiteness with the GretagMacbeth Spectrolino Spectrophotometer.

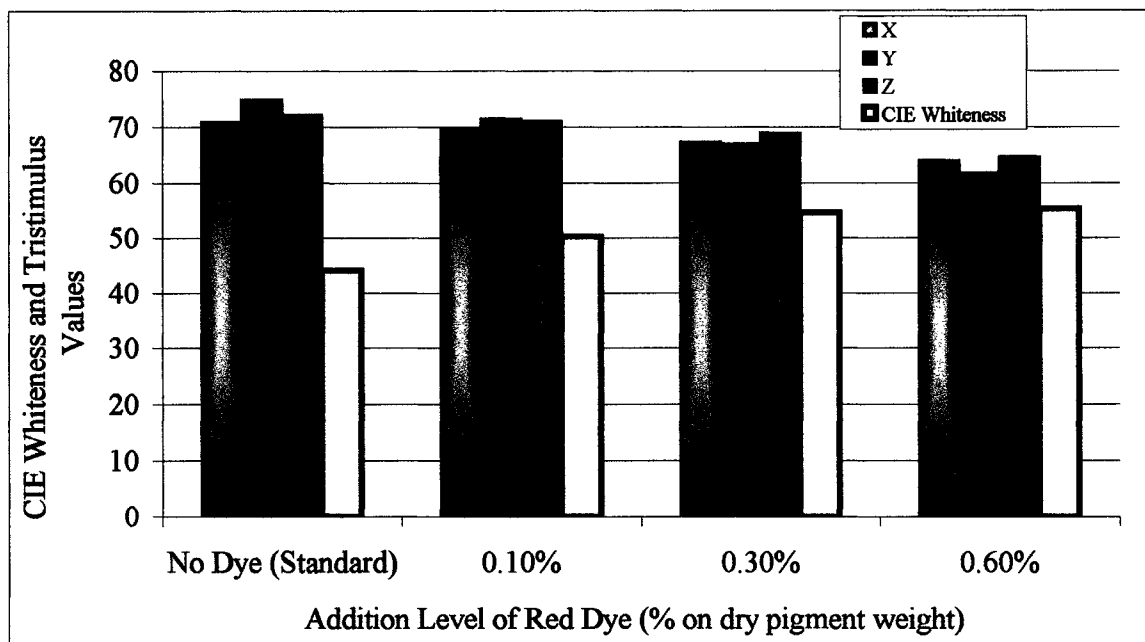


Figure 8. CIE Whiteness for Red Dye and Effect of Tristimulus Values on CIE Whiteness with datacolor Spectraflash Spectrophotometer.

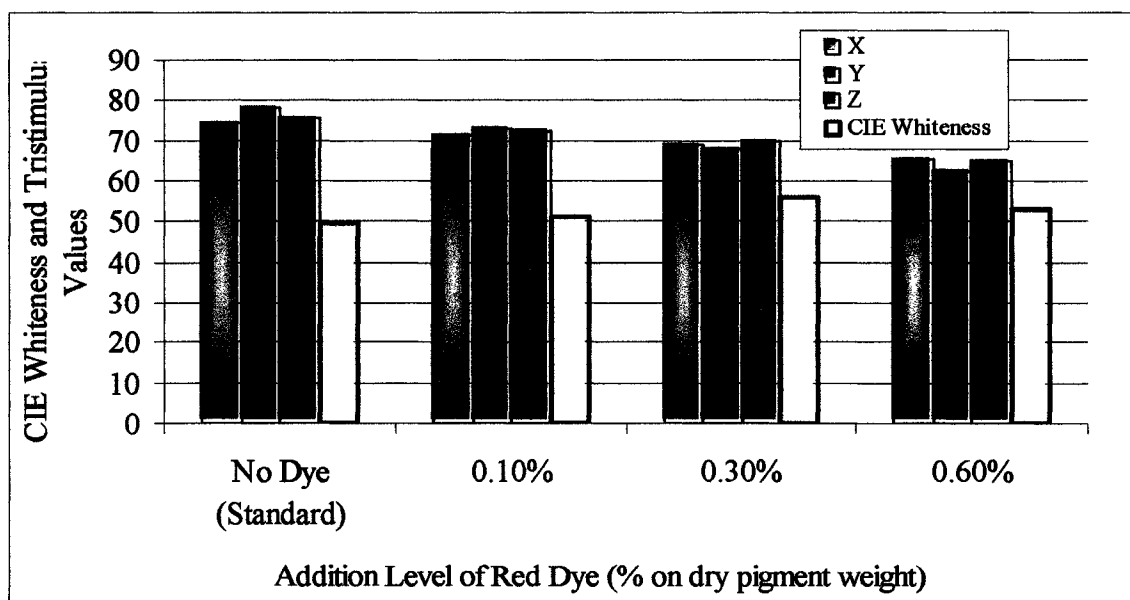


Figure 9. CIE Whiteness for Red and Effect of Tristimulus Values on CIE Whiteness with the GretagMacbeth Spectrolino Spectrophotometer.

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:

$$\text{Hunter WI} = L - 3b, \quad (3)$$

where L and b are Hunter values^(8,21).

For Ganz Whiteness

$$W = Y + 1869.3(x_n - x) + 3695.2(y_n - y), \quad (4)$$

where,

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

$$y = Y/(X+Y+Z) \quad \text{and}$$

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

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

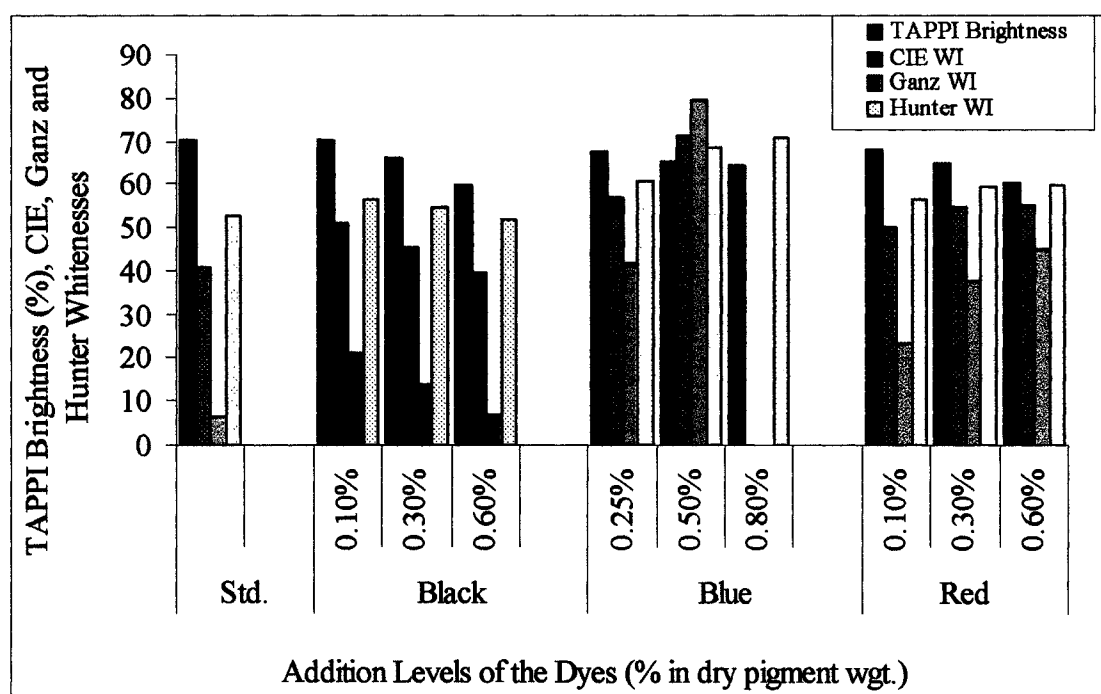


Figure 10. Blue, Black, Red Dye Effect on TAPPI Brightness and CIE, Ganz and Hunter Whitenesses Measured by the datacolor Spectraflash Spectrophotometer.

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 datacolor Spectraflash 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 low 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.

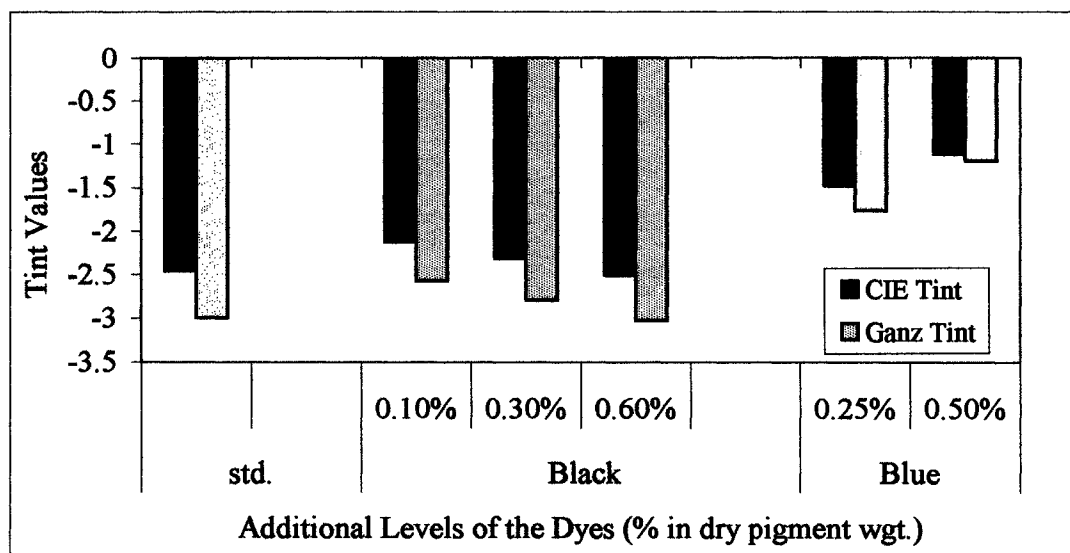


Figure 11. CIE and Ganz Tint Deviations Measured by datacolor Spectraflash Spectrophotometer.

It should be noted that the metric is different for both scales. The threshold for distinguishing different whiteness is defined in Ganz scale as being 5 points, for CIE whiteness it is about 2.3 to 2.4 points. The threshold for distinguishing different tints is 0.5 points.

The Micro S4-M and GretagMacbeth were used to acquire the data shown in Figure 12. Again, all the whiteness values exhibited a very similar distribution with the GretagMacbeth Spectrolino 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. 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.

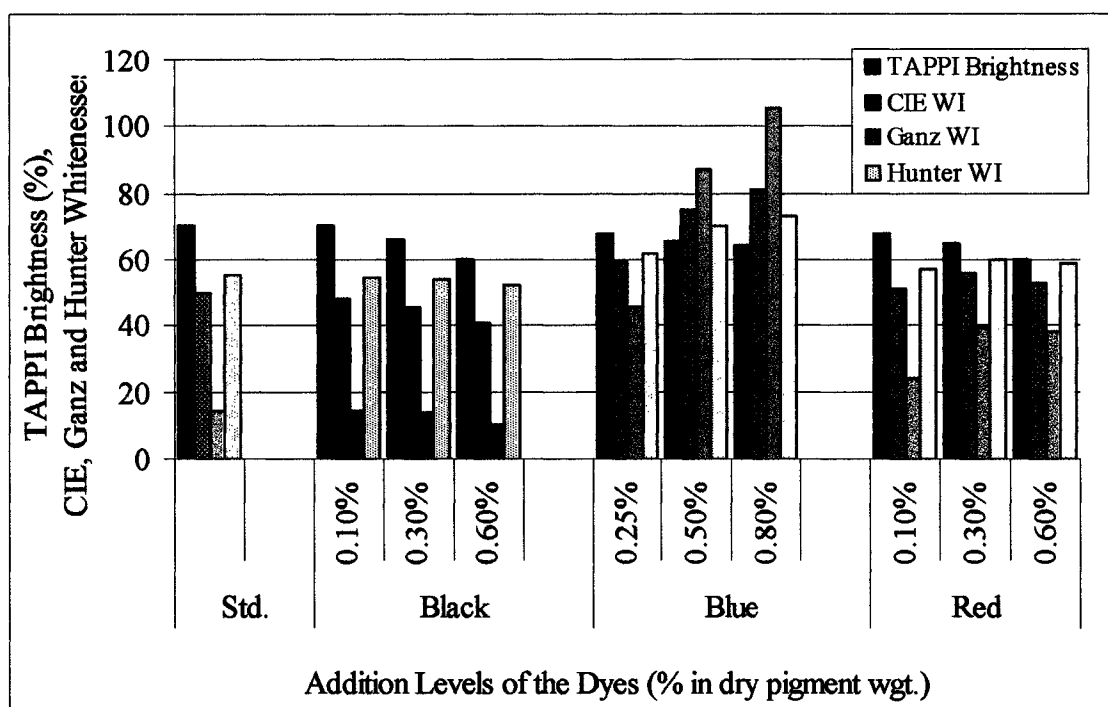


Figure 12. Blue, Black, Red Dye Effect on TAPPI Brightness and CIE, Ganz and Hunter Whitenesses Measured by GretagMacbeth Spectrolino Spectrophotometer.

The correlation coefficients of observer evaluation and CIE, Hunter, and Ganz whitenesses and TAPPI brightness were calculated for each color dye added test samples for both datacolor Spectraflash and GretagMcBeth spectrophotometers. For GretagMcBeth Spectrophotometer, 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 positive signs but TAPPI brightness.) Corresponding ranking correlations were 1 for TAPPI, -0.8 for CIE, -0.78 for Ganz and -0.6 for Hunter. (Note that, this time 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.

For datacolor Spectraflash spectrophotometer, 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. 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 given above for datacolor Spectraflash spectrophotometer seem to be in the acceptable range. However, TAPPI brightness agrees best with the observer evaluations for blue and red dye added test samples for both of the spectrophotometers used. Looking at the correlation coefficients calculated from datacolor Spectraflash spectrophotometer, all whiteness formulas seem to agree well with the observer evaluations. However, Ganz whiteness does not seem to establish a good agreement with observer evaluations for any of the dye added test samples when calculated from the data acquired from GretagMcBeth spectrophotometer. Similarly, Hunter whiteness correlates

poorly with observer evaluations for blue and red dye added test samples, while CIE whiteness struggles to 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. 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 GretagMcbeth 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.

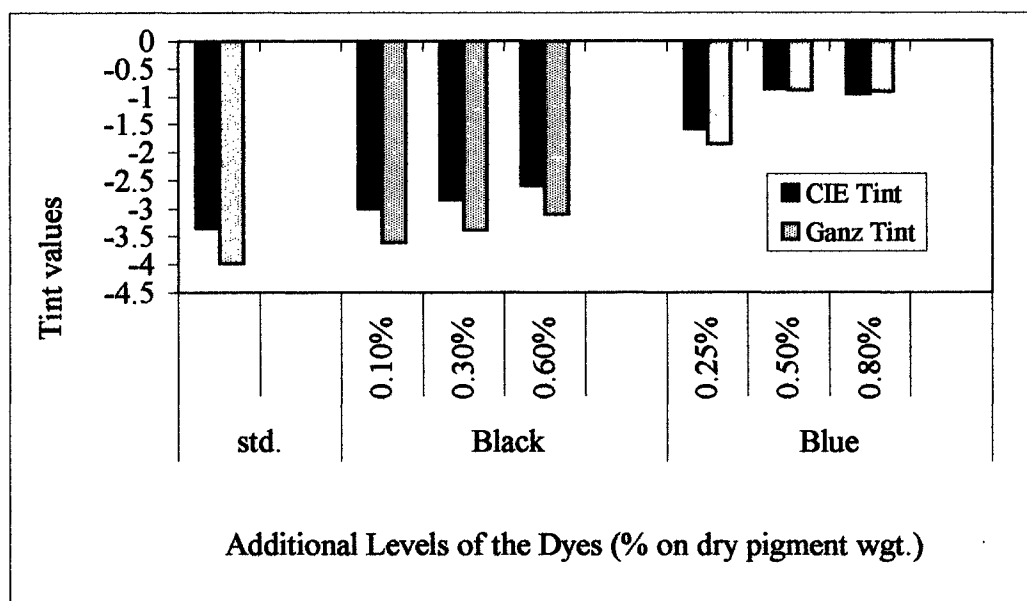


Figure 13. CIE and Ganz Tint Deviations Measured by GretagMacbeth Spectrophotometer.

L^* , a^* and b^* values are given in Figure 14. As can be seen, two spectrophotometers used are in good consensus as far as L^* , a^* , b^* values are concerned. Figure 14a and 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 14b, 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 15 shows the influence of FWA on TAPPI brightness and the corresponding reflectance with the GretagMacbeth Spectrolino spectrophotometer. Tests were made including and excluding the UV light source during the measurements.

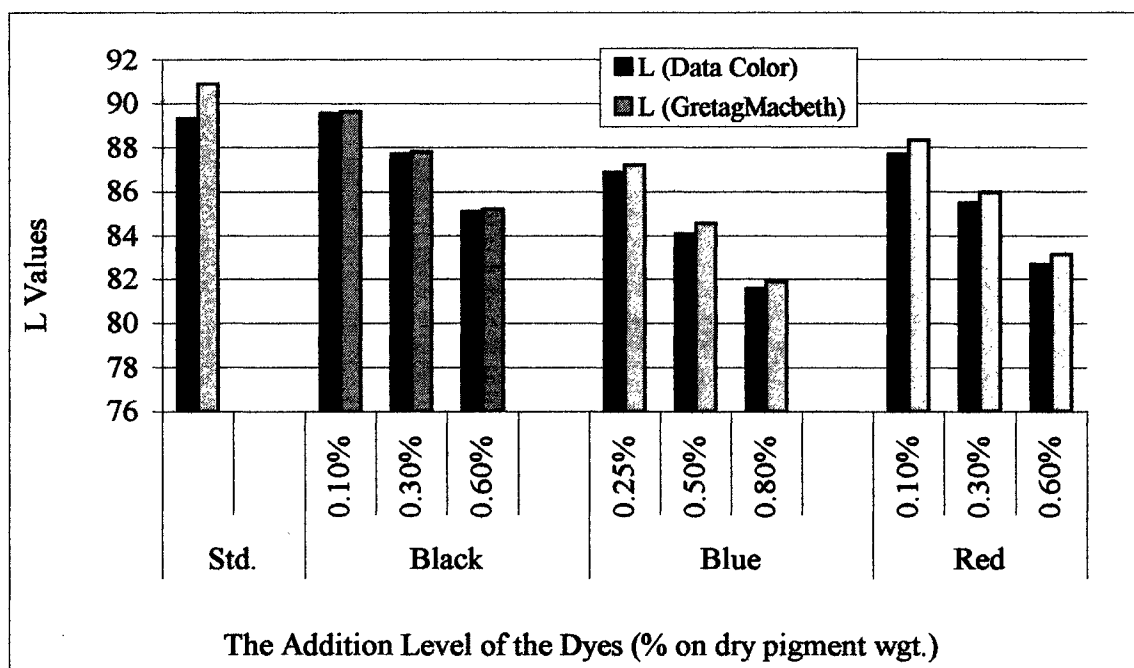


Figure 14a. Measured L^* Values Acquired by datacolor Spectraflash and GretagMacbeth Spectrophotometers.

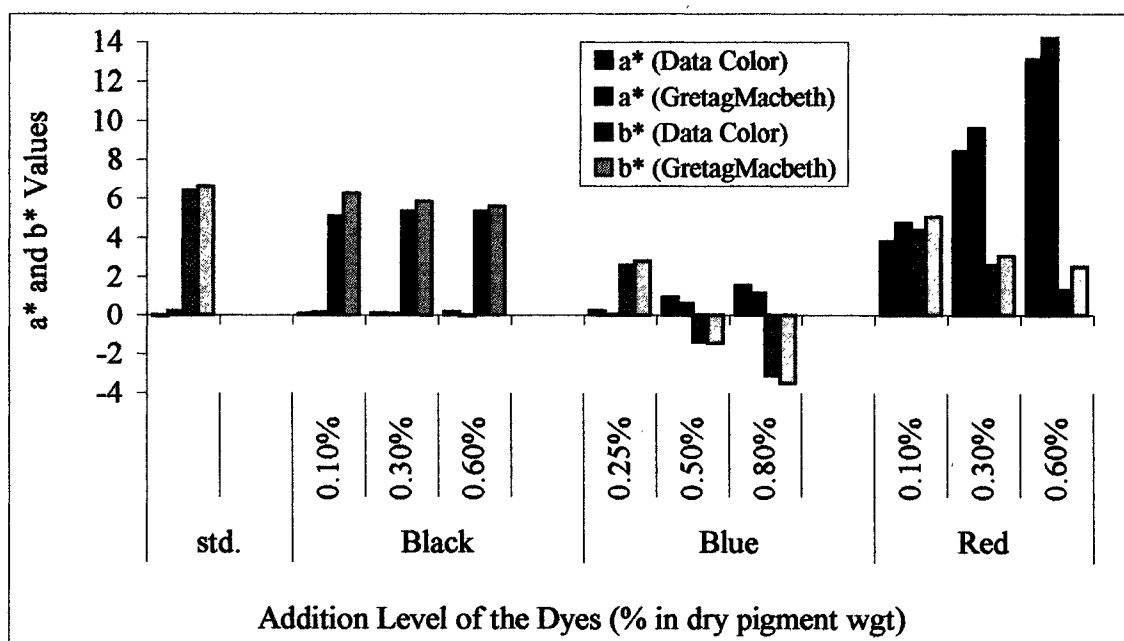


Figure 14b. Measured a^* and b^* Values Acquired by datacolor Spectraflash and GretagMacbeth Spectrophotometers.

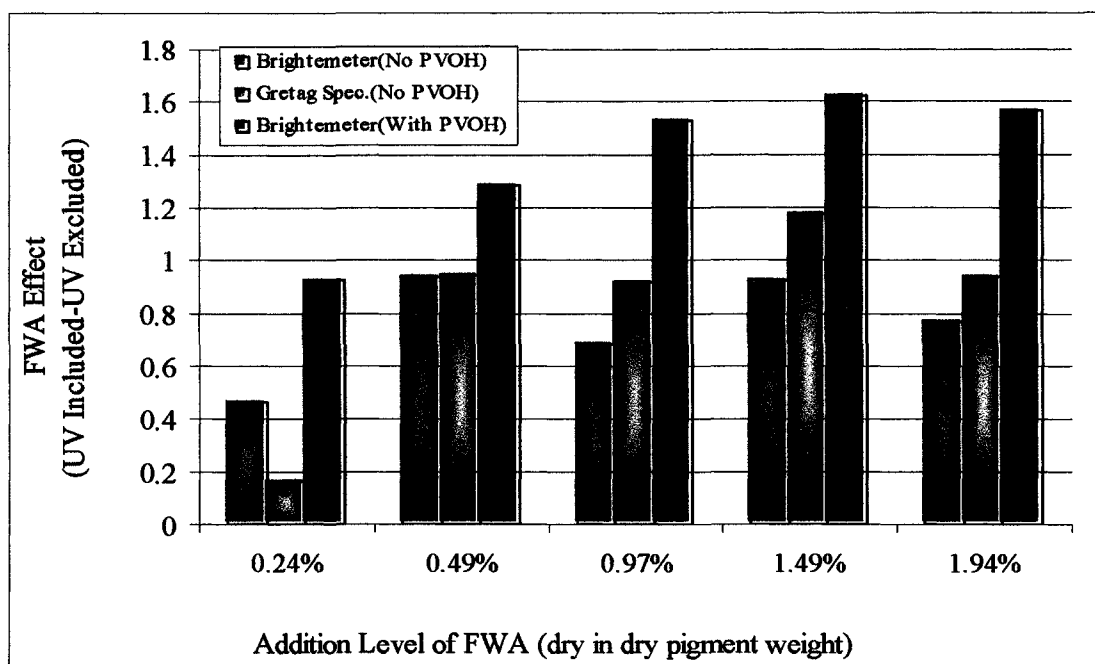


Figure 15. FWA Effect on TAPPI Brightness and the Corresponding Reflectance Values for GretagMacbeth Spectrolino Spectrophotometer (R@ 460 nm).

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 Spectrolino 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.

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.

The a^* values, shown in Figure 16b, are slightly increased 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 base-sheet (mixture of Kraft and groundwood pulp). The b^* values for all of these cases are more than twice that of the proposed SWOP guidelines (6) 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%.

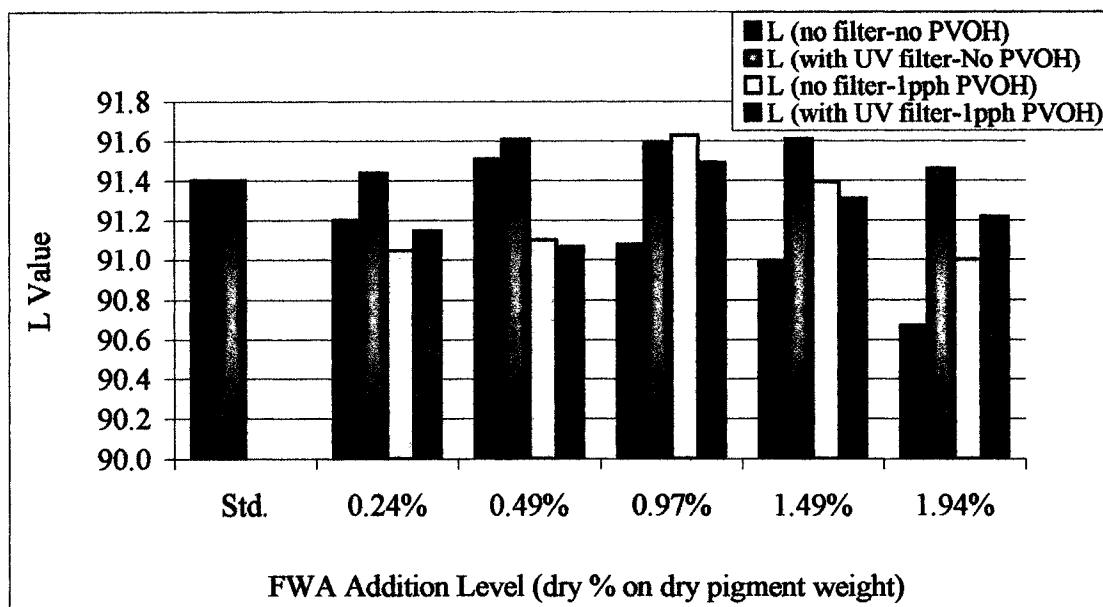


Figure 16a. FWA Effect on CIE L Values for the GretagMacbeth Spectrolino Spectrophotometer.

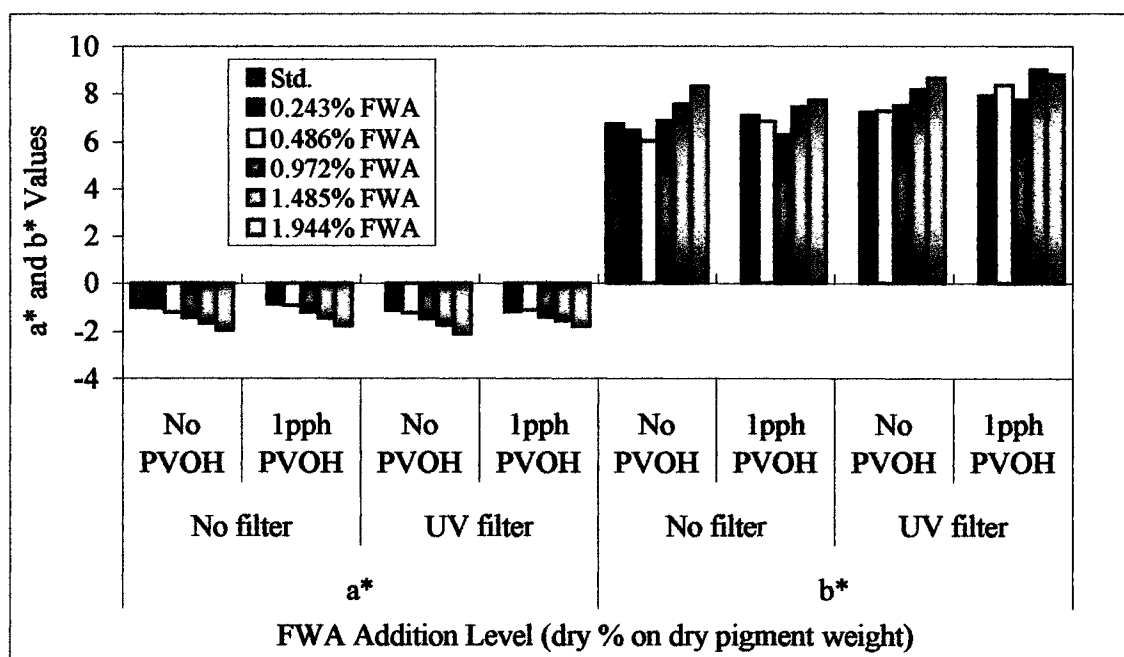


Figure 16b. FWA Effect on CIE a^*b^* Values for GretagMacbeth Spectrolino Spectrophotometer.

Above about 1% FWA, the b^* increases to a value larger than the base case, where no FWA is present. Thus, there is no benefit, and in fact there is a detriment, of FWA above about 1% on a dry basis. In all cases the beneficial effects of the FWA 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 17 shows the statistical analyses of observer evaluations of 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 no observed whiteness at all for the whiteness evaluations. Similarly, a scale of 5 implies an extraordinary green tint on the paper surface while 1 implies no green tint is 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 greening in either the colorimetry or the observer data.

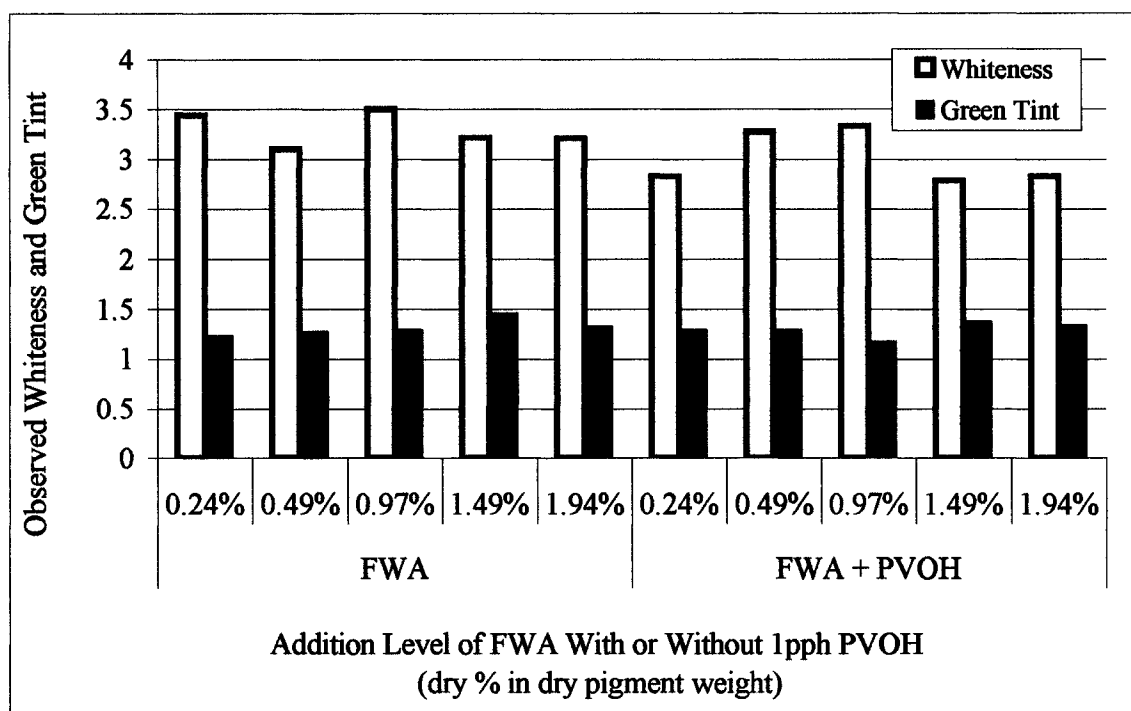


Figure 17. Observer Evaluation of Coated Light Weight Papers at Varying Addition Levels of FWA.

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 datacolor Spectraflash 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

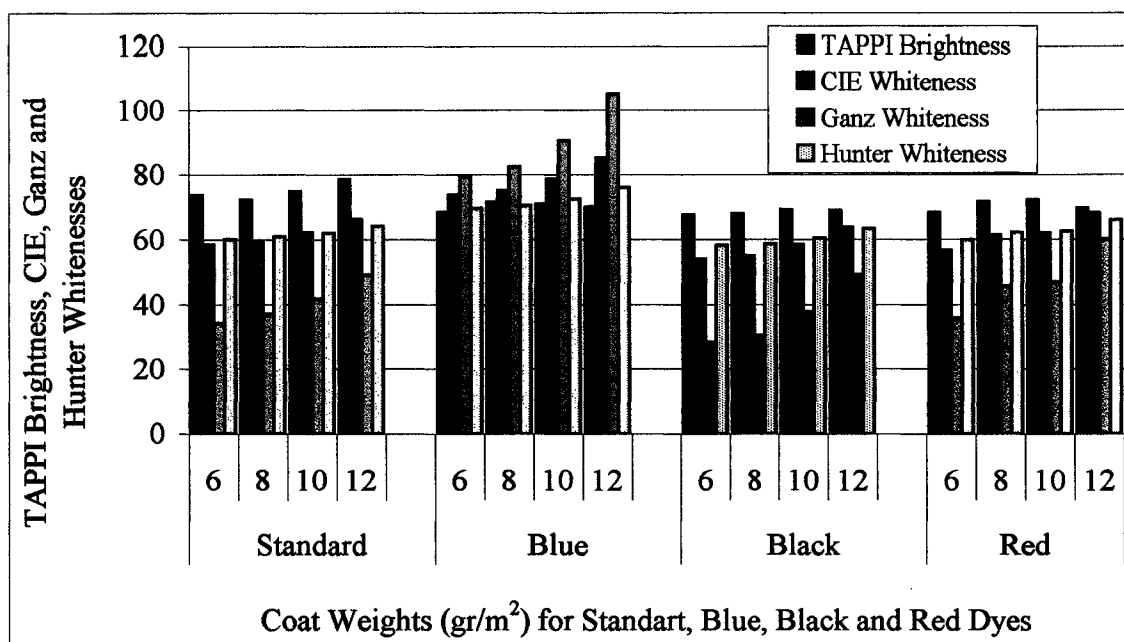


Figure 18. Coat Weight Effect for Standard Coated Papers, Blue, Black, Red Dye on TAPPI Brightness and CIE, Ganz and Hunter Whiteness Values Measured by the datacolor Spectraflash Spectrophotometer.

only slightly influenced with the increased coat weight. Changes in TAPPI brightness are considered insignificant in most cases.

The Micro S4-M and the GretagMcBeth 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 Spectrolino 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.

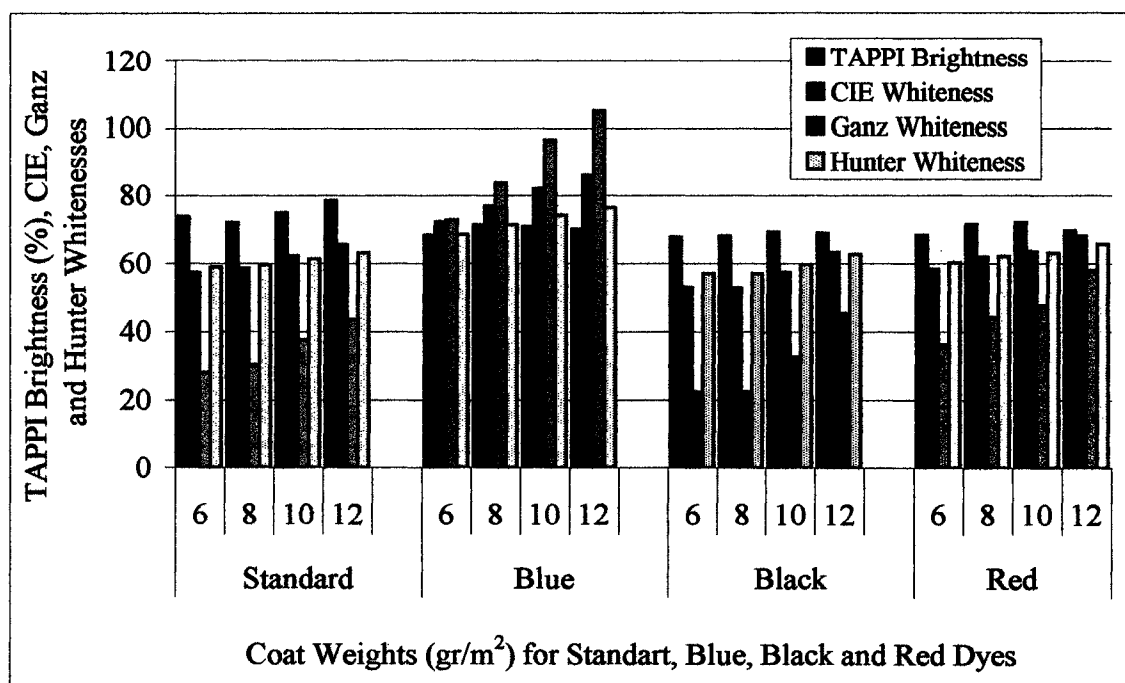


Figure 19. Coat Weight Effect for Standard Coated Papers, Blue, Black, Red Dye on TAPPI Brightness and CIE, Ganz and Hunter Whiteness Values Measured by GretagMacbeth Spectrophotometer.

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 0.6 % to 1.46% and steadily increased with increasing coat weight.

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 an 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 losing 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 .

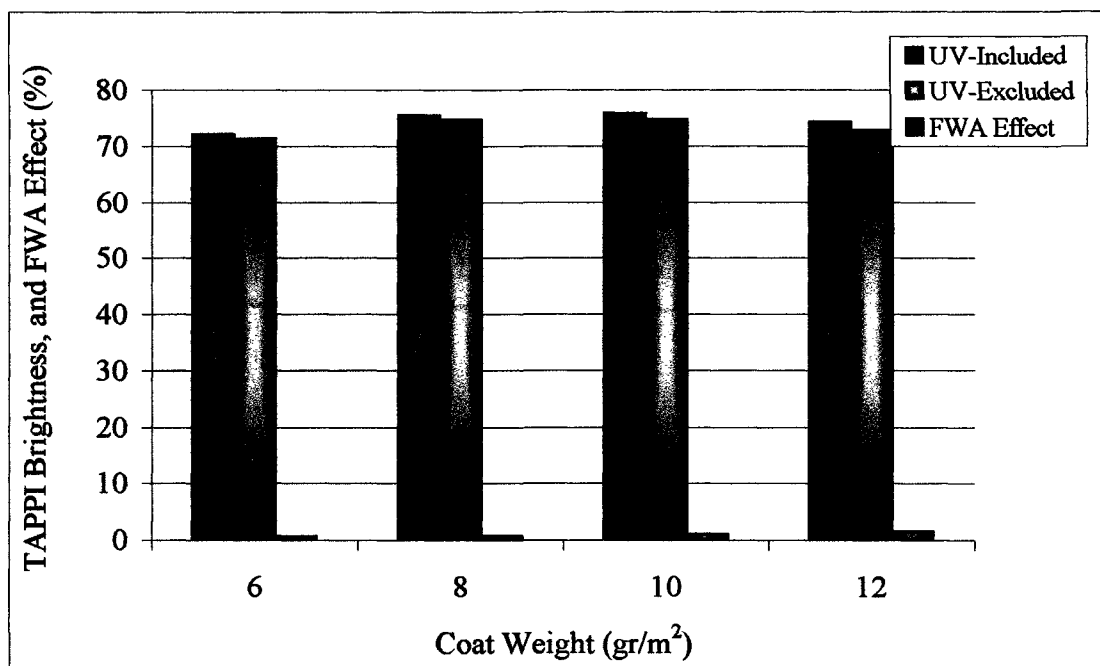


Figure 20. Coat Weight Effect for FWA on TAPPI Brightness.

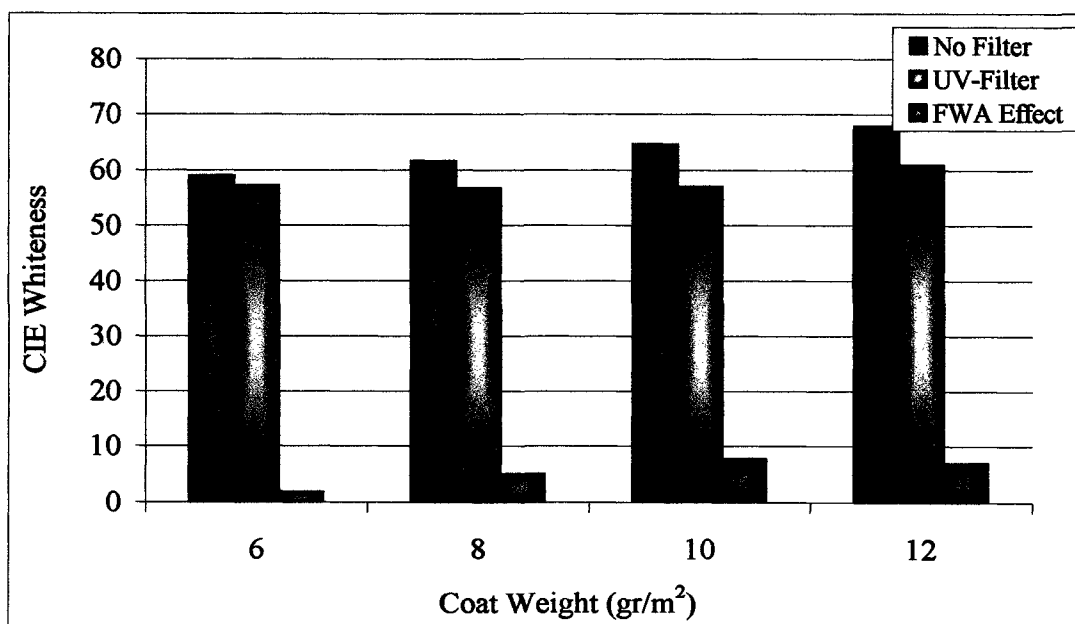


Figure 21. Coat Weight Effect on CIE Whiteness of Coated FWA Containing Paper.

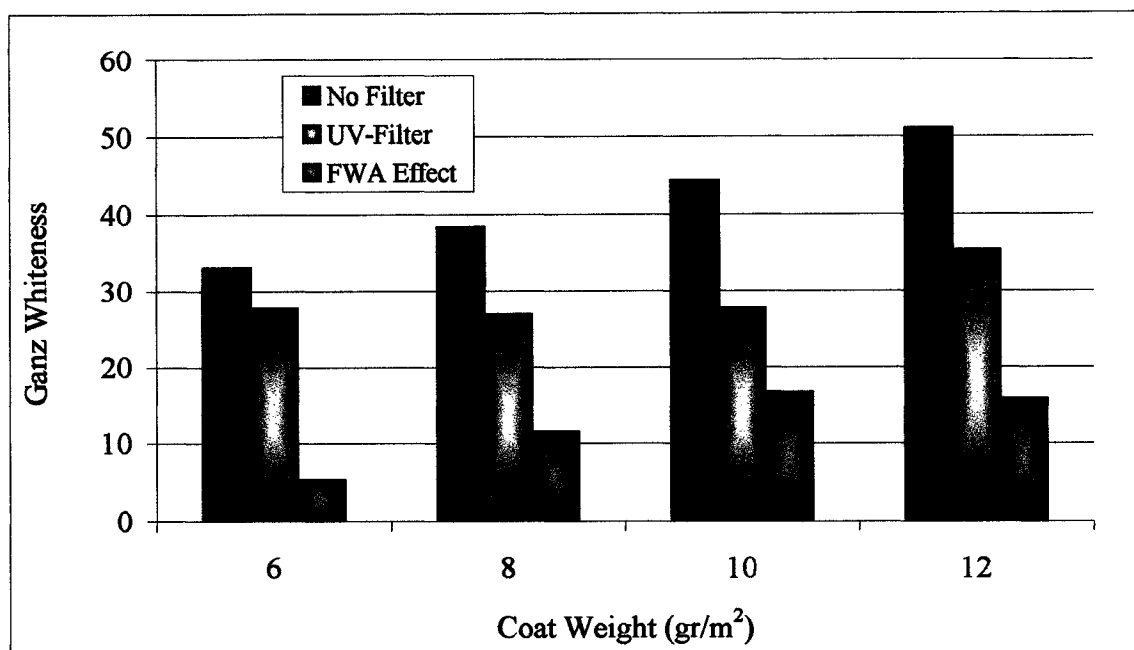


Figure 22. Coat Weight Effect on Ganz Whiteness of Coated FWA Containing Papers.

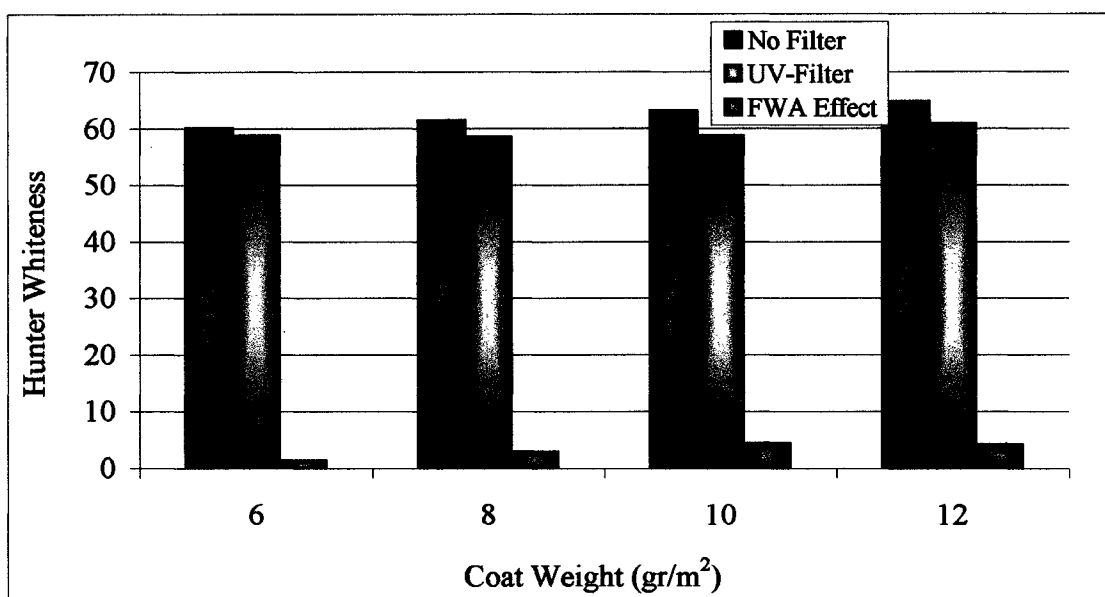


Figure 23. Coat Weight Effect on Hunter Whiteness of Coated FWA Containing Papers.

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 and economical 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.

Conclusions

It was found that in some cases, calculated CIE, Hunter, and Ganz whiteness values increased with increased amounts of color 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, even at high levels of FWA.

Appendix A

Coating Material Information

Delaminated Clay (Huber-Hydraprint)

TiO₂ (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)

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VI. WHITENESS EVALUATIONS ON TINTED AND FWA ADDED PAPERS

Abstract

There have been many whiteness formulas 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 a sample relatively as to whiter, lighter and bluer. When these formulae are applied to colored samples, they are generally meaningless. On the other hand, they satisfactorily characterize the appearance of commercial whiteness. They are mostly unsuccessful in assessing tinted samples with chromaticities placed on the borders of white colors. Previously, we showed that large differences in calculated CIE (Commission Internationale de l'Eclairage) whiteness could frequently occur when the colors of papers are slightly altered from neutral white to varying shades of whites. In the same study, observers assessed the whiteness of the tinted papers as either equivalent or very similar in appearance to each other.

In this study, three different colorants (blue, black and red), and FWA were added into coating formulations from three to four addition levels and applied to a wood-free #1 publication grade paper. The optical properties were then measured with a GretagMacbeth spectrophotometer. The CIE, Hunter, Ganz and newly proposed Fleming-

Aksoy whiteness formulae were analyzed and compared on colored papers whose properties were within the equality limits described by CIE.

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 tristimulus 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 brightimeters. 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 tristimulus measurements and having the form (1,11,12):

$$W = Y + 800(x_n - x) + 1700(y_n - y) \quad (1)$$

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 equation:

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

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 can be used only in a limited region. Criteria for whiteness are that the value of W fall within the limits given by:

$$5Y - 280 > W > 40 \quad (3a)$$

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 close 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 (7,15).

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 (12,14).

The Ganz Whiteness Formula

The whiteness formulae that Ganz proposed is as follows (6,7):

$$W = (D \cdot Y) + (P \cdot x) + (Q \cdot y) + C \quad (4)$$

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:

$$H=\text{Hue: } \delta W/\delta H$$

$$S=\text{Saturation: } \delta W/\delta S$$

$$Y=\text{Lightness: } \delta W/\delta Y$$

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).

$$D = \delta W/\delta Y \quad (5)$$

$$P = (-\delta W/\delta S) * (\cos(\phi + \eta)/\cos\phi) \quad (6)$$

$$Q = (-\delta W/\delta S) (\sin(\phi + \eta)/\cos\phi)^* \quad (7)$$

$$C = \{-W_0 * (1 - \delta W/\delta Y) - (p * x_1) - (Q * y_1)\} \quad (8)$$

All calculations are made in radiance, 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 $\lambda_0 = 470$ nm, where

$$\eta = \text{atan}(y_1 - y_0)/(x_1 - x_0) = 0.84084 * (D_{65}/10^\circ) \quad (9)$$

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.

$$\text{At } D_{65}/10^\circ \quad x_1 = 0.3138, y_1 = 0.3310, x_D = 0.11518, y_D = 0.10904$$

$$\delta W / \delta H = -\delta W/\delta S * \text{tg}\phi = -1071.8$$

$$S = (\text{tg}\psi * (x_1 - x) - (y_1 - y))/(\text{tg}\psi * \cos\eta - \sin\eta) \quad (10)$$

$$\text{Where } \psi = \phi + \eta + \pi/2 = 2.67343 \quad (7).$$

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

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

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 tint deviation formula as an additional factor to the in the calculation of whiteness to make instrumental whiteness assessments more accurate.

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

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 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 proved 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. This study aimed 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:

$$W = L - 3b \quad (12)$$

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 an imaginary blue-white and measures whiteness as the distance in color space from the sample to that ideal (2).

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 be 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 (16,17). 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.

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.

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

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/m² to a commercially produced base paper made from bleached Kraft and mechanical pulp (100 g/m² 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} (18) (near neutral) and W_{FA} (18) (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 spectrophotometric curve 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 spectrophotometric curves 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 above, a Xenon light

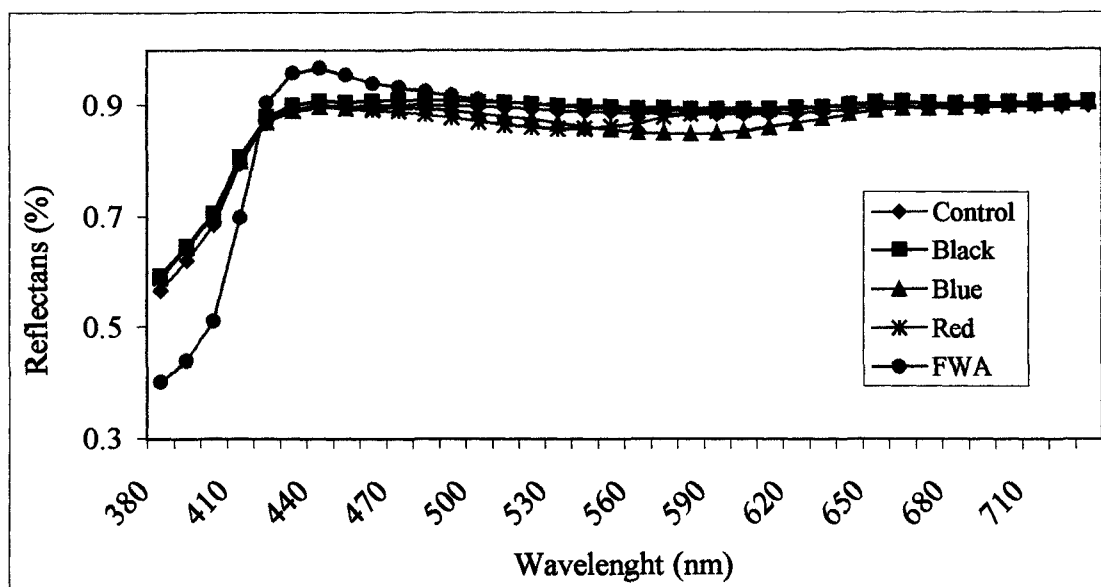


Figure 1. Color Spectra of Coated Paper, Blue, Black and Red Dyes and FWA.

source would be a better choice for measuring the effects of human observation of a FWA treated paper.

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 little white to 5-extremely 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 white to the observers.

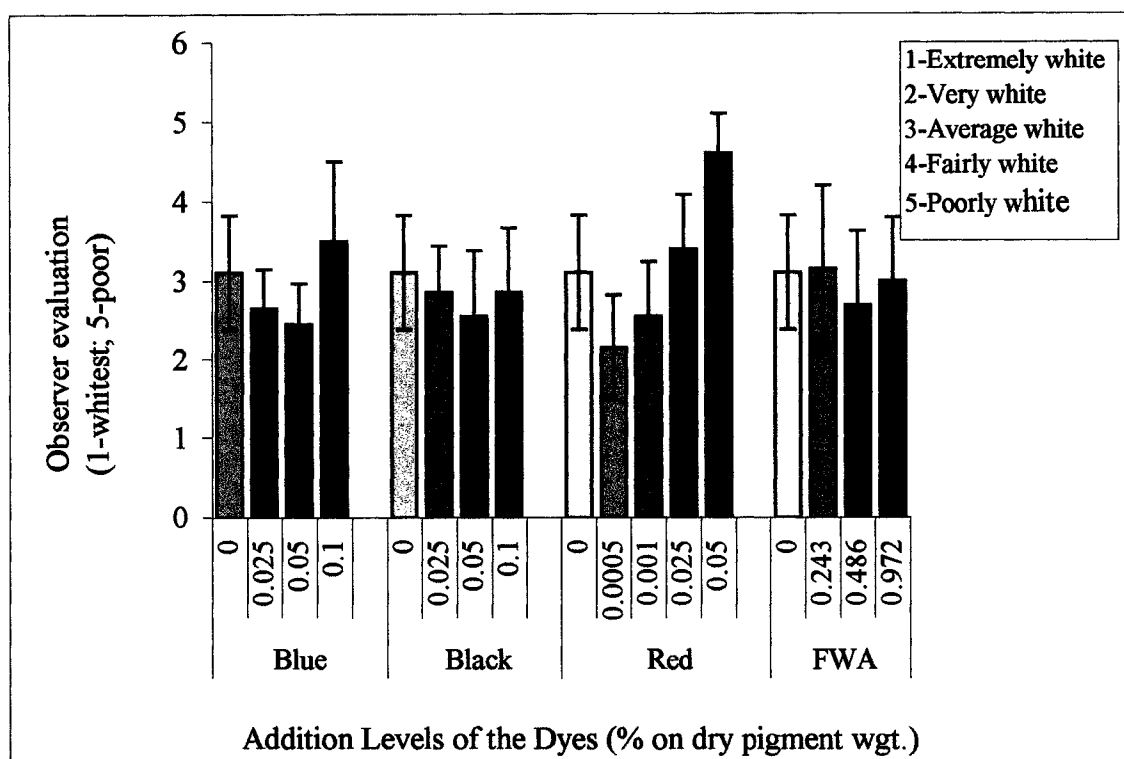


Figure 2. Observer Evaluation of Coated Publication #1 Grade Papers at Varying Addition Levels of Blue, Black and Red Dyes.

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 D65/10° and C/2°, respectively. All whiteness values but N_{FA} and W_{FA} increase as the addition level of blue dye is increased. This increase is more pronounced for the Ganz whiteness. For the blue tinted samples at D65/10°, the correlation coefficients for N_{FA} with the average rank data were -0.58. The corresponding correlation coefficients were 0.46 for Ganz, .44 for CIE, -0.44 for Hunter -0.43 for W_{FA} . The corresponding rank correlations were -0.35 for W_{FA} and -0.2 for CIE, Ganz and Hunter, and 0.2 for N_{FA} .

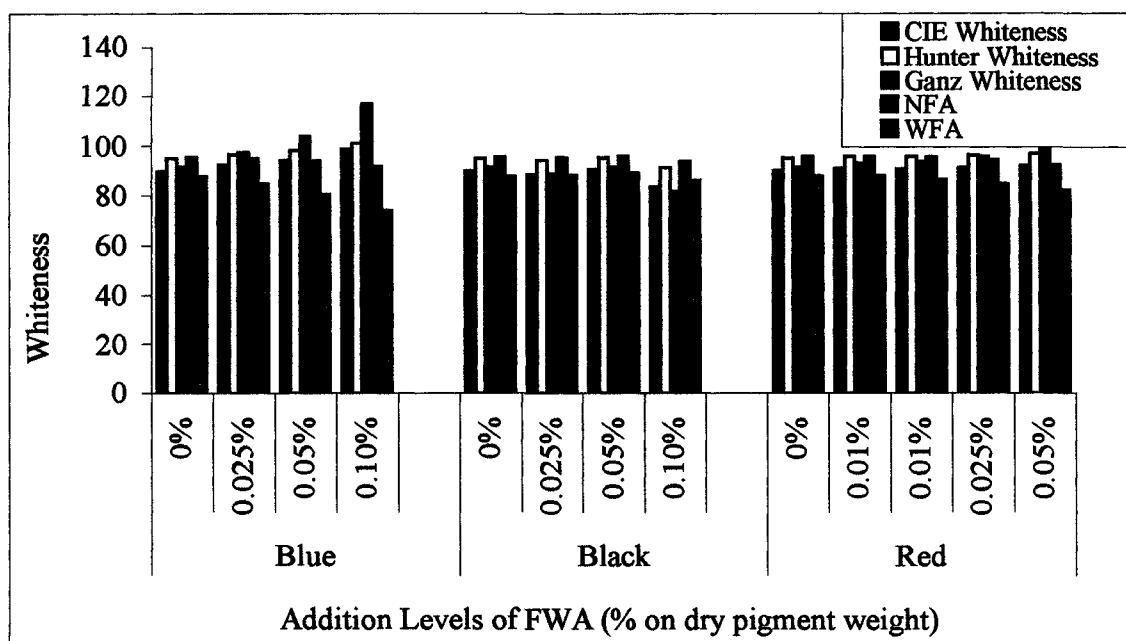


Figure 3. CIE, Hunter, Ganz, N_{FA} and W_{FA} Whitenesses for Blue, Black, Red Dye # 1 Publication Grade Papers at $D_{65}/10^\circ$.

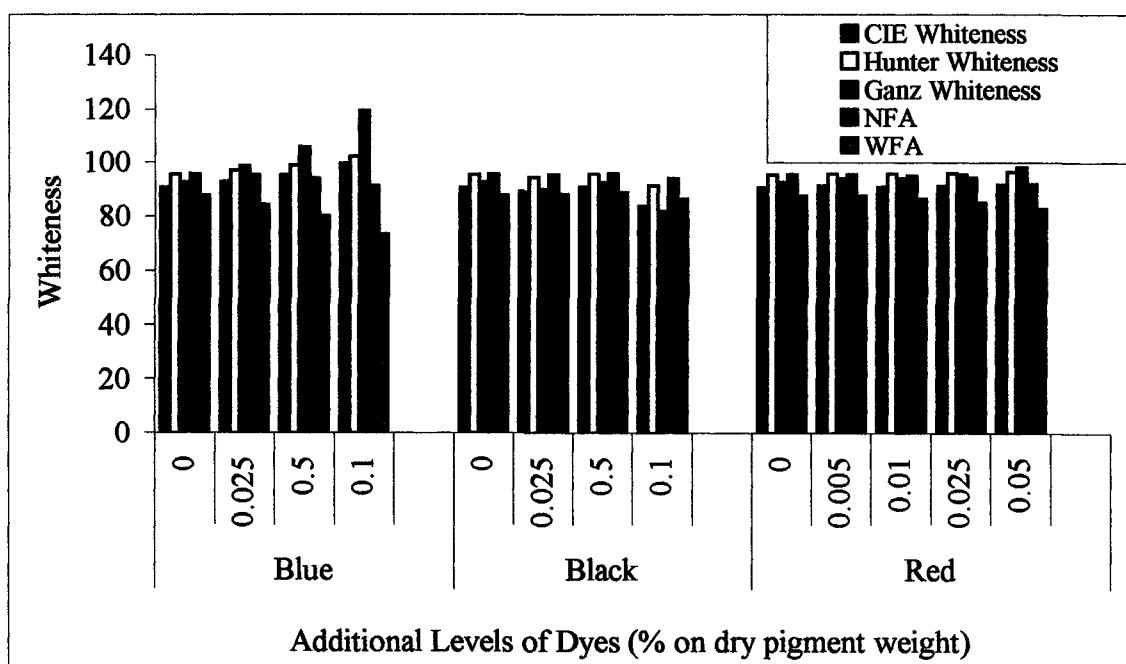


Figure 4. CIE, Hunter, Ganz and N_{FA} and W_{FA} Whitenesses for Blue, Black, Red Dye # 1 Publication Grade Papers at $C/2^\circ$.

All whiteness values remained mostly unchanged after addition of the red dye. At D65/10°, N_{FA} exhibited the best agreement with the observer assessments with a correlation coefficient of -0.94 followed by W_{FA} with a correlation coefficient of -0.90. The corresponding correlation coefficients for Ganz, Hunter and CIE were 0.83, 0.72 and 0.61 (with an opposite sign), respectively. Again N_{FA} produced the highest rank correlation with 0.9, followed by W_{FA} with -0.86. Rank correlations for Ganz were -0.7, for CIE and Hunter were -0.6.

Whiteness values varied insignificantly with black dye addition in both figures. Corresponding correlation coefficients and ranking correlations for black dye added samples were fairly small for all whiteness formulas but W_{FA} . At D65/10°, correlation coefficients were -0.47 for W_{FA} , -0.23 for N_{FA} , and -0.11, -0.09 and -0.04 for CIE, Hunter and Ganz, respectively. Ranking correlations were -0.29 for W_{FA} , -0.51 for Ganz and 0.1 for N_{FA} , Hunter and Ganz. It should be noted that compared mean ranks from observer evaluations and whiteness values were in such a narrow region. Similarly, correlation coefficients and ranking correlations were calculated for C/2°. The acquired data were fairly consistent and very much the same with the D65/10° data.

The correlation coefficients for the red dye tinted samples were comparatively high while variation 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} has given the highest correlation coefficients in each test sample group except the black tinted samples where the highest correlation coefficient belongs 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.

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 equality 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).

It should be noted that the metric is different for both scales; the threshold for distinguishing different whiteness is defined by the Ganz scale as being 5 points, for CIE whiteness it is about 2.3 to 2.4 points. The threshold for distinguishing different tints lies at 0.5 points.

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 than the black.

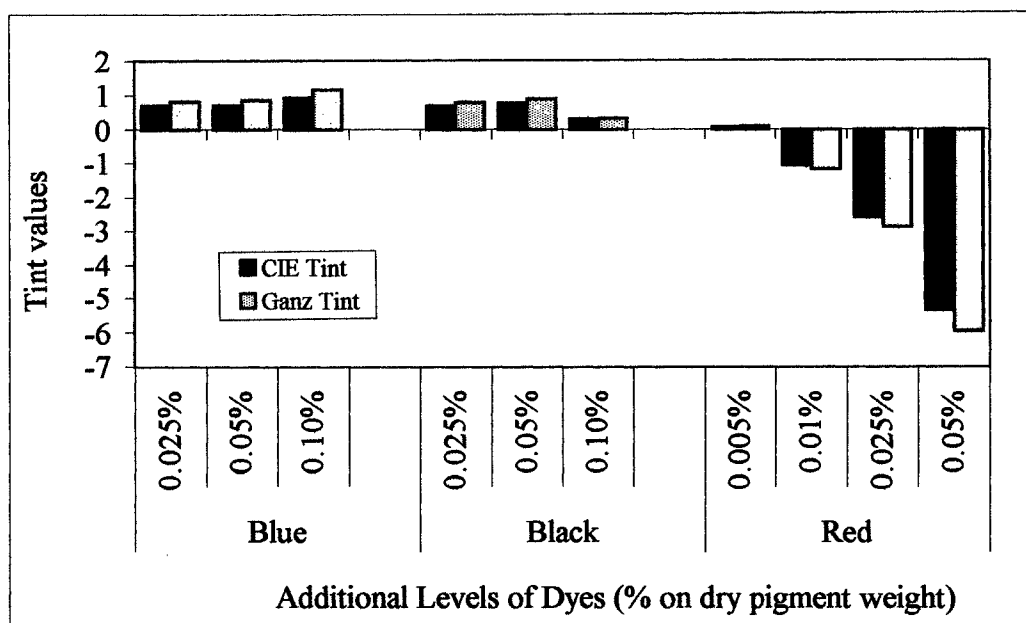


Figure 5. CIE and Ganz Tint Values for Blue, Black, Red Dyed #1 Publication Grade Papers at D65/10°.

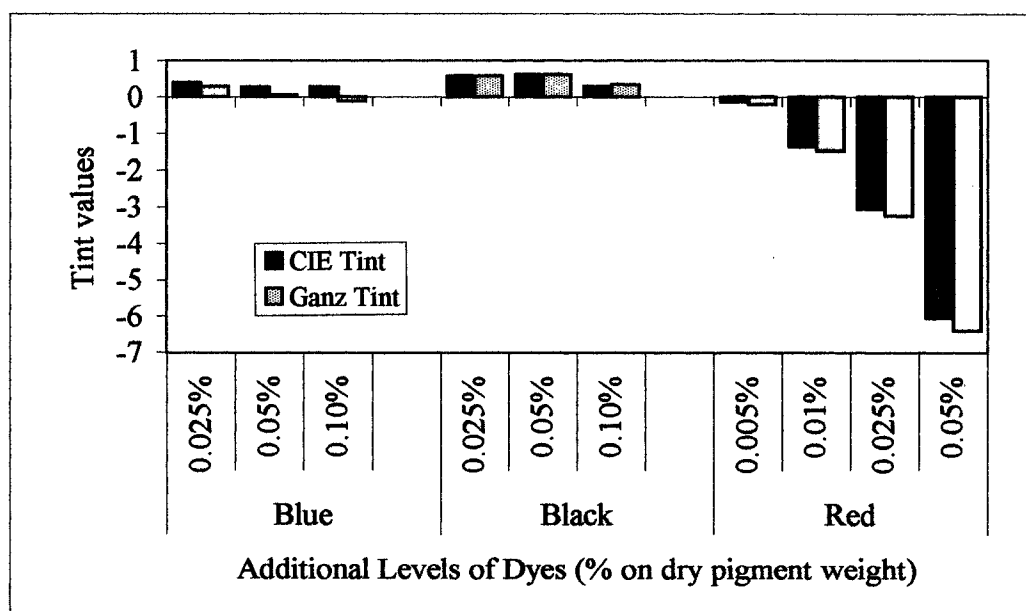


Figure 6. CIE and Ganz Tint Values for Blue, Black, Red Dyed #1 Publication Grade Papers at C/2°.

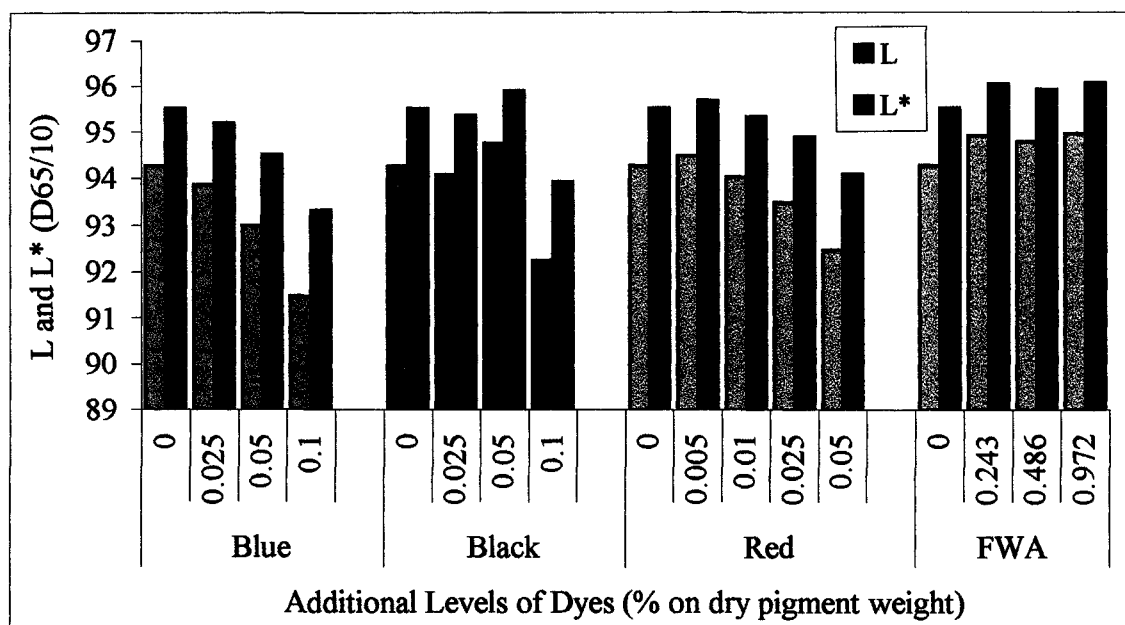


Figure 7. CIE and Hunter L Values for Blue, Black and Red Dyed #1 Publication Grade Papers at D65/10°.

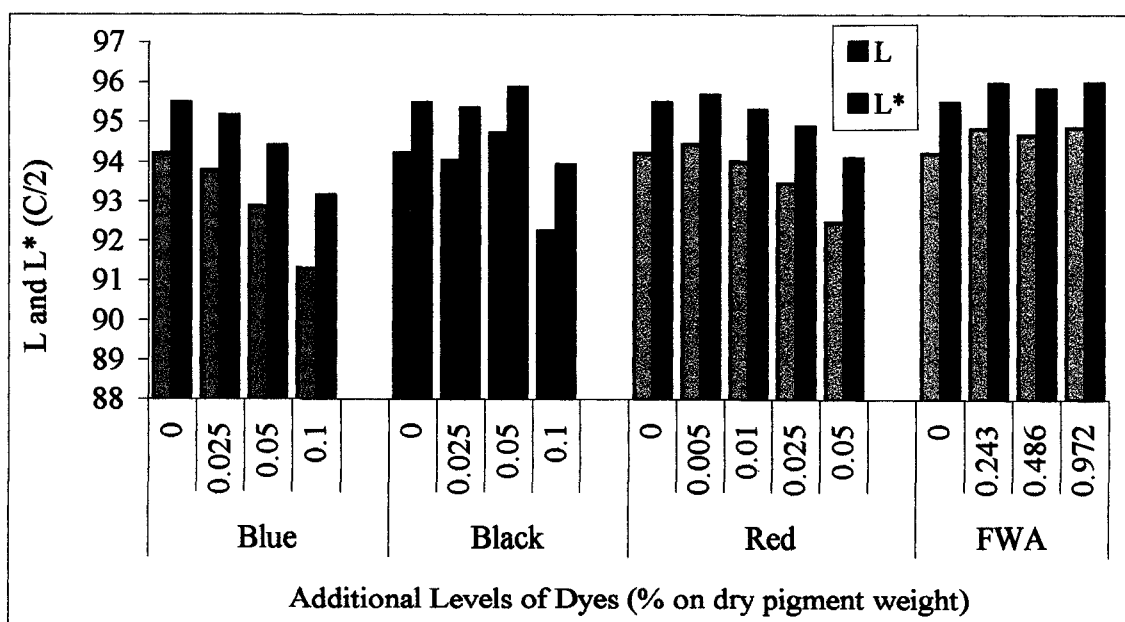


Figure 8. CIE and Hunter L Values for Blue, Black and Red Dyed #1 Publication Grade Papers at C/2°.

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. 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.

Again, the b values for the black and FWA samples were random and changes in the values with dye level were insignificant. Both the “a” and “b” values were around 0 for the black dyed samples.

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 the Fleming-Aksoy whiteness values, 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 and Hunter whiteness values increased. This increase was more pronounced for the Ganz values. The N_{FA} and W_{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

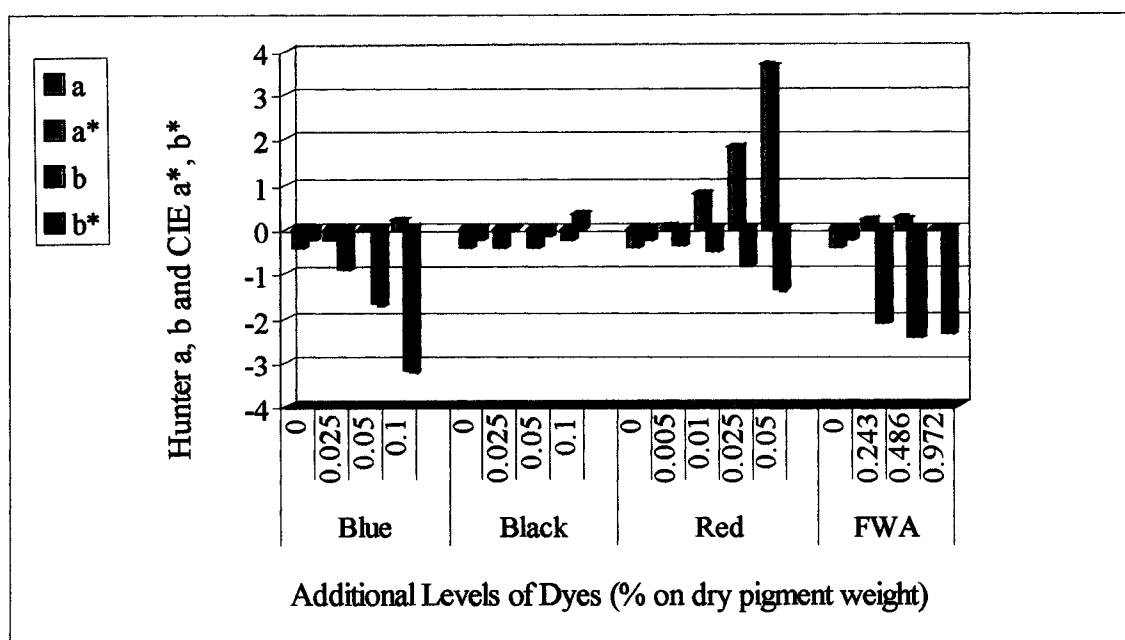


Figure 9. CIE and Hunter a and b Values for Blue, Black and Red Dyed #1 Publication Grade Papers at D65/10°.

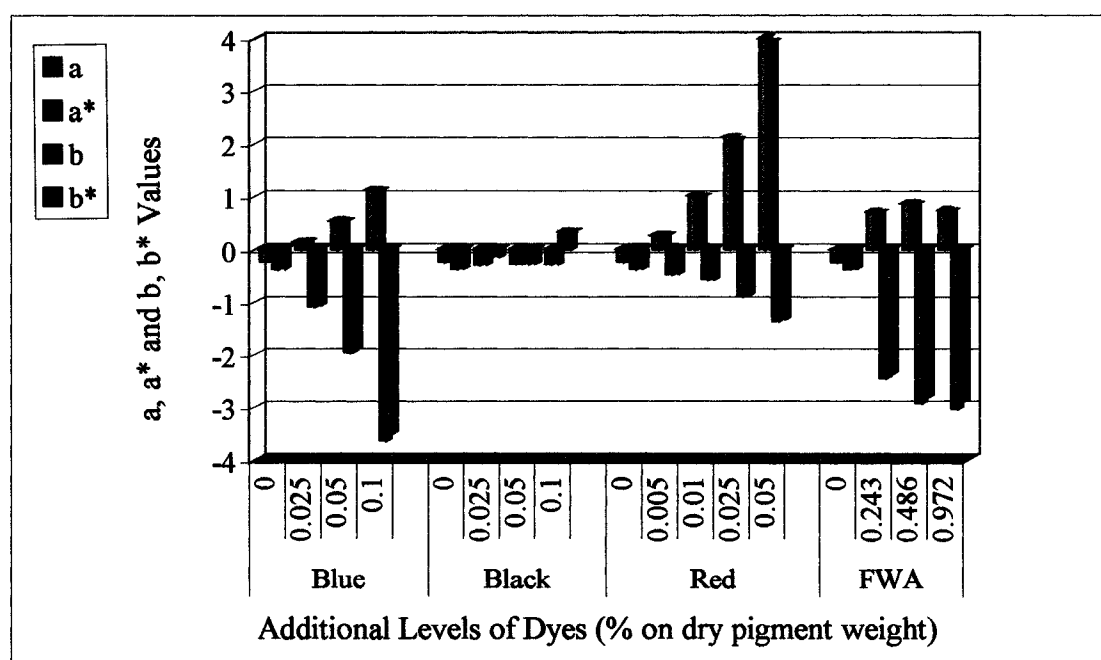


Figure 10. CIE and Hunter a and b Values for Blue, Black and Red Dyed #1 Publication Grade Papers at C/2°.

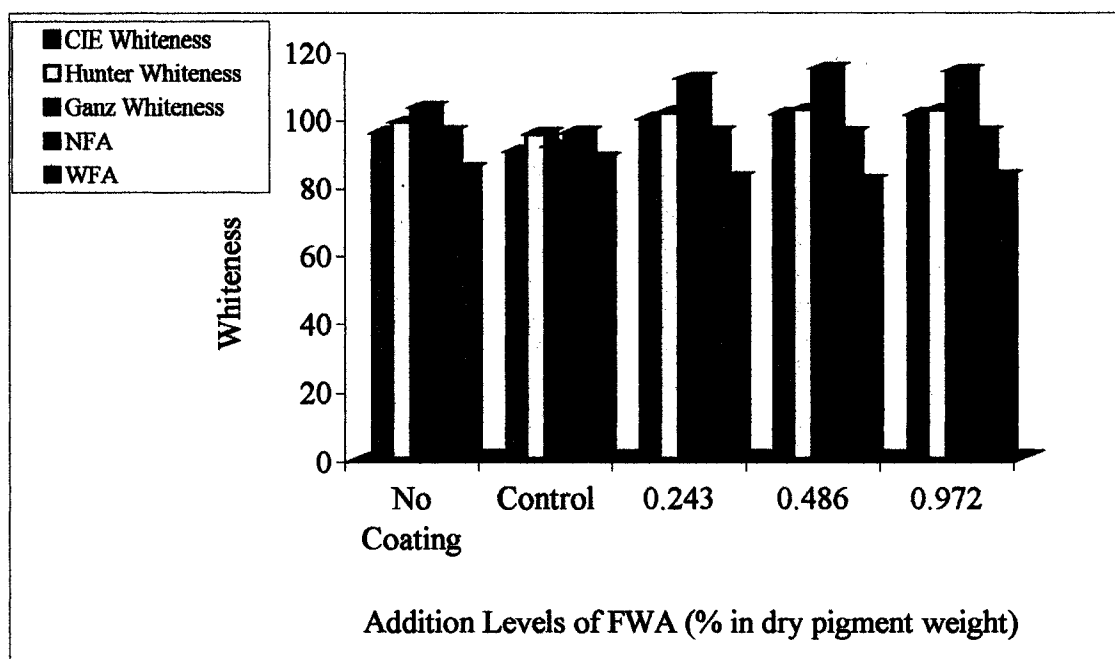


Figure 11. CIE, Hunter, Ganz, N_{FA} and W_{FA} Whiteness Values of FWA #1 Publication Grade Papers at D65/10°.

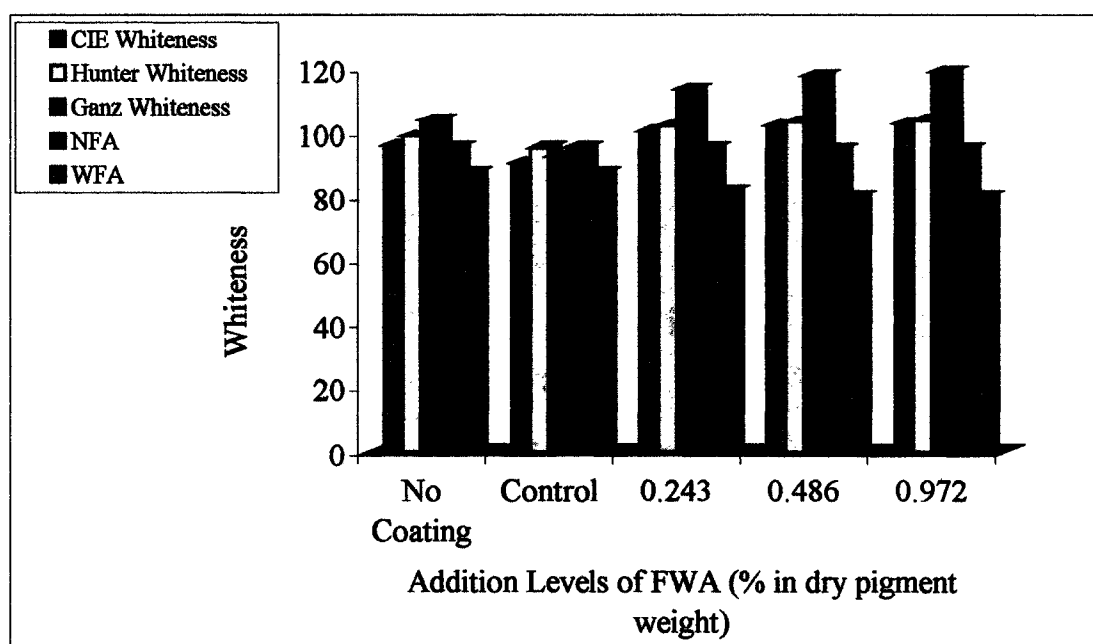


Figure 12. CIE, Hunter, Ganz, N_{FA} and W_{FA} Whiteness Values of FWA #1 Publication Grade Papers at C/2°.

the neutral whiteness and the formula does not choose any color component over any other as a preference color component.

The correlation coefficients for the average rank data are 0.99 for N_{FA} , 0.47 for W_{FA} , -0.45 for CIE and Hunter and -0.47 for Ganz. The rank correlations were 0.98 for N_{FA} , 0.65 for W_{FA} and -0.63 for Ganz, and -0.62 for CIE and Hunter.

The tint values for FWA dyed samples were all well within the equality 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 D65, 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 and Hunter whitenesses. The N_{FA} and W_{FA} whiteness remained near constant regardless of how much FWA was added.

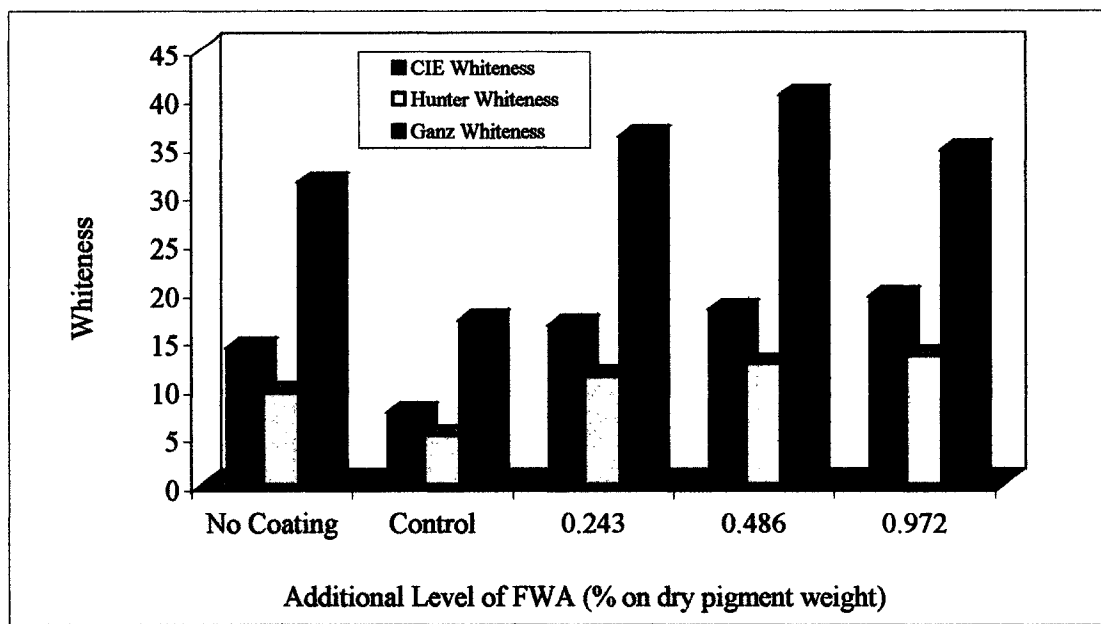


Figure 13. Fluorescent Effect at D65/10°.

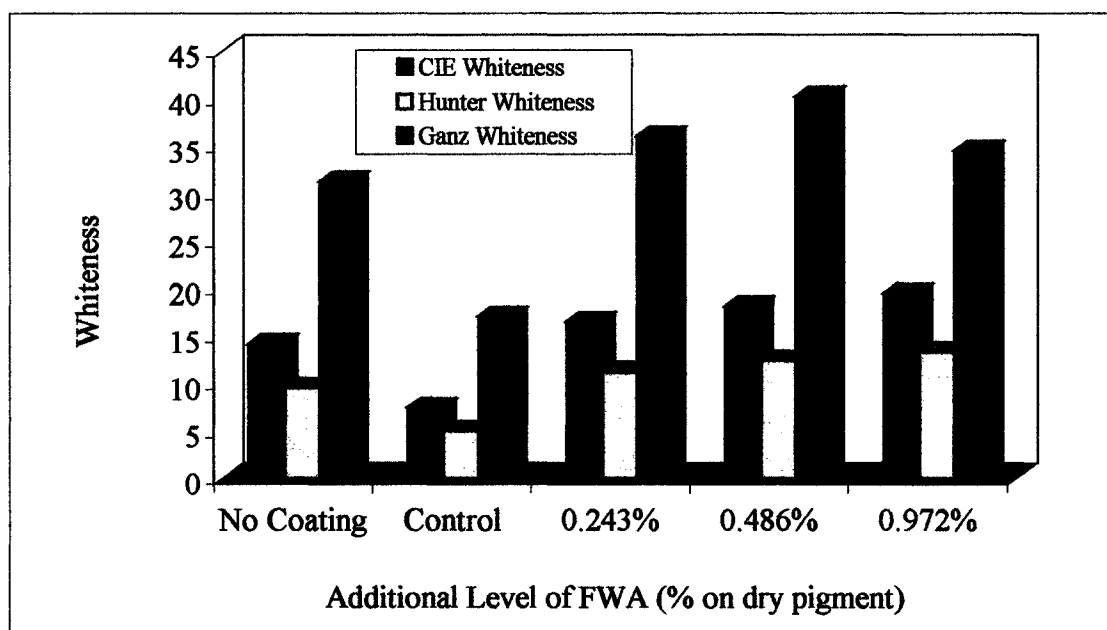


Figure 14. Fluorescent Effect at C/2°.

Conclusions

The N_{FA} and W_{FA} whiteness values exhibited the best correlation with observer assessments overall. All other whiteness values increased 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 best with the observer assessments for the FWA treated samples. The correlation between the observer assessments and all the whiteness formulas studied correlated well for red tinted samples. The change in whiteness values were a lot 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. However, the correlation coefficient for the F_{WA} was moderately higher than that of the CIE, Hunter and Ganz whiteness formulas. Again, the correlation coefficient of the N_{FA} was significantly higher than that of the CIE, Hunter and Ganz whiteness formulas for the black dye samples. For these observer evaluations, the W_{FA} and N_{FA} formulas showed a clear improvement over the CIE, Hunter and Ganz formulas.

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 W_{FA} and 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 CIE, Hunter and Ganz whiteness values increased as the addition level of FWA increased.

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VII. NEW MEASURES OF WHITENESS THAT CORRELATE WITH PERCEIVED COLOR APPEARANCE

Abstract

Most whiteness formulas currently in use satisfactorily characterize the appearance of commercial whiteness. However, when these formulas are applied to colored samples they are generally unsuccessful in assessing tinted samples with chromaticities placed on the borders of white colors. In this study, new formulas expressing whiteness are proposed. These are compared with CIE, Hunter and Ganz whiteness formulas and TAPPI brightness, through perceptual evaluation and instrumental measurements and analyses. Both of the proposed whiteness formulas matched well with 48 randomly selected observer assessments for printed samples, the one that is based on a maximum at neutral white being in a lesser degree. On the other hand, CIE, Hunter and Ganz whiteness formulas had a poorer correlation with the observers' evaluation. TAPPI brightness also agreed well with the observers' assessments, but it cannot be strictly correct because of its reliance on a narrow wavelength range. Relatively saturated chroma values are associated with the maximum whitenesses with the evaluated CIE, Hunter and Ganz whiteness formulas. The proposed whiteness formulas don't suffer from this abnormality.

Introduction

Over the years, many studies have been carried out and many formulas proposed for whiteness. However, disagreements and arguments have never ended (1,2). One important argument is about description of perfect whiteness and which directions of departure from it should be favored or avoided (1-3). The arguments are further confused by the semantic difference between “white samples” and “whiteness of samples” (1,3). A white sample is characterized by high levels of luminosity and no saturation- therefore no hue at all (3). On the other hand, samples showing high whiteness are characterized by high levels of luminosity and finite saturation-with a blue hue (3). As such, whiteness is characterized as being contrary to yellowness.

In addition, widespread usage of fluorescent whitening agents, to improve the whiteness of objects, has compounded the disagreements in evaluating whiteness (1-5). That is because whiteness depends on observers, and for the same observer, it also depends on the evaluation methods applied (1-3). It also depends on the individual observer preference and many other varying conditions (2,3).

Any whiteness assessment technique is first based on the perceptual evaluation and psychometric techniques (3). Then instrumental measurement and analyses are made and a correlation between the perceptual evaluation and instrumental measurements is searched. There have been many attempts to approximate observer preferences in regards to tint or hue of the object by assigning different weight proportions in formula parameters (6,14).

Technical Considerations

Chromaticity Coordinates and the Chromaticity Diagram

Three color-matching functions were defined by the CIE (*Commission Internationale de l'Eclairage*) in 1931 (15). These correspond to human red, green and blue color perception and are usually called the 2° observer functions, because the CIE visual observations were conducted with a visual area subtending a

2° visual angle (1). In 1964 (16), the CIE defined an additional set of color matching functions corresponding to a 10° observer. These functions are generally used to estimate the human cone receptor's reaction to incident radiation from an object, if the radiation is known (1,2,6,7,17).

Spectrophotometers measure the amount of radiation versus wavelength and, therefore the cone responses can be estimated. The X, Y and Z tristimulus values are calculated in terms of the spectral response (15,16). X represents the red response, Y represents the green response and luminosity, and Z represents the blue response. Tristimulus colorimeters attempt to filter light to reproduce the human light cone response and X, Y, Z values can be calculated (15-17).

Each tristimulus value (X,Y,Z) is a primary of an axis in a three dimensional space and all together a sample's tristimulus values define a position in that three-dimensional space. A two-dimensional chromaticity diagram is obtained by performing two sequential projections. Tristimulus values are converted into two variables giving a two dimensional map. That is, magnitudes of tristimulus values are transformed into ratios of tristimulus values or in other words into chromaticity coordinates (1,7),

given by:

$$x = X/(X+Y+Z) \quad (1a)$$

$$y = Y/(X+Y+Z) \quad (1b)$$

$$z = Z/(X+Y+Z) \quad (1c)$$

Only two of the three chromaticity coordinates or projection values are needed to describe the color in chromaticity space, since the sum of the tristimulus values equals 1. They are usually x , and y chromaticity coordinates in the CIE system. The x and y values are usually plotted on the chromaticity diagram (1,2). The points in this diagram are indications of the hue and saturation of the corresponding colors. One of the tristimulus values, usually the Y value, also must be specified. The line connecting the points representing the chromaticities of the spectrum colors, spectrum locus, of the chromaticity diagram looks like a horseshoe as shown in Figure 1.

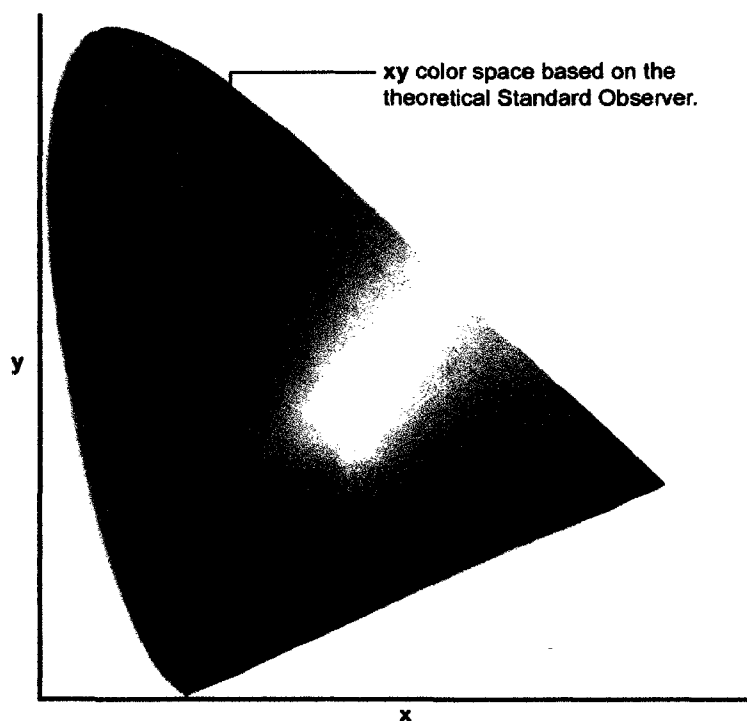


Figure 1. Chromaticity Diagram.

The CIE tristimulus system and CIE chromaticity diagram are not based on steps of equal visual perception. In other words, equal distances on the diagram do not correspond to equal visual differences, because equal chromaticity values can have arbitrary intensities. The projected values of x and y are not even perceived equally visually spaced, even for the same values of x and y . This is one of the biggest disadvantages of CIE tristimulus and chromaticity systems. However, there have been several studies conducted and proposals have been made to approach to equal perception. The CIE tristimulus system and the CIE chromaticity diagram do not intend to describe color appearance based on color perception. Rather they both intend to provide the information whether two samples match either in regards to their tristimulus values or their chromaticities. These systems do not tell what the samples look like or how the samples differ if they do not match. In reality, a given chromaticity can have a wide variety of appearances depending on the viewing conditions, and illumination (1).

As explained and shown above, two out of three dimensions of color can be shown in the chromaticity diagram. A three dimensional CIE color space is made by plotting axis Y rising from the illuminant point of the chromaticity diagram (Figures 2a, 2b). Therefore, the three-dimensional chromaticity diagram can be formed by the usage of two chromaticity coordinates x , y and Y , where all the real colors lie within, with exception of the black color. While the color white is located on the top of an achromatic axis in this diagram, the color black can lie anywhere because it is not well defined through the mathematical definition where X , Y , Z tristimulus values are all zero and corresponding x and y coordinates can be anywhere within the diagram (7).

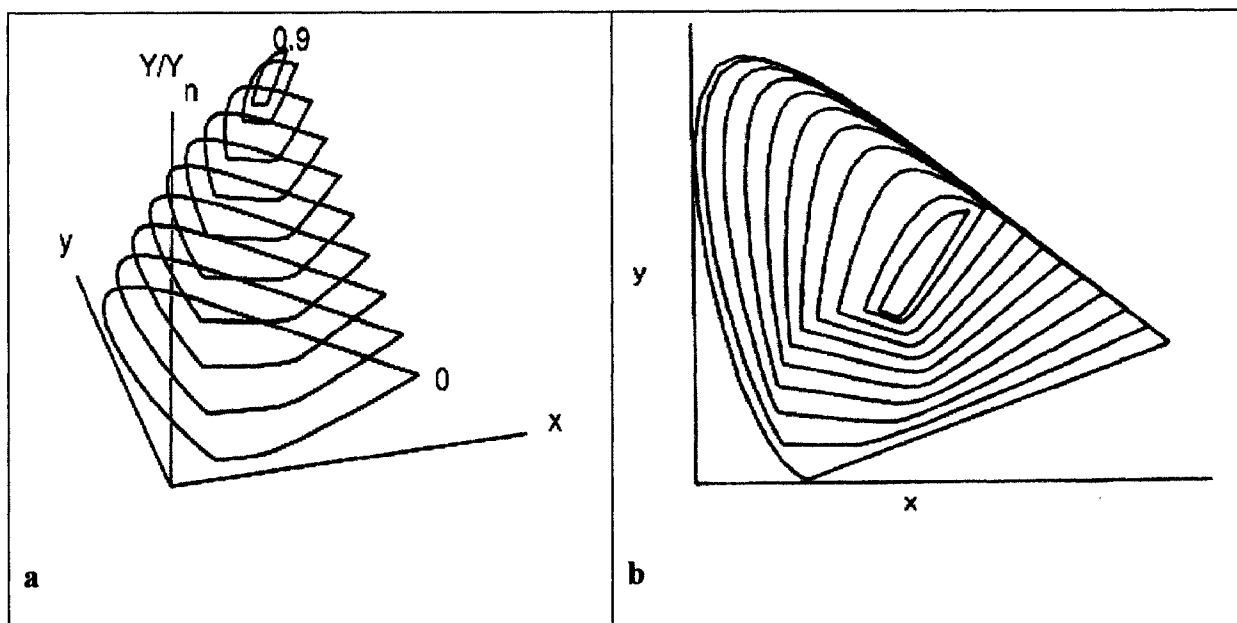


Figure 2. (a) Added Y on Chromaticity Diagram,
(b) Added Y on Chromaticity Diagram (Looking Down).

Source: Roy S. Berns, *Principles of Color Technology*, John Wiley & Sons, New York 2000.

Opponent-Type Systems

There have been several proposals made in transforming the CIE tristimulus system. In 1939, Breckenridge et. al. (18) developed uniform chromaticity diagrams in which neutral colors, including the reference white, would plot at the intersection of the diagram's coordinate axes. The position of a color relative to the origin would indicate its hue and chroma (saturation). Later, Hunter (6,7,19) adopted this concept and improved it step by step until he proposed the L, a, b color space in 1948 (19). L represents lightness, a represents redness or greenness and b represents blueness or yellowness. The Hunter L, a, b system achieved significant popularity by some industries (Figure 3) (6,7,19,20).

Although L , a , b coordinates are opponent coordinates in the Hunter system, they are not derived from opponent theory. Adams' (21) chromatic-value space was based on a Hering (22) type opponent color vision theory. Nickerson (23) et al. modified Adams' chromatic value space by optimizing constants for their own color-difference data, rearranging one of the chromatic axes to result in opponent properties similar to Hunter L , a , b . With the suggestions by Glasser (24), the ANLAB equation was formulated. In 1976, the CIE (25) introduced two new transformations of the chromaticity diagram that were modified to the ANLAB space for easier calculation. They are the L^* , a^* , b^* system (CIELAB) and the L^* , u^* , v^* system (CIELUV). L^* again indicates lightness, a^* and u^* indicate redness or greenness, and b^* and v^* indicating blueness or yellowness. Cylindrical polar coordinates; $CIE L C_{ab} H_{ab}$ and $CIE L C_{uv} H_{uv}$, were also defined by CIE. Both $CIE L C_{ab} H_{ab}$ and $CIE L C_{uv} H_{uv}$ correlate with lightness, chroma and hue, respectively, while only C_{uv} correlates with saturation. This is because as CIE defined saturation, which is derived from the chromaticity diagram, it is defined only for CIELUV.

Nevertheless, the ratio C_{ab}^*/L^* is sometimes assumed to correlate with saturation. Both systems were modified for the CIE standard observer 1964 (10°) and illuminant where for the illuminant L^* is always 100, a^* (u^*) and b^* (v^*) are always 0. In general, usage of the two equations is not recommended when the illuminant is much different from average daylight. Today, both systems, as well as Hunter L , a , b are frequently used in color matching of materials. However, it should be noted that there are still no perfect color space systems. None of the above-explained systems provide equal visual differences as equal distances on the color diagram for all regions of the color space (1,7).

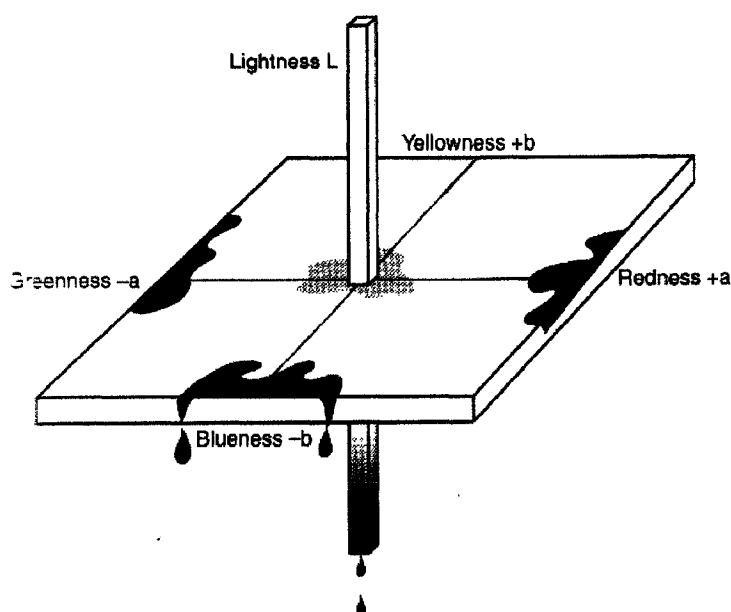


Figure 3. L, a, b Color Space.

Source: Roy S. Berns, *Principles of Color Tech.*, John Wiley & Sons, New York 2000.

One Dimensional Color Spaces

Color properties like hue, lightness, and saturation have been used to describe a single color property. Consequently, there have been many systems developed to describe the color of a variety of objects with a single number over the years. Frequently these objects differ in a single respect, such as saturation, and their color varies with this amount over a comparatively narrow and well-defined range (1,7).

Describing a particular color property usually entails visual or instrumental comparison of the test object to a series of standards. If the selected standards have color and spectral reflectance or transmittance curves similar to those of the test object, the comparison is easily possible and the position of the test object on the scale can be easily

and precisely established. In cases like that, one-dimensional scales (single-number) are useful. One very important condition for a precise, accurate one-dimensional scale is that the test sample must be similar in both color and spectral properties to the set of standards used to calibrate and maintain the scale. As long as this condition is satisfied, one-dimensional or single-color scales work reasonably well. If the test sample differs in color and/or in spectral properties from that of the standards, then it becomes very difficult, if not impossible, to make a dependable judgment of the position of the sample on the scale. In this case, the test sample and the standard form a metameric pair and one-dimensional color scale may produce erroneous and misleading results (1,7).

Whiteness Scales

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 (18,26). Whiteness is associated with a region in color space where objects are recognized as being white (1,27). The degree of whiteness is measured by the degree of departure of the object from a perfect white. As noted above, there have been disagreements on what perfect white is and which directions of departure from it should be preferred or avoided (1-3). In addition, usage of fluorescent whitening agents to improve whiteness of objects adds to the discrepancies (1-5). Whiteness of a material with a fluorescent whitening agent strongly depends on the spectral properties of the illumination for both visual evaluations and instrumental measurements. For these reasons, no single formula has been widely accepted for whiteness (1-3,12).

Whiteness

Whiteness is an attribute of colors of high luminous reflectance and low purity, situated in a relatively small region of the color space. The color white is distinguished by its high lightness, its very low (ideally zero) saturation. As stated earlier, when judging whiteness it is felt to be more attractive with a blue cast rather than yellow cast at a comparable luminance (3,28,29). Depending on the hues of near whites, the perception may differ. For example, an object with a blue cast will be perceived whiter than an object that has a yellow cast, where saturation and lightness are the same for both objects (27,28). Whiteness depends on observers and observer preferences (8). Visual assessment is impaired by individual preferences. Instrumental whiteness assessment will be absolute only if the uncertainties of measurement and of evaluation are overcome (9). The concept also depends on the assessment methods applied such as, ranking, pair comparison, difference scaling, and ratio scaling for a particular observer. Many varying conditions such as the level and spectral power distribution of sample irradiation, the color of the surrounding whites, and the desired appearance of various products have also direct impact on the whiteness perceived (8). The intensity of fluorescence of FWA added samples, for example, depends on the spectral power distribution of the illumination, especially in the UV region. Differences among visual assessments, measurements and different measurement devices also result from differences in spectral power distribution of the illumination (9). On the other hand, the general agreement is that samples are considered less white or darker if they are yellower and darker (8).

According to Ernst Ganz (9), three uncharacteristic observations are made if samples are compared where they differ only moderately in whiteness:

1. Different observers may give different weights to lightness and blueness. A sample can be ranked for its whiteness although a difference in lightness and/or blueness may be clearly perceived.
2. Some observers prefer whites with a greenish while some prefer reddish tint. This causes contradictory evaluations of whitenesses where there is a hue difference in a given sample. At the same time samples with an intermediate bluish or neutral tint are assessed more consistently.
3. There is in general agreement among observers for hue differences, which is assessed independent of the perceived difference in whiteness.

These three effects could explain why samples with different luminous reflectance, purity, and dominant wavelength can be ranked linearly for their perceived whitenesses under given conditions by observers, although no general agreement on whiteness can be reached (8).

It is important to note that whiteness must be defined based on perceptual evaluations and psychometric techniques before instrumentally measuring whiteness. In reality, the appearance of an object is evaluated by the observer. Therefore, an objective measure cannot be built until the subjective reality has been analyzed (30).

Instrumental measurement of whiteness simulating a psychometric scale is accompanied by an additional term that indicates to what extent and in what direction the appearance of the sample deviates from the maximum whiteness (30).

Whiteness Formulae

Over the years, many studies have been carried out and many formulae proposed. It has been realized through the studies that whiteness is entirely based on experience with the reflection of light of all wavelengths and that no measurement with a single filter in any particular region of the spectrum can ever be sufficient as a whiteness measurement. The visual experience of whiteness is done through color assessments and the instrumental measurement of whiteness is based on color measurement (1).

In whiteness measurements, the problem is to develop a single formula that gives an appropriate weighting to the tristimulus values. Many formulas have been developed, most of them have attempted to add the X, Y, Z tristimulus values in different algebraic proportions in order to achieve a weighting towards the blue region corresponding to subjective experience (3). Another problem is that the perfect reflecting diffuser is not perfectly white. The human eyes, in combination with the brain, classify white that is slightly bluer than an object that reflects perfectly over the whole visual range (1,29,31). Selection of a single whiteness formula would not be sufficient, since the perception of the appearance of an object varies from one individual to another. In addition, there is no general agreement in the evaluation of whiteness (9).

Whiteness evaluations made at uniform chromaticity spacing are less problematic, because only a small part of the color space is taken by white colors. There, chromaticity spacing correlates well with human perception (9).

Whiteness determined by colorimetric measurements through a whiteness formula is not an exact quantity. Its value depends on the spectrophotometer used, properties of the whiteness formula used and illumination state. Therefore, differences in whiteness

values are considered significant, only if the same instrument is used for the measurements (30).

Since it is not possible for a producer to fabricate a stable source that has the relative power distribution of D_{65} with adequate accuracy, there have been methods developed to convert to illuminant D_{65} through the use of the spectral radiance factors that are measured with a source of different, but known, relative spectral power distribution.

A device for controlling the relative UV contents of the sample irradiation for use by spectrophotometers attained an approximation to a stable relative spectral power distribution. The excitation of the fluorescence of a stable white reference sample is attenuated sufficiently to keep the tristimulus values of this sample constant with an adjustable UV filter (9).

Attempts have been made to standardize the calculation of whiteness, although colorimetry of fluorescent samples is still problematic (1-3). Most formulae used today assess a sample relatively as to whiter, lighter and bluer. When these formulas are applied to colored samples they are generally meaningless. On the other hand, they satisfactorily characterize the appearance of commercial whiteness. They are mostly unsuccessful in assessing tinted samples with chromaticities placed on the borders of white colors (32,33). However, there are formulas developed for dealing with such cases. They produce ellipses that are equivalent lines that should be centered on the unknown preferred white in the chromaticity chart. This point is not reached under normal viewing conditions, because of lower UV content of the illumination source in comparison to daylight. This limits the excitation of fluorescence (21).

Any whiteness formula defines surfaces of constant whiteness in the color space and they are based on luminous reflectance Y and on transformed chromaticity coordinates, such as colorimetric saturation (9).

While whiteness is a qualifying assessment, tint deviation is a descriptive assessment and thus not a simple quality judgment. Tint deviation describes the hue of the sample in comparison with the equally white step of the white scale to which the formula parameters relate. Therefore, tint deviation is mainly a descriptive assessment and does not entail quality judgment. It directly depends on the tint of the white scale being used as the reference (13).

The tint is assessed visually and chosen by colorimetric means, because the whiteness value does not characterize a white by itself. The influence of the relative UV content in the measurement on the evaluation of tint is negligible.

CIE Whiteness

Beginning in 1931, CIE started extensive studies to solve the problem created by the excess of equations available. Using results from Ganz (8,9), in 1981 the CIE recommended an equation for the whiteness W , related to basic CIE tristimulus measurements, and having the form (1,10,11):

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

where x and y are the CIE chromaticity co-ordinates and x_n and y_n are the co-ordinates for the perfect reflecting diffuser at the given illumination. For example, at $D_{65} 10^\circ$, $x_n = .313795$ and $y_n = .330972$ (14).

This equation is complemented by the tint 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 or 1964 CIE standard observer, respectively. A positive value of T indicates greenishness and a negative value indicates reddishness.

These equations can be used only in a limited region. Criteria for whiteness are that the values of W fall within the limits given by:

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

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 470 nm (3,13,14) in the CIE chromaticity diagram and the inequalities 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 (8-11). According to this definition, the perfect reflecting diffuser has a whiteness of 100 and a zero tint value.

One clear disadvantage in CIE whiteness is that this system of equations does not clarify whether the whiteness has any component of bluishness or yellowishness. A standard measure for yellowness is given by ASTM E-0313 or DI-1925 (1,3,34,35):

$$YI = 100(C_x X - C_z Z)/Y, \quad (4)$$

where $C_x = 1.301$ (D_{65} 10°) or 1.277 (C 2°) and $C_z = 1.150$ (D_{65} 10°) or 1.059 (C 2°).

In this equation, zero as given by this equation, is associated with the visual zero between bluishness and yellowness.

The CIE suggests that the formula should only be used for relative evaluations and these 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 close as possible to a desired illuminant (13,14). This also improves the matching of different measuring instruments for whiteness. The tint deviation or hue value can still not be adequately matched (14).

Whiteness and tint formulae proposed by the 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 (9,27).

If the sample illumination is stabilized, assessment 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 (13,14).

Contributions of Luminance Factor and of Chromaticity to Whiteness

Color information that is independent of the luminance or luminance factor is called chromaticness, hence the chromaticity diagram. However, chromaticities should correlate to some extent with the stimulus hue, and chroma (saturation) (1,2).

Other than whiteness formulas and tint values, the third value characterizing a white sample is the luminance factor Y (9). This kind of whiteness can be characterized by the contribution of chromaticity.

$$C=W-Y \quad (5)$$

where $C > 0$ and $W > Y$ for bluish whites and

$C < 0$ and $W < Y$ for yellowish whites

To prevent application of whiteness formulas to colored samples the following limits were proposed: (9)

$$Y > 70 \quad (6a)$$

$$W > 40 \quad (6b)$$

$$-6 < T < 6 \quad (6c)$$

Equation 1 was proposed as a standard whiteness formula of neutral hue preference.

Two supplementary whiteness formulae, one for green hue preference

$$W = Y + 1700(x_n - x) + 900(y_n - y) \quad (7a)$$

and one for the red hue preference

$$W = Y - 800(x_n - x) + 3000(y_n - y) \quad (7b)$$

are required to cover all evaluations (9).

The above three formulations can be used with colorimetric data evaluated for standard illuminant D_{65} and both CIE 1931 2° and CIE 1964 10° observers.

Two standard tint formulas were proposed for a D_{65} illuminant, one each for the CIE 1931 2° and CIE 1964 10° standard observers (7) respectively, were proposed.

$$T = -1000(x - x_n) + 1700(y - y_n) \quad (8a)$$

$$T = -900(x - x_n) + 800(y - y_n). \quad (8b)$$

Whiteness Region in the Chromaticity Diagram for CIE Whiteness

As mentioned earlier, whiteness can be thought of as a region in the chromaticity diagram. This region is a rectangle having four corner points. The x and y values at the corner points in the chromaticity diagram can be calculated for a given Y value by using CIE tint and whiteness inequality conditions (inequalities $-3 < T < 3$).

Applying the tint condition 6b, we have

$$(20/13)(x-x_n) + 3/650 > y-y_n > (20/13)(x-x_n) - 3/650 \text{ for } 2^\circ \quad (9a)$$

$$(18/13)(x-x_n) + 3/650 > y-y_n > (18/13)(x-x_n) - 3/650 \text{ for } 10^\circ \quad (9b)$$

For $x = x_n$, these both become

$$3/650 > y-y_n > -3/650 \quad (10)$$

From the Whiteness condition 6a, we have

$$(280-4Y)/1700 < y-y_n + (8/17)(x-x_n) < (Y-40)/1700 \quad (11)$$

For $x = x_n$ and $Y = 100$, this becomes

$$-6/85 < y-y_n < 3/85 \quad (12)$$

If the intersection points for x and y are calculated for a given Y value, the whiteness region can accurately be determined. For the 10° observer, this is

$$y-y_n = (18/13)(x-x_n) \pm 3/650 \quad (13a)$$

$$y-y_n + (8/17)(x-x_n) = (Y-40)/1700 \quad (13b)$$

$$(280-4Y)/1700 \quad (13c)$$

After solving these 4 equations, we obtain 4 values of $x-x_n$,

$$x-x_n = 13(Y-40)/41000 - 51/20500 \quad (14a)$$

$$= 13(Y-40)/41000 + 51/20500 \quad (14b)$$

$$= 13(280-4Y)/41000 - 51/20500 \quad (14c)$$

$$= 13(280-4Y)/41000 + 51/20500 \quad (14d)$$

and

$$y-y_n = (18/13)[13(Y-40)/41000 - 51/20500] + 3/650 \quad (15a)$$

$$= (18/13)[13(Y-40)/41000 + 51/20500] - 3/650 \quad (15b)$$

$$= (18/13)[13(280-4Y)/41000 - 51/20500] + 3/650 \quad (15c)$$

$$= (18/13)[13(280-4Y)/41000 + 51/20500] - 3/650 \quad (15d)$$

Similar results can be obtained for the 2° observer.

For Y=100, the four corner points within the whiteness region are found to be:

$$(x-x_n, y-y_n) = (0.01359, 0.01420) \quad (16a)$$

$$(-0.00861, 0.01654) \quad (16b)$$

$$(-0.00385, -0.00995) \quad (16c)$$

$$(-0.00883, -0.00761) \quad (16d)$$

For these,

$$\begin{aligned} W_{CIE} &= Y + 800(x_n - x) + 1700(y_n - y) \\ &= 40, 40, 220, 220 \end{aligned} \quad (17)$$

For D₆₅, 10° the four corners are:

$$(W_{CIE}, C) = 40, 13.8 \quad 40, 14.5 \quad 220, 30.3 \quad 220, 29.0 \quad (18a)$$

$$(x, y) = (0.3353, 0.3452) \quad (0.3224, 0.3475) \quad (0.3099, 0.3210) \quad (0.3050, 0.3234) \quad (18b)$$

$$(L^*, a^*, b^*) = (100, -1.2, 13.8) \quad (100, -4.7, 13.7) \quad (100, 9.6, -28.7) \quad (100, 5.2, -28.5), \quad (18c)$$

where $C = (a^{*2} + b^{*2})^{1/2}$ is the Chroma.

Likewise for D₅₀, 10°:

$$(W_{CIE}, C) = 40, 15.5 \quad 40, 15.8 \quad 220, 32.1 \quad 220, 31.1 \quad (19a)$$

$$(x, y) = (0.3692, 0.3846) \quad (0.3642, 0.3870) \quad (0.3121, 0.3056) \quad (0.3072, 0.3080) \quad (19b)$$

$$(L^*, a^*, b^*) = (100, -1.3, 15.5) \quad (100, -4.5, 15.2) \quad (100, 9.2, -30.7) \quad (100, 5.1, -30.7) \quad (19c)$$

These results point out the weakness in the CIE Whiteness formula. Clearly, all of these corner points of the “whiteness” region are far from white by any sensible measure. Relatively saturated chroma values (>30) are associated with the maximum whiteness values. Such results are clearly absurd. Similar conclusions are reached, if we use more moderate Y values.

For example, many commercial papers, such as publication grades, have Y approximately 83 or greater. Thus, the corresponding calculated values for Y=83 are:

for D_{65} , 10°

$$(W_{CIE}, C) = 40, 9.3 \quad 40, 9.9 \quad 135, 12.3 \quad 135, 11.4 \quad (20a)$$

$$(x, y) = (0.3299, 0.3487) \quad (0.3249, 0.3510) \quad (0.2998, 0.3070) \quad (0.2948, 0.3093) \quad (20b)$$

$$(L^*, a^*, b^*) = (93.0, -3, 9.3) \quad (93.0, -3.7, 9.2) \quad (93.0, 4.7, -11.4) \quad (93.0, 8, -11.4) \quad (20c)$$

and at D_{50} , 10°

$$(W_{CIE}, C) = 40, 10.4 \quad 40, 10.8 \quad 135, 13.1 \quad 135, 12.5 \quad (21a)$$

$$(x, y) = (0.3638, 0.3772) \quad (0.3589, 0.3795) \quad (0.3337, 0.3355) \quad (0.3287, 0.3378) \quad (21b)$$

$$(L^*, a^*, b^*) = (93.0, -4, 10.4) \quad (93.0, -3.5, 10.2) \quad (93.0, 4.4, -12.4) \quad (93.0, 9, -12.4) \quad (21c)$$

Chroma values more than 13 for the high CIE whiteness corners are obviously far from white. Clearly, a new Whiteness formula is needed to avoid such results.

The four positions at each white point for Y=100, that define the white boundary is shown in Figures 4a and 4b. The planes in the whiteness region for a 5 point incremental change in Y from 100 is also shown in Figures 5a and 5b. The range of Y in commercial printing papers can be between 70 and 100.

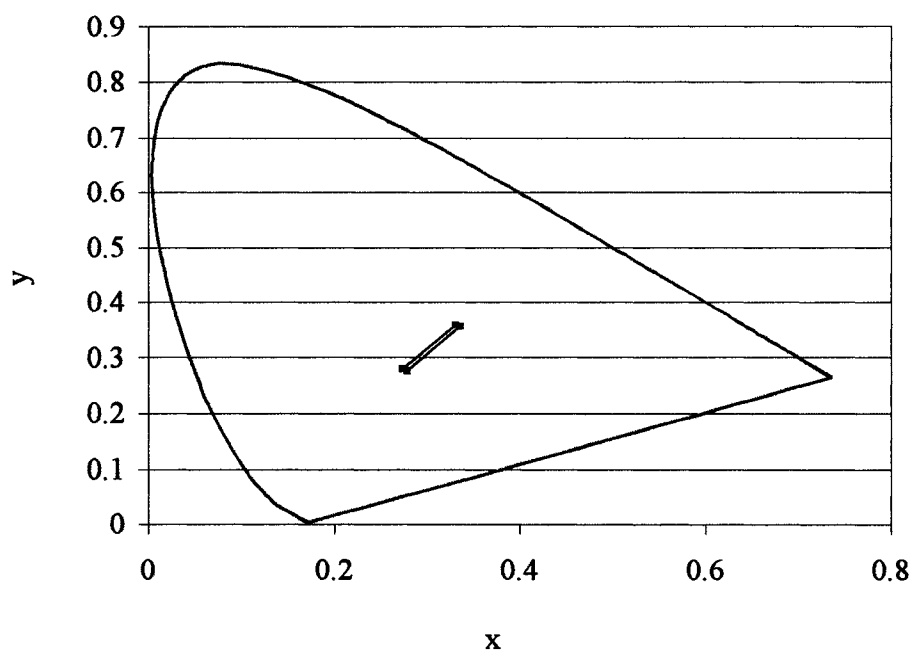


Figure 4a. Four Corner Positions at Each White Point for $Y=100$ @ $D50/10$.

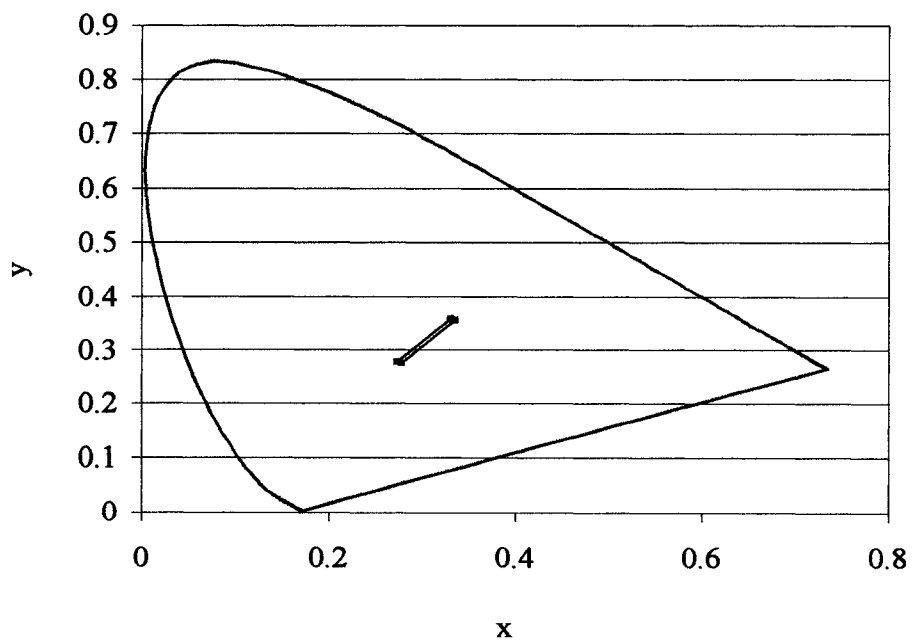


Figure 4b. Four Corner Positions at Each White Point for $Y=100$ @ $D65/10$.

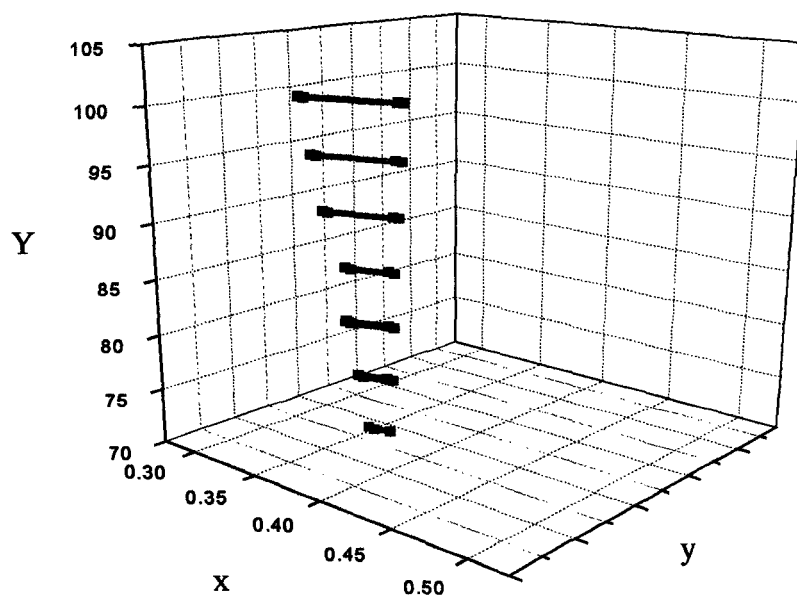


Figure 5a. Planes in the White Region at Varying Y Values @ D50/10.

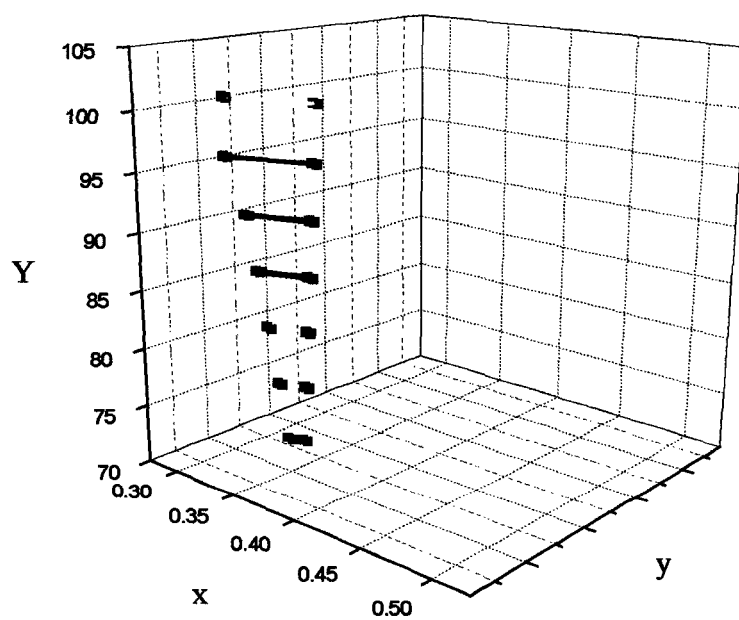


Figure 5b. Planes in the White Region at Varying Y Values @ D65/10.

New Whiteness Formulae

Previously, we showed (32,33) that large differences in calculated CIE Whiteness could frequently occur, when the colors of papers are slightly altered from neutral white to varying shades of whites. In the same study, observers assessed the whiteness of the tinted papers as either equivalent or very similar in appearance to one another.

We propose new formulae that will reduce the large calculated differences among slightly tinted papers, within the whiteness region in the chromaticity diagram, and to establish a better correlation between the calculated values and perceptual visualization assessments. One formula will measure nearness to neutral white, while the second will characterize whiteness in the sense discussed above. That is, high whiteness is associated with high luminescence and moderate saturation with a blue cast.

For nearness to neutral white, the Luminance factor L and Chroma (related to saturation) are selected as the appropriate variables in this formula, since whiteness is directly dependent on and characterized by these two properties. An exponential decay function is proposed to reduce large differences in calculated whiteness values in slightly colored papers.

For nearness to neutral white, we propose a formula of the form,

$$N_{FA} = L * e^{-\lambda(C/C_0)^2} \quad (22)$$

where C_0 is a characteristic chroma value, presumably related to the saturations at the four corners of the whiteness region and λ is a coefficient to be determined.

For $C = C_0$, $N_{FA} = L * e^{-\lambda}$, if we assume $e^{-\lambda} = 1/2$, then $\lambda = \ln 2 = .693$, this yields the working form for our Whiteness formula:

$$N_{FA} = L^* (1/2)^{(C/C_0)^2} \quad (23)$$

For whiteness, we will employ a similar form. We propose a whiteness formula of the form

$$W_{FA} = W_0 e^{-\lambda[(a^*-a_1^*)^2 + (b^*-b_1^*)^2]/C_2^2} \quad (24)$$

where W_0 , a_1^* and b_1^* are to be determined and C_2 is a characteristic chroma, possibly different from C_0 .

We will determine W_0 , a_1^* and a_2^* by requiring that W_{FA} be equal to W_{CIE} from equation 1 for $a^*=b^*=0$ and the derivatives with respect to a^* and b^* be equal to those obtained from equation 1. In order to do this, we must express W_{CIE} in terms of a^* and b^* . Using the definitions of CIELAB (23) in terms of the tristimulus values (13), we obtain

$$W_{CIE} = Y + (a^*W_a - b^*W_b)/D \quad (25)$$

where

$$W_a = \alpha[3(Y/Y_n)^{2/3} + 3(Y/Y_n)^{1/3}a^*/500 + (a^*/500)^2]/3 \quad (26a)$$

$$W_b = \beta[3(Y/Y_n)^{2/3} - 3(Y/Y_n)^{1/3}b^*/200 + (b^*/200)^2]/3 \quad \text{and } (26b)$$

$$D = Y/Y_n + x_n a^*/500[3(Y/Y_n)^{2/3} + 3(Y/Y_n)^{1/3}a^*/500 + (a^*/500)^2] - z_n b^*/200[3(Y/Y_n)^{2/3} - 3(Y/Y_n)^{1/3}b^*/200 + (b^*/200)^2] \quad (26c)$$

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

Equations 25 and 26 should be compared with the expression obtained by Ganz and Pauli (34):

$$W_{CIE} = 2.41L^* - 4.45b^*[1 - 0.0090(L^* - 96)]^4 - 141.4 \quad (27)$$

which was determined by regression analysis of the CIE whiteness formula for $D_{65} 10^\circ$

with respect to a^* and b^* . Equation 25 is rigorous and is equivalent to the usual CIE formula.

We see from equation 25 that for $a^*=b^*=0$:

$$W_{\text{CIE}} = Y \quad (28)$$

$$\partial W_{\text{CIE}} / \partial a^* = W_a / D = \alpha(Y/Y_n)^{-1/3} \quad (28a)$$

$$\partial W_{\text{CIE}} / \partial b^* = -W_b / D = -\beta(Y/Y_n)^{-1/3} \quad (28b)$$

For D_{65} 10° , the derivatives become

$$\partial W_{\text{CIE}} / \partial a^* = .0258(Y/Y_n)^{-1/3} \quad (29a)$$

$$\partial W_{\text{CIE}} / \partial b^* = 4.336(Y/Y_n)^{-1/3} \quad (29b)$$

If we expand Y to first order in $L-96$, we obtain for W near $a^*=b^*=0$

$$W_{\text{CIE}} = 2.411L^* + (.02670a^* - 4.490b^*)[1 - .00893(L^* - 96)] - 141.448 \quad (30)$$

in good agreement with equation 27. As implied by Ganz and Pauli's regression, the a^* term is negligible for practical purposes.

The corresponding derivatives of equation 24 for $a^*=b^*=0$ are

$$\partial W_{\text{FA}} / \partial a^* = 2\lambda a_1^* Y / C_2^2 \quad \text{and (31a)}$$

$$\partial W_{\text{FA}} / \partial b^* = 2\lambda b_1^* Y / C_2^2 \quad (31b)$$

Equating equations 28 and 31, we obtain

$$W_0 = Y e^{\lambda C_1 / C_2^2} \quad (32a)$$

$$a_1^* = \alpha C_2^2 / (200\lambda)(Y_n/Y)^{4/3} \quad \text{and (32b)}$$

$$b_1^* = -\beta C_2^2 / (200\lambda)(Y_n/Y)^{4/3} \quad (32c)$$

where $C_1 = (a_1^{*2} + b_1^{*2})^{1/2} = \gamma C_2^2 / (200\lambda)(Y_n/Y)^{4/3}$, with $\gamma = (\alpha^2 + \beta^2)^{1/2}$. Setting $\lambda = \ln 2$ as before we end up with

$$W_{\text{FA}} = Y(1/2)^{[a^*(a^*-2a_1^*)+b^*(b^*-2b_1^*)]/C_2^2} \quad (33)$$

The WFA and CIE whiteness equations are shown in Figures 6a and 6b and compared in Figure 6c in L , a^* , b^* color space for $L=93$.

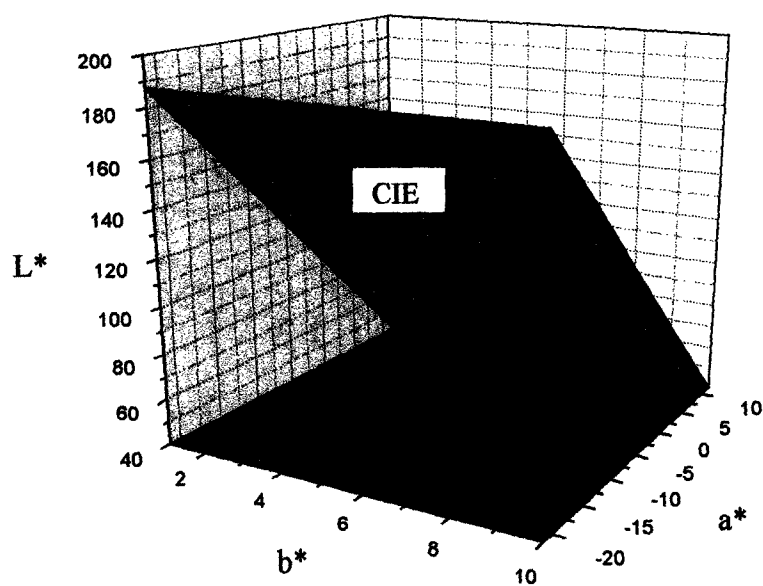


Figure 6a. CIE Equation on L , a^* , b^* Color Space.

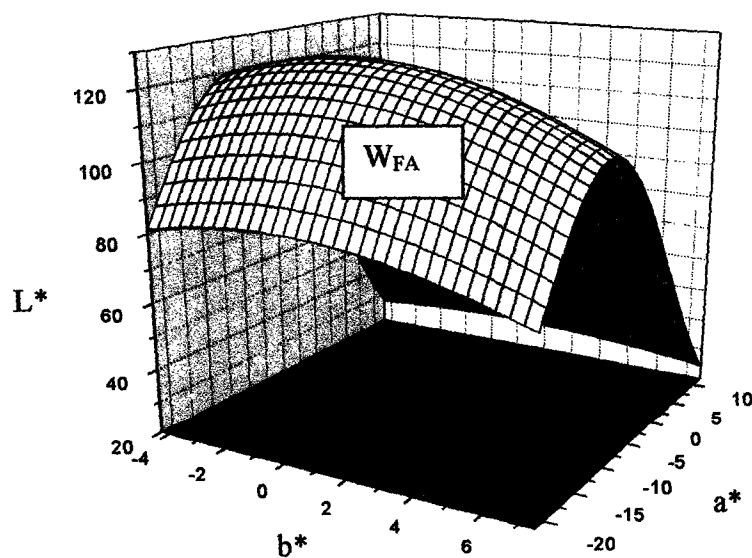


Figure 6b. W_{FA} Equation on L , a^* , b^* Color Space.

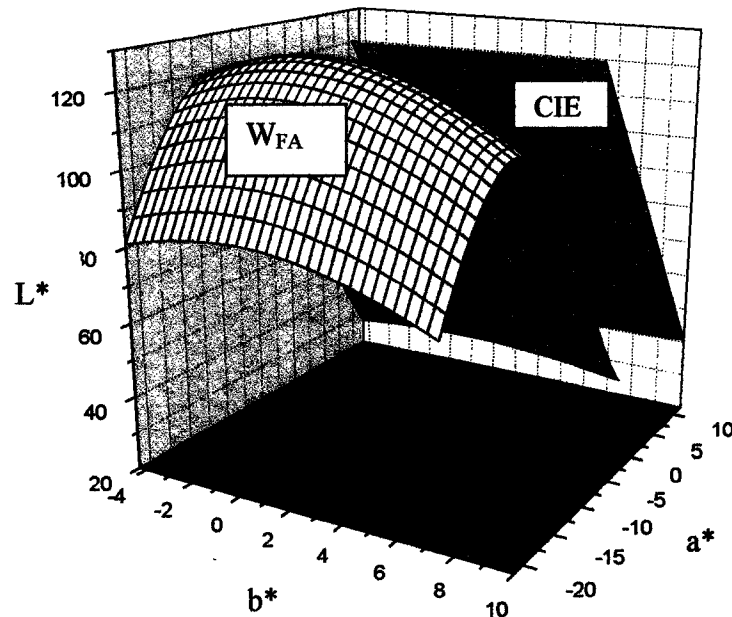


Figure 6c. Comparison of CIE and W_{FA} Equation on L^* , a^* , b^* Color Space.

The characteristics of this formula are that it has a maximum value at a_1^* and b_1^* and decays to zero far away from the maximum. With the exponential form, we don't need to explicitly include the tint formulas, because the exponential forms already reduce the values for tinted samples. Unlike the CIE and other whiteness formulas, it is a smooth function and doesn't cut off abruptly at the inequality limits. This is consistent with the known continuity and smoothness of the visible color space. Reducing the whiteness below a maximum value is consistent with the belief that increasing the blueness of a sample (reducing the b value) improves whiteness up to a point, after which the whiteness decreases.

The remaining task is to determine the characteristic chromas C_0 and C_2 . They represent the distance in a^*-b^* space at which the functions decay to half their maximum

value. These values should, in some sense represent the area of the whiteness region for given Y (or L^*) values. They should be related to the corner saturations calculated from equations 14 and 15. In what follows, we will set both C_0 and C_2 to the maximum corner saturation value. This corresponds to a large region of applicability, while discounting samples far from the maximum value. Application of these formulas will be illustrated in the following section.

Application of New Whiteness Formulae

Three commercial digital printing papers were chosen for testing of our formulae. These were Xerox Phaser 860/8200 Glossy coated paper (145 gsm), Stora Enso 4CC Silk (130 gsm) and Stora Enso 4CC Cover (160 gsm). The Phaser paper has $Y = 84.9$ ($L^* = 93.8$), $a^* = 0.7$ and $b^* = -2.5$ at D65 10° , as measured on a GretagMacbeth SpectroScan spectrophotometer. Likewise, the Silk paper has $Y = 89.0$ ($L^* = 95.6$), $a^* = .9$ and $b^* = -3.9$ and the Cover has $Y = 86.4$ ($L^* = 94.5$), $a^* = 2.2$ and $b^* = -9.4$. ICC (36,37) output profiles (38) were determined for these three papers on a Xerox Phaser 8200 solid ink printer, by measuring an ECI 2002R (39) output test chart with the SpectroScan, and calculating the profile with GretagMacbeth ProfileMaker. ProfileMaker is known to produce accurate ICC profiles (40-42).

Using the Xerox paper, as close as possible to the four corner points, a neutral point and a near to maximum W_{FA} point were printed for a nominal Y of 83 ($L = 93$). The corner values were chosen as closely as possible to the chromaticity values in Equations 20 or 21, within the gamut of the printer. This pattern is shown in Figure 7. The actual nominal and measured values of Hunter Lab and CIELAB are given in Table 1. In

addition, a modified version of Figure 7 was printed, where the Upper Middle and Lower Middle patches were interchanged.

In addition to the corners, a series of steps, with varied nominal b^* values were printed on the Silk and Cover papers, respectively. The corresponding nominal and measured Hunter Lab and CIELAB values for these steps are given in Tables 2 and 3.

Y values of the coated color samples in the chromaticity diagram are shown as in

Figure 8.

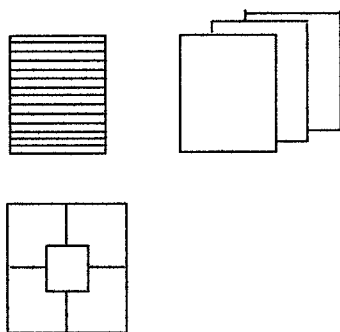


Figure 7. Patterns Printed on Xerox Phaser 8200 Printer for Viewer Observations.

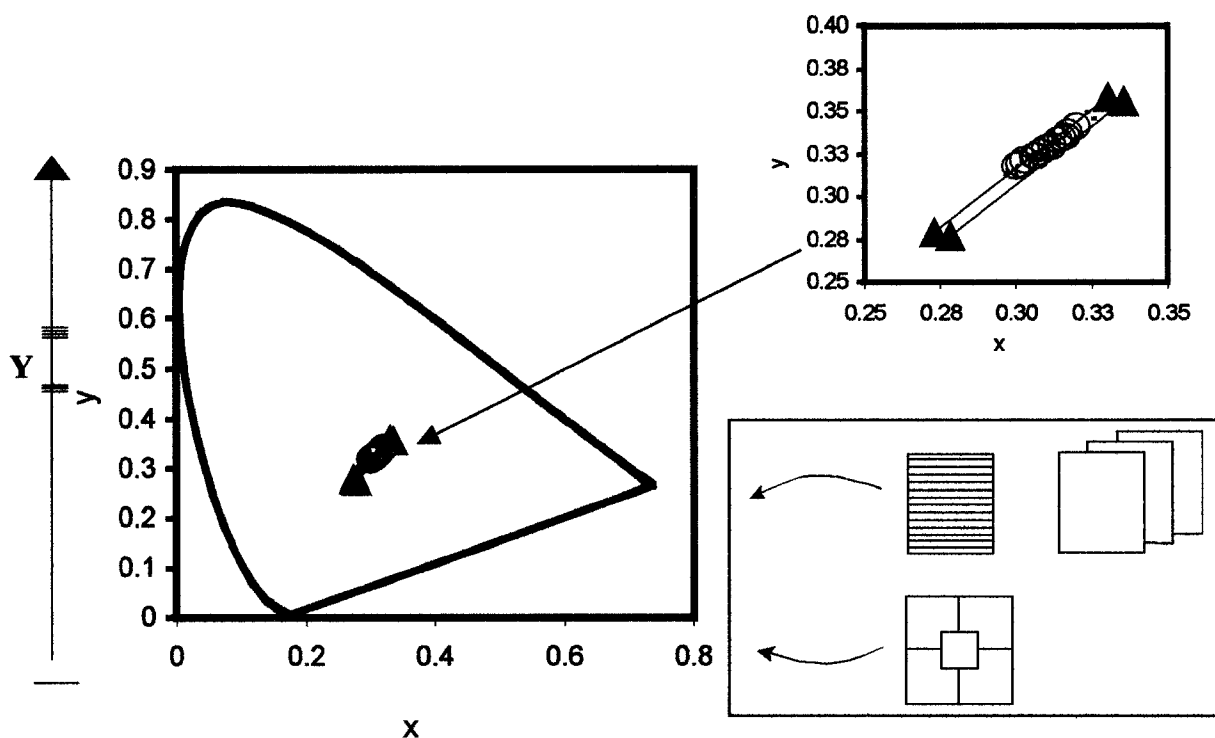


Figure 8. Coated Color Samples in the Chromaticity Diagram for Their Y Values.

Table 1. Hunter L, a, b and L^* , a^* , b^* Values Calculated from the Measured Spectra from the Printed Figure 7 for D_{50} , 2° .

		L	a	b	L^*	a^*	b^*	DE
Upper Left	Target	89.0	0.4	-4.1	91.3	0.4	-4.7	0.50
	Measured	89.1	0.0	-4.3	91.4	0.0	-4.9	
Upper Right	Target	89.0	2.0	-4.0	91.3	2.0	-4.6	0.31
	Measured	89.1	1.9	-4.2	91.4	1.9	-4.9	
Lower Left	Target	90.0	-3.0	6.8	92.1	-3.0	8.4	1.07
	Measured	90.2	-2.5	6.1	92.3	-2.5	7.5	
Lower Right	Target	88.7	0.2	5.7	91.1	0.2	7.0	0.44
	Measured	89.2	0.2	5.6	91.5	0.2	6.9	
Upper Center	Target	91.0	0.3	-2.6	92.9	0.3	-3.0	0.48
	Measured	91.0	0.4	-3.0	93.0	0.4	-3.5	
Lower Center	Target	91.2	0.1	0.0	93.1	0.1	0.0	0.09
	Measured	91.3	0.1	0.0	93.2	0.1	0.0	

In order to compare predictions of the test formulas, 48 randomly selected observers were asked to rank each printed patch for their visual appearance for whiteness. In addition, they were asked to judge the three unprinted papers for whiteness. Twenty-five of the observers evaluated the samples in a 5000 °K light booth and 23 of the observers under the daylight behind a window. We chose primarily untrained observers, because they are expected to be more representative of buyers of paper and print. However, since they are untrained, they are likely to be more varied, and thus larger samplings are needed. Recall that the original CIE color matching functions (13) were based on only 17 observers. Fewer trained observers would be required, but if they are trained according to a particular school of whiteness and formulas, it would interfere with the objectivity of the test.

Spectral reflectance values of each patch on the printed samples were measured with the GretagMacbeth SpectroScan spectrophotometer. Tristimulus values (X, Y, Z), CIE, Hunter, Ganz and proposed whiteness formulas were calculated for D₅₀, 2° and C, 2°. In addition, CIE and Hunter L, a, b values for D₅₀, 2° (the standard reference for ICC profiles), D₅₀, 2° and C, 2° and effective TAPPI brightness were calculated from the measured spectra.

Table 2. Hunter L, a, b and L*, a*, b* Values Calculated from the Measured Spectra from the Printed Steps on the Silk Paper for D₅₀, 2°.

		L	a	b	L*	a*	b*	DE	RMS DE
Step 1	Target	89.5	0.3	-6.6	91.7	0.3	-7.5	0.79	
	Measured	88.9	-0.2	-6.9	91.2	-0.2	-7.8		
Step 2	Target	90.2	0.2	-6.1	92.3	0.2	-6.9	0.55	
	Measured	90.0	-0.2	-6.3	92.1	-0.2	-7.2		
Step 3	Target	91.7	-0.3	-5.1	93.5	-0.3	-5.8	0.52	
	Measured	91.5	-0.7	-5.3	93.4	-0.7	-6.0		
Step 4	Target	93.0	-0.1	-4.2	94.5	-0.1	-4.7	0.18	
	Measured	93.1	-0.2	-4.3	94.6	-0.2	-4.9		
Step 5	Target	93.4	0.4	-3.9	94.8	0.4	-4.4	0.18	
	Measured	93.5	0.3	-4.0	94.9	0.3	-4.5		
Step 6	Target	93.3	0.1	-2.9	94.8	0.1	-3.4	0.23	
	Measured	93.5	0.1	-3.1	94.9	0.1	-3.5		
Step 7	Target	93.2	-0.4	-1.5	94.7	-0.4	-1.7	0.35	
	Measured	93.3	-0.4	-1.8	94.8	-0.4	-2.0		
Step 8	Target	93.7	0.3	-1.2	95.1	0.3	-1.3	0.25	
	Measured	93.9	0.3	-1.3	95.2	0.3	-1.5		
Step 9	Target	93.7	-0.2	0.4	95.0	-0.2	0.5	0.32	
	Measured	93.8	-0.1	0.2	95.1	-0.1	0.2		
Step 10	Target	93.6	-0.4	1.0	95.0	-0.4	1.2	0.39	
	Measured	93.7	-0.3	0.7	95.1	-0.3	0.8		
Step 11	Target	92.9	0.0	1.6	94.4	0.0	1.9	0.37	
	Measured	93.1	0.1	1.3	94.6	0.1	1.5		
Step 12	Target	93.3	-1.0	2.6	94.8	-1.0	3.1	0.68	
	Measured	93.5	-0.7	2.1	94.9	-0.7	2.5		
Step 13	Target	93.1	-1.4	3.5	94.6	-1.4	4.2	0.33	
	Measured	93.4	-1.2	3.5	94.9	-1.2	4.2		0.43

Table 3. Hunter L, a, b and L*, a*, b* Values Calculated from the Measured Spectra from the Printed Steps on the Cover Paper for D₅₀, 2°.

		L	a	b	L*	a*	b*	DE	RMS DE
Step 1	Target	91.1	1.1	-9.7	93.0	1.1	-10.8	0.51	
	Measured	90.6	0.8	-9.9	92.6	0.8	-11.0		
Step 2	Target	91.0	0.8	-8.8	92.9	0.8	-9.9	0.49	
	Measured	90.7	0.5	-9.1	92.7	0.5	-10.2		
Step 3	Target	91.2	0.9	-8.1	93.1	0.9	-9.0	0.45	
	Measured	91.0	0.7	-8.4	92.9	0.7	-9.4		
Step 4	Target	91.1	0.7	-7.3	93.0	0.7	-8.2	0.35	
	Measured	91.0	0.5	-7.5	92.9	0.4	-8.4		
Step 5	Target	90.7	-0.1	-6.1	92.7	-0.1	-6.9	0.30	
	Measured	90.6	-0.3	-6.2	92.6	-0.3	-7.0		
Step 6	Target	91.4	0.5	-5.0	93.2	0.5	-5.7	0.21	
	Measured	91.3	0.4	-5.1	93.2	0.4	-5.8		
Step 7	Target	91.3	0.2	-4.1	93.2	0.2	-4.7	0.18	
	Measured	91.3	0.1	-4.2	93.1	0.1	-4.8		
Step 8	Target	91.3	0.0	-3.5	93.1	0.0	-4.1	0.16	
	Measured	91.2	-0.1	-3.6	93.1	-0.1	-4.2		
Step 9	Target	91.4	0.0	-2.5	93.3	0.0	-2.9	0.11	
	Measured	91.5	0.0	-2.6	93.3	0.0	-3.0		
Step 10	Target	91.3	-0.1	-2.0	93.2	-0.1	-2.3	0.06	
	Measured	91.4	-0.2	-2.0	93.2	-0.2	-2.3		
Step 11	Target	91.6	0.1	-0.9	93.4	0.1	-1.1	0.23	
	Measured	91.8	0.1	-0.8	93.6	0.1	-0.9		
Step 12	Target	91.5	-0.2	-0.2	93.4	-0.2	-0.2	0.21	
	Measured	91.7	-0.1	0.0	93.5	-0.1	0.0		
Step 13	Target	90.9	0.0	0.8	92.8	0.0	1.0	0.48	
	Measured	91.1	0.0	1.2	93.0	0.0	1.4		
									0.32

For each of the printed samples, L, L* and Y values were kept essentially constant for each printed patch, while a, b and a*, b* values were varied. The achieved L, L* values were in the range of 89-96 and the Y values were in the range of 79-89 for D₅₀, 2°, with similar values for D₆₅, 2° and C, 2°.

Results and Discussion

Figure 9 shows the whiteness evaluation of the 48 observers for the printed pattern in Figure 7 and its variation. As seen from the Figure, an overwhelming number of 46 observers assessed the one of the center areas as the whitest. One of these areas is nearly neutral (Table 1) and is the maximum for N_{FA} , while the other is the maximum for W_{FA} . Tint values varied from -1 to 2.5 and $5Y-280-W_{CIE}$ varied from 7 to 81 , all within the CIE bounds.

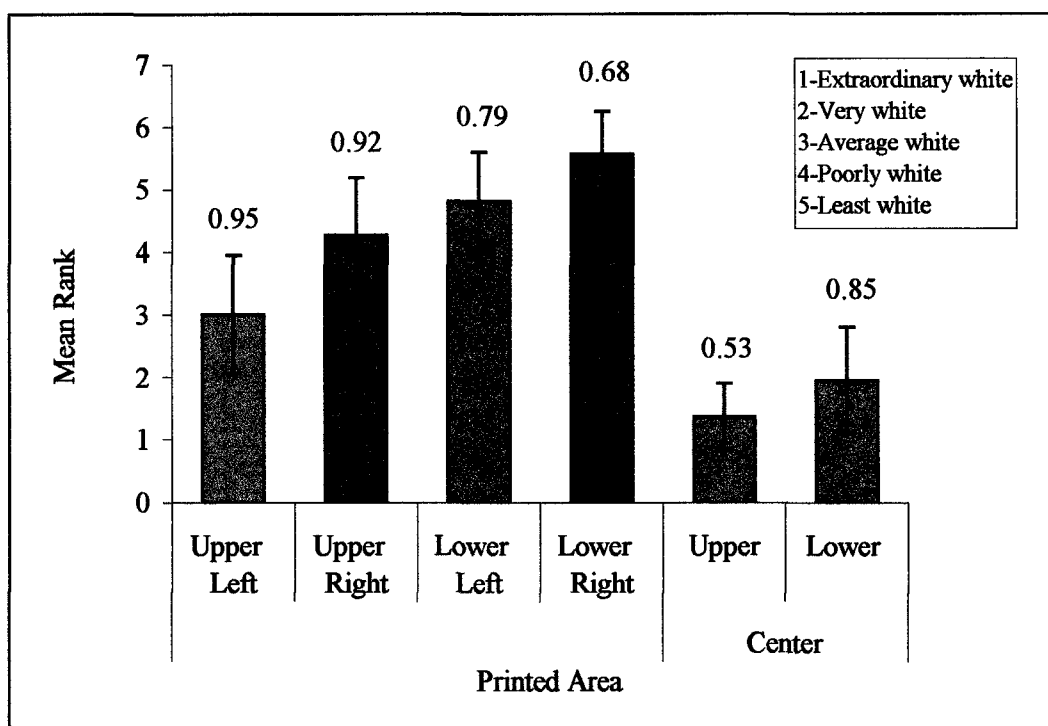


Figure 9. Observers' Evaluation for Print of Figure 7.

The calculated CIE, Hunter, Ganz and proposed whiteness values along with TAPPI brightness are given in Figures 10 a,b, and c for each printed area of Figure 4 for $D_{65}/10^\circ$, $D_{50}/2^\circ$ and $C/2^\circ$, respectively. As seen in the Figure, the proposed whiteness formulas are in good agreement with the observer evaluation data for each printed area on the sample. The correlation coefficients, rank correlations and combined correlations for the printed areas (4 corners) are given in Table 4. NFA, WFA and TAPPI brightness showed significantly higher correlations than CIE, Hunter and Ganz whiteness values for the printed areas on the sample. Although the observer evaluations under the daylight behind a window exhibited slightly lower correlations than the observer evaluations under the light booths, the difference is insignificant for the printed samples.

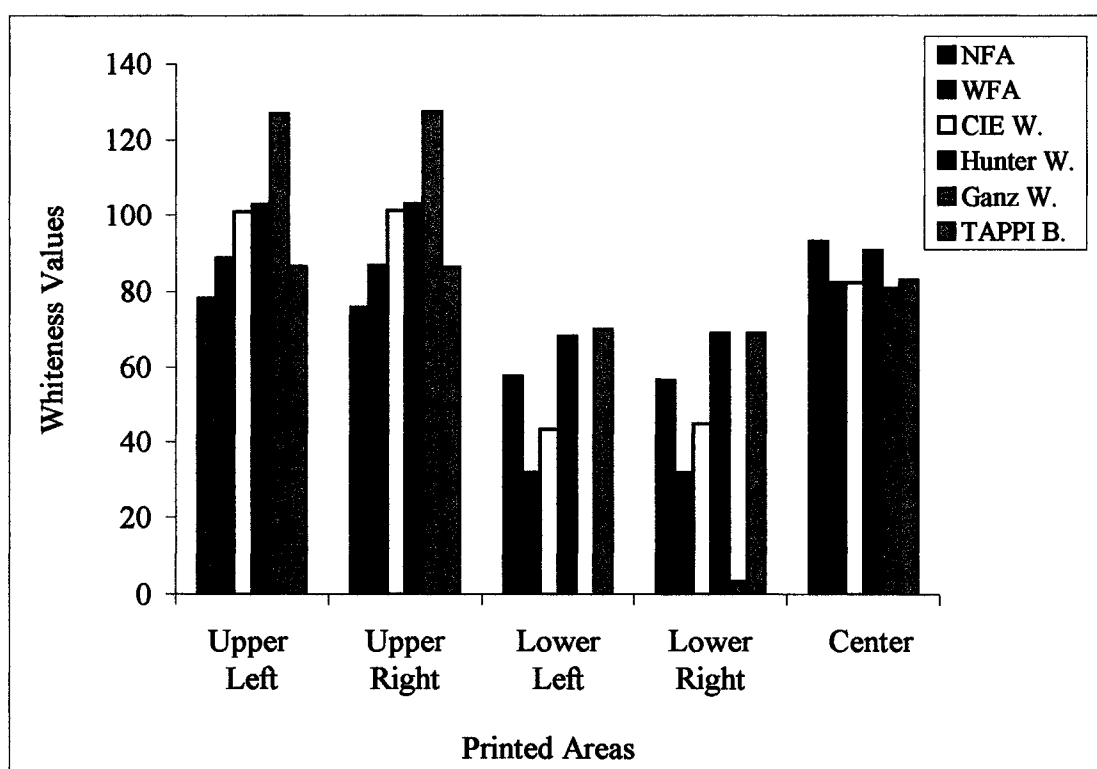


Figure 10a. Whiteness Values for D_{65} , 10° .

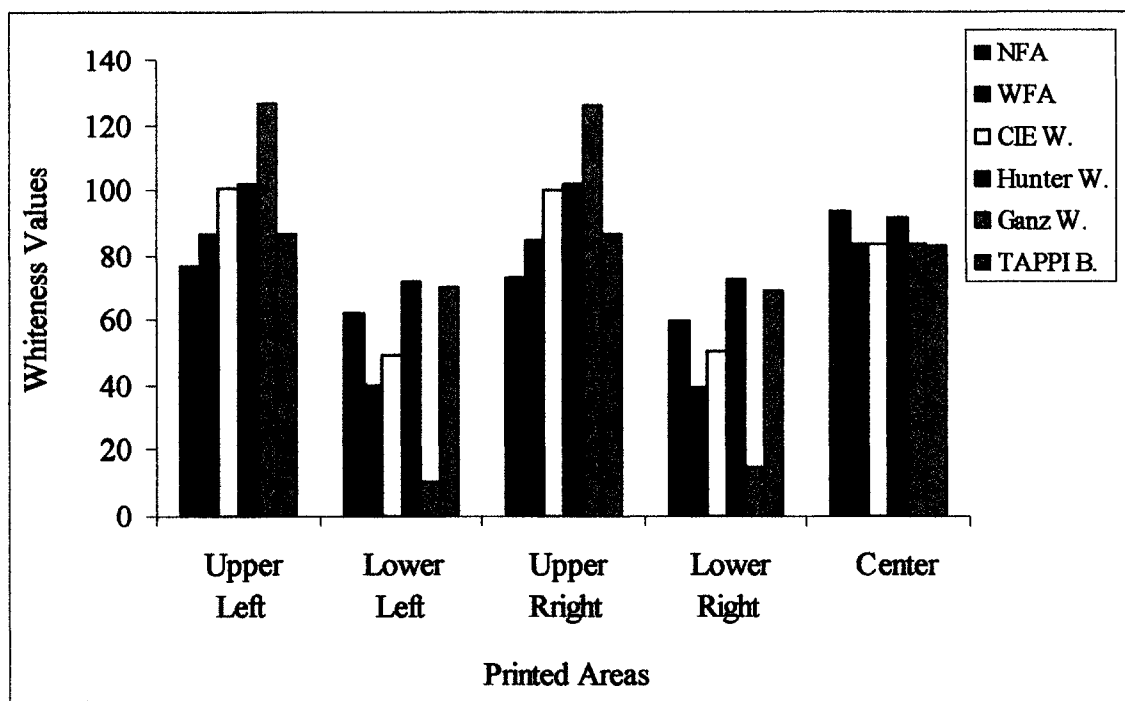


Figure 10b. Whiteness Values for D₅₀, 2°.

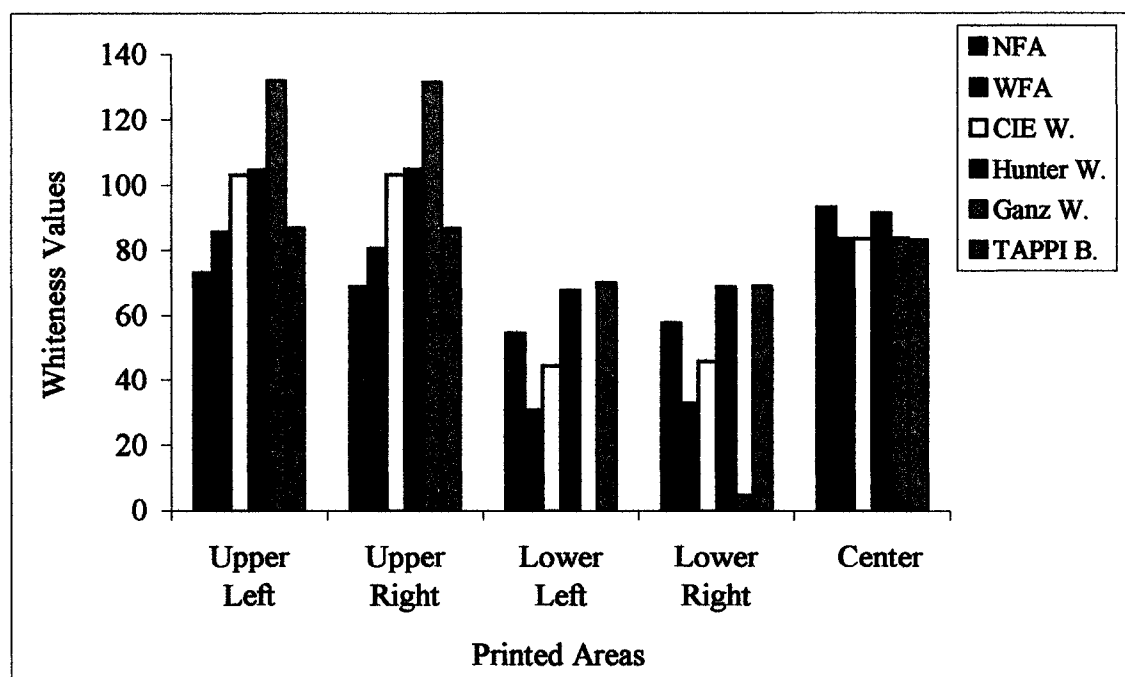


Figure 10c. Whiteness Values for C, 2°.

Table 4. Corresponding Correlation Coefficients for the Printed 4 Corners.

		NFA	WFA	CIE	Hunter	TAPPI	GANZ
Under light booth (25 observers)	Corr.Coeff.	-0.95	-0.87	-0.76	-0.75	-0.84	-0.74
	Ranking Corr.Coeff.	0.94	0.83	0.43	0.43	0.83	0.43
	Combined Corr. Coeff.	-0.95	-0.87	-0.76	-0.75	-0.84	-0.74
Under daylight (23 observers)	Corr.Coeff.	-0.90	-0.76	-0.64	-0.62	-0.73	-0.61
	Ranking Corr. Coeff.	0.91	0.77	0.29	0.29	0.77	0.29
	Combined Corr. Coeff.	-0.89	-0.76	-0.63	-0.62	-0.73	-0.61
Combined Observer Conditions	Corr. Coeff.	-0.93	-0.83	-0.71	-0.70	-0.8	-0.68
	Ranking Corr. Coeff.	0.94	0.83	0.43	0.43	0.83	0.43
	Combined Corr. Coeff.	-0.93	-0.82	-0.71	-0.7	-0.79	-0.68

The correlation coefficients, rank correlations and combined correlations for the printed papers are given in Table 5. Negative values result from increasing whiteness corresponding to a low rank order. All of the formulas except the N_{FA} were in good agreement of the assessments of the printing papers. All of the papers were well within the CIE bounds (3a,b).

Table 5. Corresponding Correlation Coefficients for the Printed Papers.

		NFA	WFA	CIE	Hunter	TAPPI	GANZ
Under light booth (25 observers)	Corr. Coeff.	0.8	-0.99	-0.95	-0.94	-0.99	-0.93
	Ranking Corr. Coeff.	-0.5	1	2	1	1	1
	Combined Corr. Coeff.	0.8	-1	-0.94	-0.93	-0.99	-0.92
Under daylight (23 observers)	Corr. Coeff.	0.84	-0.98	-0.97	-0.97	-1	-0.96
	Ranking Corr. Coeff.	-0.5	1	1	1	1	1
	Combined Corr. Coeff.	0.84	-0.98	-0.97	-0.97	-1	-0.96
Combined Observer Conditions	Corr. Coeff.	0.82	-0.98	-0.96	-0.96	-1	-0.94
	Ranking Corr. Coeff.	-0.5	1	0.96	1	1	1
	Combined Corr. Coeff.	0.81	-0.99	-0.96	-0.95	-0.99	-0.94

The results for the step samples (Tables 2 and 3) were more varied. There appeared to be some confusion and mix ups of patches that were near to one another colorimetrically. This is not so surprising, because the steps were designed to have $\Delta E \sim 1$, where $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$. In addition, there was much more variation between the different observers than there was for the patterns based on Figure 7 or the papers. This undoubtedly reflects different observer preferences for samples that have high luminance and are reasonable white by all of the measures.

The correlation coefficients, rank correlations and combined correlations for the silk paper are given in Table 6. The averaged ranked observer data are consistent with two local maxima in whiteness, one near the neutral maximum of N_{FA} and the other near the bluer maximum of W_{FA} . The observer evaluations under the daylight behind a window exhibited significantly lower correlations than the observer evaluations under the light booths. This reduced overall correlation values significantly.

Table 6. Corresponding Correlation Coefficients for the Cover Papers.

		FNA	WFA	CIE	Hunter	TAPPI	GANZ
Under light booth (25 observers)	Corr.Coeff.	-0.22	-0.86	-0.6	-0.57	-0.8	-0.53
	Ranking Corr. Coeff.	0.31	0.8	0.35	0.35	0.68	0.35
	Combined Corr. Coeff.	-0.18	-0.83	-0.59	-0.57	-0.78	-0.53
Under daylight (23 observers)	Corr.Coeff.	-0.76	-0.14	0.35	0.36	0.04	0.41
	Ranking Corr. Coeff.	0.7	0.22	-0.4	-0.4	0	-0.4
	Combined Corr. Coeff.	-0.65	-0.15	0.27	0.28	0	-0.32
Combined Observer Conditions	Corr. Coeff.	-0.56	-0.59	-0.16	-0.14	-0.46	-0.09
	Ranking Corr. Coeff.	0.46	0.67	0.04	0.04	0.47	0.04
	Combined Corr. Coeff.	-0.46	-0.53	-0.16	-0.15	-0.43	-0.1

The W_{FA} gives a much better correlation with the observer data than N_{FA} , having correlation coefficients of -0.86 versus -0.22 and rank correlation coefficients of 0.80 versus 0.31 for the light booth evaluation. On the other hand, the W_{FA} and N_{FA} gives a close correlation with the observer data, having correlation coefficients of -0.59 versus -0.56 and rank correlation coefficients of 0.67 versus 0.46, respectively for the combination of the two observer evaluation conditions. All of the steps are within the CIE inequalities, except for steps 1, 2 and 3, which have tint values slightly greater than 3. However, these would be in bounds if their a^* values were increased slightly (less than .4 in each case). Thus, these steps are visually indistinguishable from ones that are in bounds.

The correlation coefficients, rank correlations and combined correlations for the cover paper are given in Table 7. Compared to observation under light booth, correlation coefficients for observations under sunlight behind a window were fairly low. This caused overall calculated correlation coefficients values to fall significantly. It seems that confusion and mix-ups of patches that were near to one another calorimetrically was much more apparent for the observation made under sunlight behind a window. The averaged ranked observer data show local maxima in whiteness, near step 4 and step 6, as predicted by our W_{FA} formula. However there is also a local maximum in the observer data at step 1, the bluest printed sample, would be expected from the CIE, Hunter, Ganz formulas and from TAPPI brightness.

Table 7. Corresponding Correlation Coefficients for the Cover Papers.

		FNA	WFA	CIE	Hunter	TAPPI	GANZ
Under light booth (25 observers)	Corr.Coeff.	0.77	-0.86	-0.93	-0.92	-0.94	-0.92
	Ranking Corr. Coeff.	-0.815	0.8	0.9	0.9	0.9	0.9
	Combined Corr. Coeff.	0.62	-0.77	-0.79	-0.78	-0.8	-0.78
Under daylight (23 observers)	Corr. Coeff.	-0.3	-0.01	0.17	0.17	0.13	0.18
	Ranking Corr. Coeff.	0.37	0.03	-0.17	-0.17	-0.17	-0.17
	Combined Corr. Coeff.	-0.22	-0.08	0.09	0.1	0.05	0.1
Combined Observer Conditions	Corr. Coeff.	0.42	-0.65	-0.61	-0.6	-0.64	-0.6
	Ranking Corr. Coeff.	-0.53	0.63	0.65	0.65	0.65	0.65
	Combined Corr. Coeff.	0.28	-0.54	-0.46	-0.45	-0.49	-0.45

The user data were even more varied for the cover paper than the silk paper. As a result, the average rankings, and hence the predicted ranking order, were very sensitive to the weight of averaging. For the observations under booth light, for example, if a rank weighted average is used WFA has a correlation coefficient of -.92, while if the inverse of the average inverse rank is used the correlation coefficient is -.54. For TAPPI brightness the correlation coefficient is -.67 for rank weighting and .78 for inverse weighting. For the rank averaging, the coefficients were .67 for CIE and .66 for Hunter

and Ganz. For inverse weighting, the coefficients were .76 for CIE and Hunter and .75 for Ganz. Because the reliability of the observers is variable, it is hard to know the correct weighting. It doesn't make much difference for the other printed samples, but as we see the cover paper samples are very sensitive. A better estimate of the correlations is to take arithmetic averages of the straight, rank and inverse average coefficients. This yields coefficients of .77 for WFA, .79 for CIE, .80 for TAPPI brightness and .78 for Hunter and Ganz. There isn't a great deal of difference between these values and none are very compelling. Clearly, it is not possible to differentiate among the various formulas based on this sample. Additional test patches would need to be constructed to definitively differentiate between the various formulas.

All of the steps are within the CIE bounds, except for steps 1, 2 and 5, which have tint values slightly greater than 3. As with the silk paper, these can be brought into bounds by increasing their a^* values by about .5 or less. Because these are visually indistinguishable from patches that are within bounds, the tint deviation is an unlikely cause for the variability of the observer data for the cover paper. In fact, many observers found steps 1 and 2 to be among the whitest samples.

For all of the 41 patches rated by the viewers under booth light, W_{FA} and TAPPI brightness each gave an average correlation coefficient of -.87, while CIE, Hunter and Ganz showed average correlation coefficients of only -.77, -.76, -.75, respectively (Table 8). The corresponding averages over straight, rank and inverse weighted averages are -.83, -.82, -.73, -.72 and -.70 for W_{FA} , TAPPI, CIE, Hunter and Ganz, respectively. The combination of observations under booth light and under sunlight behind a window, TAPPI brightness and N_{FA} gave an average correlation coefficient of -.71, -.65 and .64,

while CIE, Hunter and Ganz showed average correlation coefficients of only -.52, -.49 and -.46, respectively. The corresponding averages over straight, rank and inverse weighted averages are -.65, -.59.5, -.47.5, -.46.5 and -.44.5 for W_{FA} , TAPPI, CIE, Hunter and Ganz, respectively.

Table 8. Corresponding Weighted Average Correlation Coefficients.

		WFA	CIE	Hunter	TAPPI	GANZ
Under light booth (25 observers)	Average Corr. Coeff.	-0.87	-0.77	-0.76	-0.87	-0.75
	Average Straight, Rank and Inverse Corr. Coeff.	-0.83	-0.73	-0.72	-0.82	-0.70
Under daylight (23 observers)	Average Corr. Coeff.	-0.34	-0.09	-0.08	-0.22	-0.06
	Average Straight, Rank and Inverse Corr. Coeff.	-0.37	-0.14	-0.13	-0.27	-0.11
Combined Observer Conditions	Average Corr. Coeff.	-0.71	-0.52	-0.51	-0.65	-0.49
	Average Straight, Rank and Inverse Corr. Coeff.	-0.65	-0.47	-0.46	-0.6	-0.44

Conclusions

The proposed colorimetric whiteness, N_{FA} and whiteness, W_{FA} , formulas matched well with 48 randomly selected observer assessments for samples printed based on Figure 7. The CIE, Hunter, and Ganz showed significantly worse correlations, while the TAPPI brightness showed a good correlation, though slightly worse than N_{FA} and W_{FA} . However, for samples that are much closer to neutral and the “paper whites”, the results are less definitive. While W_{FA} exhibited the best correlation, TAPPI brightness correlated only slightly better than N_{FA} . The CIE, Hunter and Ganz formulas correlate much less well than W_{FA} , TAPPI or N_{FA} .

For the observer evaluations, the W_{FA} formula showed a clear improvement over CIE, Hunter and Ganz formulas. The surprising thing is that the TAPPI whiteness, which is based on apparent reflection at a single wavelength, correlates so well. Because of its dependence on a single region of the spectrum, it can lead to absurd results. If we consider a hypothetical reflectance spectrum that is the same as the cover paper for wavelengths less than 500 nm and then decreases linearly from 88% at 510 nm to 25% at 730 nm, such a sample would have the same TAPPI brightness as the cover paper! However, its colorimetric values would be $L^*=89.5$, $a^*=-9.4$ and $b^*=-17.9$. This sample is far outside the CIE bounds ($T=21.6$ and $5Y-280-W_{CIE}= -64.2$). W_{FA} for this hypothetical sample is 2.8, consistent with the obvious blue to cyan of this sample. Although some refinements and testing are still in order, the W_{FA} formula is clearly an improvement over the other whiteness assessments. An important advantage is that it doesn't have to rely on a tint formula, since it automatically weights highly tinted

samples lower than less tinted samples. In a future publication (42), we will compare observer observations of whiteness of coated paper samples with the W_{FA} formula.

Correlation coefficients found were the highest for each tested whiteness formulas when observer evaluations were executed under a light booth. Observer evaluations made under daylight behind a glass significantly reduced the correlation coefficients for each whiteness formula investigated. Observer evaluations executed under daylight behind a glass other than a standard light booth added discrepancies to the test results. Still the reduction in the correlation coefficients were significantly smaller for WFA and NFA than for other whiteness formulas tested where observer evaluations were executed under day light behind a glass.

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VIII. CONCLUSIONS

The study made on Zirconium containing insolubilizers on silica containing ink-jet coating yielded the following conclusions. Anionic zirconium species of AZC and KZC added to ink-jet coatings had some influence on the rheology of the coating formulation, KZC giving a slightly higher viscosity. Both zirconium species interacted with the silica and PVOH in the suspension solution, or in the coating. However, these interactions were weak and easily broken down at higher shear rates. The zirconium insolubilizers increased the viscosity of the PVOH and decreased the viscosity of the silica pigments. Both AZC and KZC probably worked as secondary dispersants with the silica pigments with charge repulsion between pigments preventing agglomeration. Since the zirconium containing ink-jet coatings exhibited more fluid-like behavior, no problems in high-speed paper coating applications are expected. Addition levels of the AZC and KZC were not found to greatly influence the rheology of the final coating composition and coating components. Thus, from a rheological viewpoint, there is no limitation on the amount of anionic zirconium species that can be used in ink-jet coating formulations, within the range of experimented addition levels (from 5% to 10% in dry binder weight).

In the first phase of optical measurements and evaluations study, tinted and FWA added LWC grade paper were used. 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 and calculated whiteness values. 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.

In the second phase of the optical measurements and evaluations study, near neutral (N_{FA}) and high luminance moderately saturated (W_{FA}) whiteness formulas were proposed and tested. Three commercial digital printing papers were chosen and printed for testing of the proposed formulas. N_{FA} and W_{FA} formulas matched well with 48 randomly selected observer assessments for printed samples. W_{FA} exhibited the highest correlation. The CIE, Hunter, and Ganz showed significantly worse correlations, while the TAPPI brightness showed a good correlation, though slightly worse than W_{FA} . However, for samples that are much closer to neutral and the “paper whites”, the results are less definitive. The CIE, Hunter and Ganz formulas correlated much less well than W_{FA} , N_{FA} and TAPPI.

The W_{FA} formula showed a clear improvement over CIE, Hunter and Ganz formulas. The TAPPI whiteness, which is based on apparent reflection at a single

wavelength, correlated well. Although some refinements and testing are still in order, the W_{FA} formula is clearly an improvement over the other whiteness assessments. An important advantage is that it doesn't have to rely on a tint formula, since it automatically weights highly tinted samples lower than less tinted samples.

In the third phase of the optical measurements and evaluations study, tinted and FWA added # 1 publication grade paper were used for further testing of the N_{FA} and W_{FA} whiteness formulas. N_{FA} and W_{FA} whiteness exhibited the best correlation with observer assessments overall while CIE, Hunter and Ganz formulas again showed poorer correlation with observer assessments. N_{FA} and W_{FA} whiteness formulas appeared to be a clear improvement over studied commercial whiteness formulas once again.

Fluorescent effect of uncoated paper was quenched after coating the sheets looking at the CIE, Hunter and Ganz whiteness values. N_{FA} and W_{FA} whiteness formulas did not detect any changes in whiteness as the addition level of FWA increased. This is probably due to added blue shade to the surface of the measured samples with the usage of FWAs. CIE, Hunter and Ganz whiteness values increased as the addition level of FWA was increased.

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