



Whiteness Assessment: A Primer

Concepts, Determination and Control of Perceived Whiteness

Dr. Claudio Puebla

Axiphos GmbH

Germany

Copyright Notice © 2001-2006 Axiphos GmbH, Germany, all rights reserved

Information in this document is subject to change without notice and does not represent a commitment on the part of Axiphos GmbH.

This recompilation does not claim to be exhaustive and/or complete; it is regularly updated, please refer to the date of last version.

This information and our technical advice –whether verbal, in writing or by way of trials- are given in good faith but without warranty and this also applies where proprietary rights of third parties are involved. Our advice does not release you from the obligation to verify the information currently provided and to test our products as to their suitability for the intended processes and uses. The application, use and processing of our products and the products manufactured by you on the basis of our technical advice are beyond our control and, therefore, your entirely own responsibility. Our products are sold in accordance of our General Conditions of Sale and Delivery.

Preface

Measured by the number of colors perceived by the eye, the color white is by far the most encountered one in the human environment. Regardless of the area examined, textiles, paper, plastics or detergents, the color white is clearly the preferred color in many utilitarian and aesthetical applications.

On the other hand no much literature is readily available on this important theme, reflecting a series of serious problems encountered in the assessment and most remarkably in the instrumental measurement of white surfaces.

The emergence of Fluorescent Whitening Agents (FWA) during the fifties and their massive application during the decades thereafter has been without doubt responsible for the enormous impetus experienced in this area. The addition of fluorescence makes it necessary to step up from white color to whiteness, adding a stronger psychophysical accent than encountered with other colors, and posing a challenge to visual assessment.

In fact fluorescence adds a new dimension to the industrial color area and, given the importance of white objects, it creates a subspace of its own denoted as whiteness. On the other hand, fluorescence poses a challenge to measuring instruments; as a matter of fact many of the problems encountered in the whiteness area originate in inadequacies of instrumental assessment.

The emergence of new techniques based on the availability of cheap and fast computer power brings solutions to many of the problems that the user comes across while dealing with whiteness, thus adding fresh ideas and impetus to an old area to be rediscovered.

Much has to be done also on wide spreading information about whiteness concepts and literature.

The present booklet evolved from an electronic "help file" intended to serve as a quick tool to clarify basic concepts; the content has been revised and augmented to give better comprehension and presentation of concepts, some figures and diagrams have been added to provide a basic text for start dealing with the "problem" of whiteness.

Dr. Claudio Puebla
Managing Director
Axiphos GmbH, Germany

June 2003

Contents

Part I - Basic principles

Chapter 1 - Introduction	6
1.1. - About light	7
1.2. - Assessing colors	8
Chapter 2 - The color white	11
2.1. - White vs. whiteness	13
2.2. - On near-whites	14
2.3. - On yellowness	15
2.4. - On color mixing	16
Chapter 3.- On whiteness	19
3.1. - The color of substrate	20
3.2. - Introduction to fluorescence	21
3.3. - The concept of shading	22
3.4. - A general picture of whiteness	23

Part II - Measuring whiteness

Chapter 4. - Where are objects showing whiteness located?	25
4.1. - Critical comments about whiteness formulas	26
Chapter 5. - One-dimensional whiteness formulas	27
5.1. - Berger whiteness formula	27
5.2. - Whiteness index (ASTM)	27
5.3. - Stensby whiteness formula	28
5.4. - Taube whiteness formula	29
Chapter 6.- Two-dimensional whiteness formulas	30
6.1. - Method of Ganz and Griesser	30
6.2. - Formula after CIE	31
Chapter 7.- Instrumental assessment	33
7.1. - Adjusting UV to daylight conditions	34
7.2. - Calibration standards	35
7.3. - Triplet effect	37

Part III - Applications

Chapter 8.- Achieving high-whiteness values	38
8.1. - Tools for the evaluation of whiteness	38
8.2. - The importance of shading	41

8.3. - Evaluation of fluorescence on metamerism effects	41
8.4. - Matching whiteness of pairs	42
Appendix (Books, reviews and norms)	47
Books	47
Reviews	48
Reports	49
Related norms	50
Selected literature (1990-2001)	52
Glossary	57
Index	64

Part I. - Basic principles

Chapter 1. - Introduction

Color perception is a basic function of living (and especially human) beings necessary for appreciation of natural environment; information provided by the color perception mechanism is processed by the brain resulting in vital information for operation, behavior and ultimately survival of the species.

While vision is quite widespread in nature, color vision is limited to those species with color receptors; color perception depends on the spectral distribution of the detected light i.e. intensities at each of the wavelengths within detection range. Color receptors probe the distribution and react producing signals with different intensities that are processed by the brain originating the color perception phenomena.

In general the process can be resumed as one stimulus (light) producing some electrical signal (color receptors in the eye) that is processed in the brain to evoke some biologically sensible conscious awareness; this relationship is matter of study of a discipline called psychophysics.

The human eye has three color receptors (connected to vision of green, red and blue) called "cones" and one more sensitive to light intensity, called "rods". Physically, color description is based on modeling the interactions between the light source illuminating the object, the object itself and the response of the color receptors. Description of color is thus related to a triad of numbers as follows:

- **luminosity**: this is related to the relative intensity of the light coming from the object and is connected to the response of the rods; its value is also connected to the concepts of white (high value) and black (low value).
- **chroma**: this is the amount of color perceived by the eye, it is also known as color saturation; colors from monochromatic sources possess the highest possible saturation values.
- **hue**: this number accounts for the observed color and its value is also given as an angle going from red, yellow, to green and blue; sometimes it is related to monochromatic sources characterized by the so called "dominant" wavelength.

Within this context each color can be assigned unique values of luminosity, chroma and hue; two colors having the same triad of values are said to be equivalent, in the sense that they are perceived as being the same under the given illumination and viewing conditions.

The color white has been matter of much controversy due to its unique characteristics and difficulties encountered in its production.

As approached by classical colorists, white is indeed one of the basic colors in all color systems; it is normally defined as the contrary of black and as such it is recognized as having the highest luminosity of all colors.

The total absence of hue and color saturation has been seen suspiciously to the point that traditionally it has not been considered as a color at all and given the property of being achromatic i.e. "without color"; by the same

token black has been regarded not only as no color but also as no luminosity and just next to void.

Most of the color systems consider white (and also black) only in an auxiliary sense as limit when color dilutes into "no color".

White can be considered as a color with following characteristics:

- the highest luminosity
- no saturation at all
- no hue

1.1. - About light

In order to perceive the sensation known as color, the responsible receptors sensitive to light of different wavelengths must be excited by an external stimulus i.e. light coming from a given object.

It is the light as a whole coming from the object that stimulates the receptors to different extent and is responsible for originating color perception. Depending on the origin of the light from the object, the latter can be classified as:

- **passive diffuser or reflector:** light is coming from a certain source located at certain distance away from the object and is reflected from it in all directions (diffuser) or specularly (reflector) towards the eye. In general light interacts with the object and its spectral distribution is changed as result of absorption and scattering processes within the material of the object; as a result light color changes after the interaction with the object. If no changes result and light is elastically reflected (i.e. no losses), the object is called perfect diffuser. If all reflection directions are evenly distributed it is further denoted as Lambertian diffuser.
- **self-luminous:** many objects have the property to emit light upon certain excitation:
 1. **incandescence:** all objects emit light when heated; this is in general a result of solely temperature, nature or constitution of the object are not involved in the light production process; the ideal radiator is known as "black body".
 2. **fluorescence:** many molecules possess the property to emit light after they have been excited by a light ray i.e. they have absorbed light. The light emitted is called fluorescence if the emission follows within picoseconds time scale. In general the energy of the emitted light is lower than the absorbed one, the rule follows that emission occurs always at higher wavelengths than absorption.
 3. **phosphorescence:** with some molecules the emission process endures longer in time as result of internal processes within them; the emission process persists from seconds to hours.

Since color perception depends on light (and its spectral distribution) coming from the observed object, it is important to consider its origin when dealing with color assessment; in this context light can originate by following process on the object:

- **passive diffusion:** the light observed originates outside the object itself, the object acts as a modulator of the incoming rays changing their spectral distribution depending on level of interaction. Color perceived is the result of interaction of incoming ray and nature of the object.
- **self-luminescence:** the incoming light excites molecules to emit the radiation perceived later as color. In general the spectral distribution of the exciting light has no influence on the spectral distribution of the emission, remarkably this is the case for fluorescent whitening agents. Departures from this rule appear when more than one excited-state is involved in the emission process.

In general terms however, light detected by the eyes that ultimately fires the color perception, is a mixture of reflected (and/or diffused) light and emission from the object; the eye cannot discriminate between both sources. As general result and due to the nature of the light detected by the eye, color cannot be considered a physical property of the observed object.

1.2. - Assessing color

Characterization of a color can be done either visually or through an instrument; in either case results must be accompanied with information about conditions under which the assessment has been performed.

Light sources vs. illuminants

While the CIE and other organizations have published norms defining illuminants, it is responsibility of the assessing laboratory to calibrate the light sources used for visual assessment.

Illuminants are defined as a table of relative intensities by the standardizing organization; the CIE recommended illuminants are daylight D_{65} and incandescent type A (see corresponding norms in the Appendix). Many other illuminants exist depending of the industrial area; most of them were at some time standardized illuminants of the CIE but have lost relevance from the scientific point of view because they do not offer much additional information to the color assessment process. They still are very important in many industrial sectors because many of them are directly related to light sources.

Light sources are physical devices that produce light used for the assessment; their spectral distribution must match the one characterizing the corresponding illuminant in order to validate the assessment. Much confusion exists however on the correct way to calibrate light sources, since this represent an economical factor.

Calibration of light sources should be done preferably examining their spectral distribution; calibration according to color temperature should be avoided, especially when dealing with whiteness.

A large variety of light sources can be found in the market, some of them claim to be close to one of the standardized illuminants, others in the best case just follow fashion or esthetics.

Defining daylight

According to the CIE, daylight is defined according to the tables of illuminant D_{65} ; the region of definition extends into the ultraviolet (UV) region down to 300 nm (although strictly for visual assessment only the region between 380 and 760 nm is relevant). The UV region is however important when dealing with fluorescent whites, since fluorescence originates from the absorption in the UV region.

Although it is quite difficult to "produce daylight" in its whole extension in the lab to be used in the visual assessment, it is absolutely mandatory to meet certain requirements concerning spectral distribution when dealing with whiteness; following guidelines should be followed:

- **make sure that the observation light has a "true" daylight simulator:** many booths are equipped with simulators of illuminant C that are denoted as "daylight" in the sense that C is a good approximation for D_{65} ; though ignoring the lack of intensity in the UV region that leads to mismatch of samples containing different amounts of FWAs
- **do not trust calibrations made on color temperature basis:** due to costs, some booths are equipped with fluorescent lamps denoted as "daylight", "cool white", etc. According to their specifications they have a color temperature similar to D_{65} ; they are normally three-band phosphorous pigments with tri-stimulus values close to D_{65} , but their spectral distribution differ notably from the D_{65} one.
- **be careful with color rendering indices (CRI):** the closer the CRI is to the value 100, the smaller is the difference of certain number of metameric pairs; notice that CRI closer to 100 does not automatically mean that the spectral distribution of the lamp is closer to that of daylight.
- **be careful when turning on the UV lamp:** since most of the booths do not have a daylight simulator for the whole spectral region, they are provided with an additional UV lamp to be turned on when dealing with fluorescent white samples. The lamp irradiates in general an uncontrolled amount of UV that by no means guarantees a good match with daylight; the situation turns worse because the lamp stabilizes normally after some minutes of operation when thermal equilibrium has been reached.

Visual assessment

In general the human eye has no memory for color such that it is not possible, even for a trained person, to judge a color on an absolute basis. For this reason assessment can be done only through comparison of pairs of samples; thus the assessment is limited to a comparison of a given sample to the one considered as standard. In a general way the eye is always making a

comparison between the light coming from the object and that coming from the environment; this is extremely important when assessing samples with high luminosity and low saturation values as in the case of white.

Furthermore the adaptation of the eye must be taken into account along with a standardized environment in order to produce reliable assessment:

- **Environment:** it is advisable to use an observation booth with an interior painted in non-reflecting grey. No colored objects (other than the pair under assessment) should be positioned in the booth; observer and other persons should also wear neutral (grey) clothes, this is especially important when assessing white samples.
- **Light sources:** the pair should be assessed under more than just one light source in order to establish the presence of metameric effects. Illuminant metamerism is the phenomena by which two samples appear to have the same color under one light source but they depart from each other when the light source changes. Light sources must be controlled and recalibrated on a periodical basis.
- **Whiteness:** the assessment of whiteness must be conducted in several steps in order to isolate and assess each of the contributions to whiteness. In this respect is important to build and maintain a well trained assessment panel that has been given special instruction in assessing whiteness

Instrumental assessment

An instrument is able to assess color on an absolute basis, provided that it has been properly calibrated; this is just a different way of saying that any measurement is referred to certain standard that has been certified and its data is traceable back to certain standardization institution.

Considering how the sample is illuminated, two different families of geometries can be distinguished:

- **directional illumination:** under this geometry the sample is illuminated by a light ray coming in a certain angle, the sample being observed (by the detector) under a different angle; the set illumination axis, object and observation axis form a plane. Due to certain unavoidable level of anisotropy of the sample, some degree of dependence of results on the orientation of the sample is observed under this geometry; for this reason it is recommended to take an average of different sample orientations in order to cancel out this effect. Following configurations are currently used:
 1. **geometry 45°/0°:** sample is illuminated in an angle of 45° and observed under 0° from the normal; this geometry is encountered in the paper assessment area as required by many Tappi methods. Samples are observed in a one-dimensional way, any optical anisotropy introduces a dependence of the results on the physical orientation.
 2. **annular geometry:** to avoid the orientation dependence, some instruments have many illuminators positioned in a ring thus introducing a rotation symmetry of the illumination; this type of

annular illumination is used in instruments for continuous measurements.

- **diffuse illumination:** in order to eliminate variations originating from anisotropic effects, the sample is positioned at a port of a hollow sphere with internal walls covered with a highly diffuse reflecting white pigment; with this configuration it is assured that the sample is illuminated from all directions at the same time. Two configurations are currently used:
 1. **geometry d/0°:** the sample is diffuse illuminated and observed in an angle of 0° from the normal; this geometry is encountered in the paper area as required by ISO methods.
 2. **geometry d/8°:** the sample is diffuse illuminated and observed in an angle of 8° from the normal; the 8° observation allows a first assessment of the gloss of the sample. This geometry is encountered in textile area.

Besides geometry different types of light detection are used; one can distinguish:

- **colorimeters:** in this type of instruments light from the sample is examined (consecutively or simultaneously) by three filters simulating the tri-stimulus functions for a given illuminant. The instrument produces the values (X,Y,Z) and all colorimetric data derived from it; since the illuminant is part of the filter, colorimetric data for a different illuminant is not possible, unless the filters are replaced and a new measurement is done.
- **spectrophotometers:** this type of instruments measures the reflectance spectra of the sample, rather than analyzes the incoming light in colorimetric terms. Since the reflectance spectrum is a physical property of the sample, calculation of colorimetric data for different illuminants and observers can be easily performed through software.

Special additional conditions are needed for the instrumental assessment of whiteness; they will be discussed later (see Instrumental assessment).

Chapter 2. - The color white

Being the color with the highest value of luminosity and no (or small) chroma, white is used in all applications where visibility and contrast are needed.

The psychological significance of white is important as an information carrier, most of the significances attributed to white are:

- **neutrality:** this may have the significance of non-aggression (white flag for truce or deliberation) but also of cowardice (white flag as surrender). It is also interpreted as void, emptiness but also as a new start (in Orient white is the color of mourning though). The absence of chroma allows good combinations with all other colors.
- **high luminosity:** as a sign of cleanness and chastity, untouched, new, unused. Contrast is based on differences of luminosity and white is the ideal background for those areas where high contrast is important (printing industry). The high luminosity is also an attention-catcher to be used in fashion and art.

However it must be mentioned that the observer (unless well trained) is not in position to distinguish between (physical) color white and whiteness; it is the last concept that opens a wide horizon of applications allowing personal and cultural values to find an expression.

Whiteness must be understood as a contraposition of yellow-blue that can be explained with the significance of the limiting colors yellow and blue:

- yellow is associated with (negative) properties like old, used not fresh. In certain cultures yellow is associated with cowardice, while in Orient is reserved to erudite and monks.
- blue is associated with coolness, freshness and by the same token with something new; in general blue is sign of tranquility

It is this juxtaposition between yellow and blue that explains our preference for bluish objects over those showing yellowness, a preference that is emphasized if accompanied with an increase (even slight) of luminosity.

Preferred whites are chosen on grounds of social group and geographical and culture origin, although for several applications certain shades of whites are preferred. While people in the Orient prefer a red-shaded white, Europeans prefer it neutral, and Latin Americans rather blue shaded; on the other hand underwear is always preferred in red shaded whites.

The amount of luminosity is important too; higher luminosity values result in more (perceived) beautiful whites.

In general it can be stated:

- whiteness will always be preferred over white, unless the latter shows more luminosity making the former to appear dull.
- each cultural group will set their own standards for the "most beautiful" white.

2.1. - White vs. whiteness

Reflectance factors of the material give information on the level of interaction of the object with the incoming light, high numbers (for example near to 100%) denote low interaction, in other words low intensity losses and high reflectance.

For samples showing no losses all the incoming light will be reflected without (noticeable) intensity losses or changes in the original spectral distribution (notice that color as hue will be perceived as soon as the spectral distribution changes); if in addition to this property the surface shows a very low (or non-existing) gloss the sample is said to be a perfect diffuser, color coordinates of a perfect diffuser are

$$(Y,x,y) = (100,x_0,y_0)$$

where (x_0,y_0) are the coordinates of the achromatic point for the corresponding illuminant; notice that the definition of perfect white is dependent on the illuminant, perfect colorimetric white is thus not an invariant (this is a very important issue when dealing with color reproduction where color will be observed under different illumination conditions; establishing a "true" white point has a strong influence on the way the scenery will be perceived).

A perfect diffuser is also a perfect white i.e. with the maximum value of luminosity without any saturation or hue. This type of sample is very rare in the nature, with remarkable exceptions like fresh fallen snow or clouds. On the other extreme samples that absorb all the incoming light (total loss) will appear black, the coordinates of such perfect black are

$$(Y,x,y) = (0,x_0,y_0)$$

notice that compared to a perfect diffuser it differs just in the value of the luminosity.

In fact such an axis coming from ideal black to perfect diffuser is a natural axis for white colors; it starts with black, going up to different levels of grey and ending with a perfect white.

White samples are then characterized by showing:

- high levels of luminosity
- no saturation at all
- and consequently no hue

There are however samples that appear to the eye as being white, this is a quite subjective perception and depends strongly on illumination conditions and on the observer himself. Samples that have this property are said to be perceived as white, their color coordinates do not lie however on the black-white axis, but they show a finite saturation level with a blue hue; one speaks of these samples as showing whiteness.

Samples showing whiteness are characterized by showing:

- high levels of luminosity
- finite saturation
- blue hue

The reason for the perception of high luminescent blue samples as being white cannot be formulated on theoretical or scientific basis and has to be left to psychophysics. It must be reminded though, that samples showing whiteness are perceived as whiter referred to a sample with less whiteness in terms that it is "bluer" on a preferred axis; whiteness is not an absolute quantity.

2.2. - On near-whites

Near whites are colors with high luminosity (>65%) and having a finite chroma, however with values so small that they are not generally considered colored. According to norm ASTM E-313 chroma of near-whites are defined in terms of Munsell chroma as being:

- less than 0.5 for B hues
- less than 0.8 for Y hues
- less than 0.3 for all other hues

Notice the lower values for hues other than B or Y, in fact the axis yellow-blue is the whiteness axis and samples having hues in this region are considered either having yellowness or being white; for the former ones even the expression "off-white" has been coined.

Pigments

Practically most of the natural or synthetic white pigments fall in the category of near-whites, in general belonging to Munsell Y hues.

During the refining process, pigments are subjected to bleaching and extraction of colored (in general heavy metal) ions.

Bleaching reduces absorption of the light, increasing the light amount to be reflected; the reflectance process depends however further on the refraction index and on the particle size of the pigment.

Refraction index is a physical property of the material and cannot be changed; the higher the value the higher is the amount of light reflected. Most of the natural pigments have quite similar refraction indices (about 1.6) with the remarkable exception of Titanium dioxide ($n = 2.6$).

The influence of refraction index and particle size distribution are combined in the scattering coefficient that is responsible for the amount of light reflected by the pigment; in this context the scattering coefficient affects the hiding power of the pigment, that is the important property for obtaining higher whiteness levels. While generally mineral pigments show scattering coefficients of 130-150 sq/kg, the superiority of Titanium dioxide with values of 1000 sq/kg is clearly indicated.

Substrates of organic nature

Most of the substrates used as material in the paper, textile and plastics industries are polymers i.e. long-chain organic materials that may contain certain amount of double bonds and/or chemical groups that show light absorption; especially the concentration of double bonds lead to the phenomena of "conjugation" of the electrons belonging to the bonds; this phenomena lowers the energy needed to excite them, resulting in the appearance of absorption of visible light and consequently of color (only absorption of light between 380 and 760 nm is perceived as color).

Natural fibers as wool, linen, cotton, pulp, etc contain a sufficient large amount of light absorbing groups and are in more or less extent colored. Through a chemical treatment known as bleaching, most of the light-absorbing groups are chemically destroyed; double bonds are eliminated to large extent resulting in an overall decrease of light absorption and a disappearance of color. Total elimination of double bonds can be achieved only after prolonged chemical bleaching that is however undesirable in economic and quality terms, since chemical treatment of fibers eliminates also single bonds resulting in shorter fibers and thus in a change of physical properties of substrate.

In this context only a compromise can be reached concerning the elimination of color; bleached materials do not resemble a perfect diffuser but they show a certain extent of yellowness of certain hue; they are definitely not blue because substrates show absorption of light in the short wavelength region, resulting in a certain "off-white" appearance similar to pigments.

By the same token man-made fibers or plastics show also certain yellowness as result of double bond formation as the polymerization process progresses (inverted situation as bleaching). Since in general plastics are transparent this so-called "residual" yellowness become noticeable (for white objects) during the "filling" process with a mineral pigment, resulting in an off-white object that originates from both the mineral filler and the plastic material. Similarly to natural polymers, plastic materials can also be chemically bleached to increase whiteness giving near-white objects with high luminosity values.

2.3. - On yellowness

Yellowness is defined as "the attribute by which an object color is judged to depart from a preferred white toward yellow". By this definition the object is clearly yellow; even at a high level of luminosity it is recognized as yellow and not as white.

Evaluation of yellowness is very important because most of the materials, even after extensive bleaching, show a certain degree of yellowness.

Yellowness is at best characterized by the yellowness index; some formulas (mainly used in plastics) are given below:

Yellowness after BASF:

$$G_B = \frac{X}{0.7831} + 0.833 \cdot Z$$

Yellowness TM-1925 and DIN 6167:

$$YI = \frac{1.2750 \cdot X - 1.0584 \cdot Z}{Y}$$

Yellowness ASTM-E 313-73:

$$YI = 100 \cdot \left(1 - 0.847 \cdot \frac{Z}{Y} \right)$$

All formulas are for C/2° (note that yellowness formulas are restricted to specific illuminants and observers). Positive numbers are obtained for all yellow samples.

Basically yellowness formulas should be applied for samples with color possessing dominant wavelengths between 570 and 580 nm. Blue samples will show negative values.

Paper brightness

Yellowness can be seen as a deficiency of blue or as absorption of blue light, all formulas given above can be understood in this context.

In the paper area a related expression has been coined as paper brightness (also known as Tappi or ISO brightness) that reflects exactly the amount of yellowness in the pulp or paper sample; its general expression is given as:

$$B = \sum_{\lambda} B_{\lambda} \cdot R_{\lambda}$$

where the function $B(\lambda)$ is a bell-shaped function peaking at 460 nm with a bandwidth of about 60 nm and numerically defined in the norms (for example Tappi T-452, ASTM D 985, ISO 2469, etc.). Note that the function is normalized to the value 100 and it is strictly one-dimensional; in other words just the reflectance values within the narrow wavelength around 460 nm will determine the value of B as a single value regardless of the shape of the reflectance spectrum of the sample.

Originally determination of paper brightness was a quick method to establish the reflectance intensity in the blue light absorbing region; the method was strictly tailored control the bleaching process of pulp, where the color always goes from dark brown to pale yellow; it was done visually by using a blue filter (this is it is called blue reflectance factor) through which samples were compared against a certain standard.

For these reasons paper brightness applies only to **naturally** colored pulps, and papers and board made from pulps, it does not apply to colored materials, although some adaptation has been made to accommodate

optically whitened samples.

Contrary to its name, paper brightness is strictly not a measure of appearance. In spite of its physical (and not colorimetric) character, it is still quite widespread in the paper industry and even used in specifications as a measure of perceived white.

2.4. - On color mixing

Any color can be decomposed as a combination of three elements that are given ultimately by the tri-stimulus function describing the normal observer; it must be mentioned that in general a closer examination of the origin of the stimulus must be given to arrive to proper tri-stimulus values.

As stated above the eye is stimulated by the light coming from the object regardless of how the light was originated. The final perceived color can be seen as a result from the light source as modulated by the reflectance factors of the object and/or from self-luminance of the object; each process separately can be understood according to following scheme:

- **additive color mixing:** the desired color can be represented as the mixture of light coming from three light sources with following normed (basic) colors: blue, green and red; an example of this method is the TV screen. The main characteristic of additive color mixing is that the luminosity value of the resulting color is always higher than those of any of its components.
- **subtractive color mixing:** the desired color can be represented as the mixture of light coming from three dyed samples of following normed (absorption) colors: yellow, cyan and magenta and illuminated with a common normed light source; an example of this method is photography. The main characteristic of subtractive color mixing is that the luminosity value of the resulting color is always lower than those of any of its components.

To calculate tri-stimulus values of samples that are both reflecting and self-luminous, both effects must be separated:

$$X = k \cdot \sum_{\lambda} (R_{\lambda} \cdot S_{\lambda}^{source} + S_{\lambda}^{fluorescence}) \cdot \bar{x}_{\lambda}$$

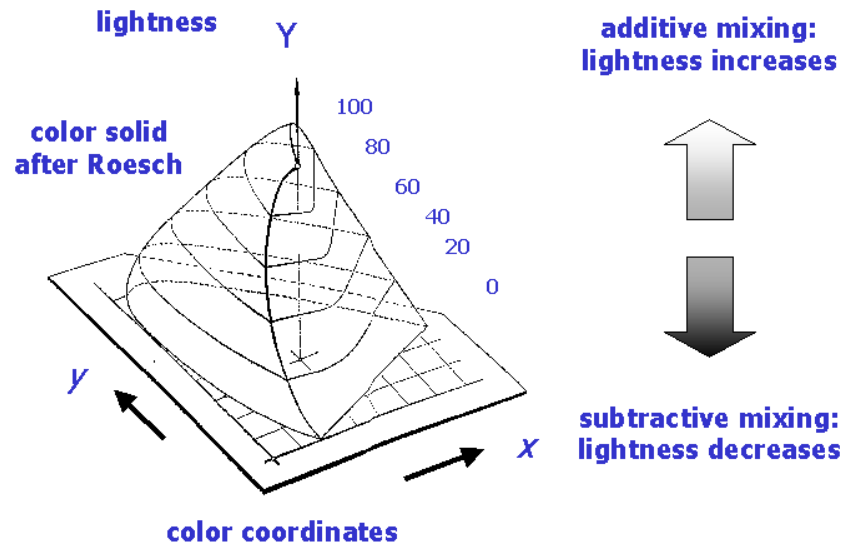
$$Y = k \cdot \sum_{\lambda} (R_{\lambda} \cdot S_{\lambda}^{source} + S_{\lambda}^{fluorescence}) \cdot \bar{y}_{\lambda}$$

$$Z = k \cdot \sum_{\lambda} (R_{\lambda} \cdot S_{\lambda}^{source} + S_{\lambda}^{fluorescence}) \cdot \bar{z}_{\lambda}$$

Notice that the self-luminous part does not depend explicitly on any illuminant; since fluorescence originates from light absorption at shorter wavelengths, its dependence on the illuminant is implicit in the amount (and in general also in the spectral distribution) of the overall intensity of the illuminant; for this reason the rule derives that "fluorescent materials can be

measured only under the illumination conditions under which they will be observed"; this is a strong limitation for the validity of the reported color values since, contrary to reflectance values, tri-stimulus values cannot be recalculated for different illuminants in a straightforward manner to assess metameric effects.

Luminosity plays an important role when choosing the proper mechanism for increasing whiteness because of the different impact of color mixing on final values of Y (or L^*). This can be summarized as shown on the following picture:



Theoretically, values for Y or L^* can be indefinitely increased by adding corresponding amounts of fluorescence i.e. using additive mixing.

This is however not the case for the application of subtractive mixing by adding shading agents because the highest attainable luminosity value is exactly that of starting point. This must be kept in mind while choosing nature and amount of shading agents; in general luminosity losses due to application of shading agents can be regained only in part by adding fluorescence.

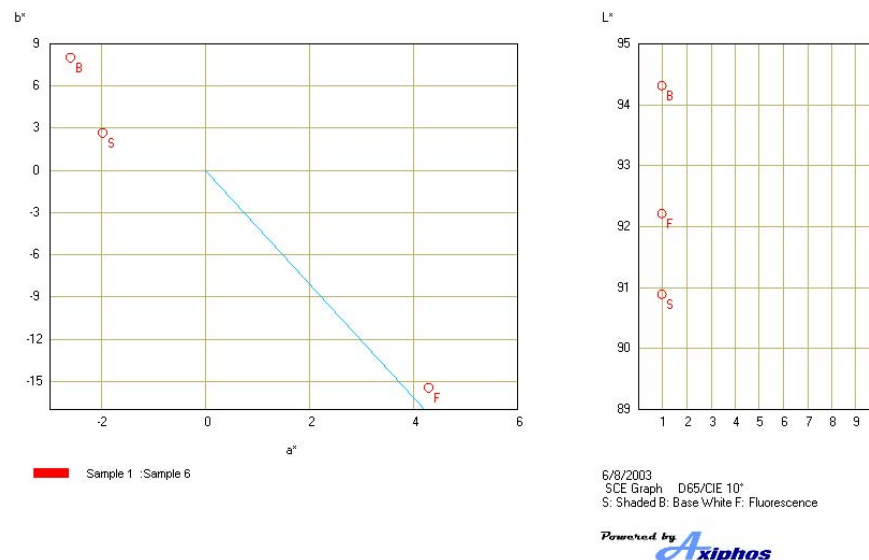
Chapter 3. - On whiteness

Whiteness is about perceived white i.e. those objects appearing white to the human observer. As such reflectance spectra of objects with whiteness depart strongly from those showing just the color white.

As stated earlier whiteness is defined as the opposite of yellowness i.e. objects showing whiteness present a blue hue. In fact only a yellow substrate can be made white by the methods presented here, since the final goal is connected to the elimination of the inherent yellowness of the substrate. The final whiteness perception can be decomposed in whiteness components:

- **Base white:** this corresponds to the amount of absorption of the substrate, this being in general yellow or showing certain amount of yellowness (that can originate also from FWA absorption). The existence of a finite amount of yellowness is however not a precondition to increase whiteness, perfect grays or a perfect white can also be added whiteness; substrate with other hues cannot be whitened using these methods.
- **Shaded white:** this corresponds to a compensation of the yellowness through addition of a blue or violet dye. In colorimetric terms, this corresponds to a subtractive color mixing process.
- **Fluorescent white:** this corresponds to a compensation of the yellowness through addition of a blue light coming from a fluorescence process. In colorimetric terms, this corresponds to an additive color mixing process.

The interrelationship between the different whiteness contributions is illustrated on the following diagram (L^* , a^* , b^*) for a fluorescent sample:



The (a^*, b^*) plane shows the relative positions of the base white (B), shaded white (S) and fluorescent white (F) i.e. total whiteness with reference to a

neutral white line shown as blue line for the D_{65} illuminant. The sample is heavily shaded as seen on the L^* diagram where the substrate with a value of over 94 falls below 91 as result of the absorption by the shading agent; notice that while shading shifts the color coordinates towards blue (lowers the value of b^*) making it to appear “whiter”, the loss of luminosity make it to appear dull.

The action of fluorescence is quite successful shifting the sample deep into the blue area; on the other hand it is able only to recover a little more than one unit on the L^* axis, in other words, in the present example fluorescence does not succeed to compensate completely the loss of luminosity due to shading.

A further point is the large UV metamerism presented by the sample, in fact color coordinates of the sample will move on approximately a line between shaded (S) and fluorescent (F) points when the amount of UV decreases for example changing to daylight “indoor” conditions. Since the shaded point (S) lies in the yellow region ($b^* > 0$) the sample will loose a large amount of whiteness and compare disadvantageously against original conditions when the final point was in the blue region ($b^* < 0$).

3.1.1 - The color of substrate

There are only three ways to make a substrate white:

1. **covering it with a white film:** the coating must be made with a material having a high opacity in order to cover the original color of the substrate. If this is the case the final white color depends solely on the properties of the coating and not on those of substrate. Since a total covering is normally not achieved certain amount of color from the substrate goes through the coating layer, total perceived color depends thus to a certain extent on color of underlying substrate
2. **substrate bleach:** this process involves the (chemical) destruction of absorbing components within the substrate, eliminating light losses. In general the bleach process ends up with a substantial gain of luminosity, but still after prolonged bleaching a certain amount of yellowness will remain
3. **color compensation:** the addition of complementary color of the substrate increases the whiteness perception. Although this process works theoretically for any substrate, industrial available dyes focus on those substrates presenting yellowness; the amount of yellowness is a limiting factor for the efficiency of the method, not all substrates can be whitened by using color compensation.

The first and second processes have a physical basis since they deal with the substrate itself in a material form; the extension of achieved whiteness is inherent to the resulting material.

Color compensation involves however directly the observer and by extension the illumination conditions, in this respect it is based on a psychochromatic process rather than a purely physical one. By the same token color compensation is more sensitive to changes in illumination conditions.

3.2. - Introduction to fluorescence

Light needed to compensate for the substrate yellowness is produced by a family of molecules known as Fluorescent Whitening Agents (FWA). These molecules have the property to absorb light in the near UV region (below 400 nm) and emit light (called fluorescence) at about 445 nm. The fact of fluorescence of blue light limits FWA to compensate only yellow substrates.

Fluorescent Whitening Agents belong to dyes family and can be incorporated into the substrate through any of following methods:

1. **exhaustion:** for cotton and other cellulose fibers presenting a surface with ionic character, ionic (normally anionic) FWAs are used that can be exhausted onto the fiber in a process similar to dyeing; this process is based on the ionic character of the substrate surface and much care must be exercised to choose the proper type to achieve maximal efficiency
2. **diffusion:** for plastic materials (not having a ionic surface) non-ionic FWAs are used that diffuse into the substrate either through incorporation during extrusion or diffusion from a bath under (normally high) temperature
3. **pigmentation:** FWA pigments are highly self-luminous and do not need the direct participation of the substrate for fluorescence production; they are incorporated physically either through mixing or more efficiently through a coating process

Besides the value of molecular quantum yield, that is given by their chemical structure, the main limitation of FWAs is given on the available UV light; in fact the amount of UV light dictates at the end the amount of fluorescence produced and the whitening power of the incorporated FWA. Thus special attention must be paid to the amount of absorption of the substrate in general and in particular in the region below 400 nm. In fact the region below 400 nm (that has no influence on the color appearance of the substrate to the human eye) dictates the amount of light left to excite the FWA; absorbing molecules present will compete with the FWA for the available light and reduce its power. In this context the use of UV absorbers (notably used in plastic and finding increase use in textiles) may annihilate the fluorescence production and the whitening effect.

In certain cases this is a desired effect (specially with certain paper qualities), for which families of fluorescence quenchers are available.

The fluorescence amount controls the extension of the final whitening effect and the position of its maximum controls the shade of the whiteness: shifting the fluorescence towards higher wavelengths results in green-shaded tones, shifting towards shorter wavelengths results in violet (redder) tones.

While the quantity of fluorescence is related to the amount of FWA, there are some limits for the amount that can be incorporated, this being a characteristic of each FWA and to be found in their specs sheets (process known as build-up); surpassing the high limit will result in green shades (so called "greening") and in many cases in a drastic drop of the fluorescence amount; following points must be taken into consideration:

- **overloading the FWA (I):** fluorescence of FWA is a process at the molecular level that involves an energy transformation process; increasing the concentration of the molecules will increase the interaction between molecules, the energy conversion may be channeled into heat instead of fluorescence resulting in an overall drop in efficiency (molecular self-quenching)
- **overloading the FWA (II):** concentration increase favors the formation of dimers, the fluorescence of such dimers lies normally at lower energies. The overall result can be seen as the development of a fluorescence shoulder positioned at wavelengths higher than 445 nm, adding a lemon green shade to the appearance (molecular association)
- **overloading the FWA (III):** as concentration increases so does the overall absorption resulting in a significant loss in the 400-420 nm region that shifts the fluorescence maximum to longer wavelengths; at a certain point the FWA is not longer able to produce enough fluorescence to compensate its own absorption, overall fluorescence and whiteness production decays drastically (self-quenching by own absorption)
- **depletion of UV:** the amount of UV present in the light source has a finite value, a high concentration of FWA may deplete it to such extent that additional FWA molecules cannot be excited. The underlying absorption of the FWA itself starts affecting the general appearance by shifting the fluorescence maximum towards higher wavelengths

In general FWA are in terms of quantum yields extremely effective and need quite low levels of application; typical values are 0.02% for plastics to 0.2% for celluloses.

3.3. - The concept of shading

Yellowness of substrate can be compensated through the addition of a violet or blue dye, color compensation results thus from a subtractive color mixing process. The type of dye used depends on the type of substrate: dyes or pigments can be used since only their color is important to achieve the effect. Quantities used for shading are measured in mgr. per kilo of substrate, posing an enormous problem for homogenization of stock or distribution within a solid substrate.

In general shading is regarded as a "cheap" way to increase whiteness, it is however a topic where much attention and care must be exercised in order not to introduce unpredictable results or difficulties during production. Following points are worth to mention:

1. **light fastness:** type of dye should match characteristics of materials and of the FWA applied in order not to introduce new variables into the system. If the application requires high levels of light fastness a corresponding dye should be chosen carefully

2. **wash fastness:** in textile area washing is considered important because garments must be cleaned and maintained; unfortunately it is common the use of dyes with low wash fastness resulting in an unrecoverable loss of whiteness
3. **violet or blue?:** the complementary color for yellowness at high luminosity values is violet, at lower luminosity values blue is more effective
4. **metameric effects:** shading will change strongly the tint perception of resulting whiteness and introduce a change in the metameric behavior of the material with respect to standard. The use of an invariant shade technique is advised in order to avoid metamerism problems during production

3.4. – A general picture of whiteness

All three effects combined: color of the substrate, amount and nature of shading agents and FWA result in a certain level of whiteness with given characteristics of the perceived white and behavior towards changes of illumination. It must be observed that alone the substrate dictates the behavior and extension of the achieved whiteness regardless on nature and amount of shading agents and FWA; in other words it builds the basis on which whiteness can be increased. For this reason determining physical and optical characteristics of the substrate is the first task to be completed before any lab work can be started

The inverse is also true: given a target white material characteristics of its substrate must be determined in order to start any work towards matching the observed whiteness.

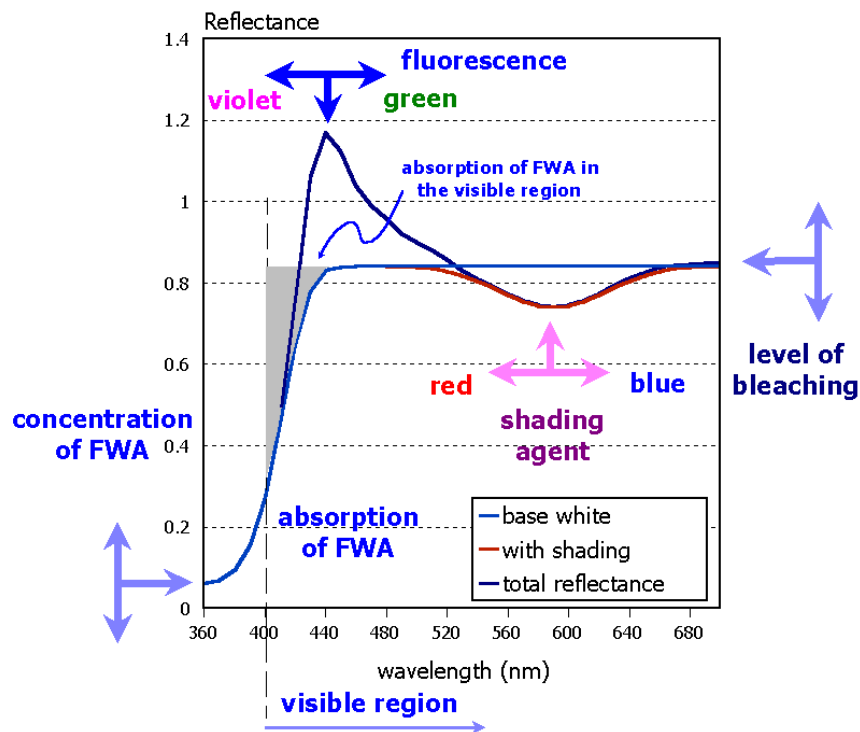
Following points are worth to mention:

1. **level of absorption:** it is not possible to whiten materials below certain level of luminosity, only through bleaching can the material reach the needed level of lightness to introduce a color compensation mechanism. This is best illustrated with recycled pulp in the paper manufacturing area: recycled paper is normally repulped and treated by a process called “de-inking” that separates colored pigments (mainly black) that are insensitive to chemical bleaching, otherwise the black particles scatter evenly within the pulp lowering luminosity and disabling any possibility to increase whiteness through fluorescence and shading agents. In general can be said that only “near-whites” are susceptible to whiteness increase
2. **colored substrates:** although the presence of colored substances do not influence the exhaustion process of FWA or shading agents they disturb or even prevent the whitening step. Only substrates belonging to a narrow area in the yellow area are whitened by the application of fluorescence and shading. In fact all commercial FWA have been developed for these type of materials
3. **UV absorbers:** many materials used during manufacture of objects absorb UV light (remarkable is the case of Titanium dioxide used not only as opacifier, but also as UV protection in plastics and synthetic fibers). Any loss of UV intensity will show as a loss in efficiency of the

FWA (actually already 2% levels of Titanium dioxide are sufficient to quench the action of the FWA)

4. **stability issues:** achieved whiteness is quite sensitive to the chemical stability of the substrate and of the whitening materials; while in general FWA are quite stable, either the substrate material or the shading agents may be not. Decay of any of these components will show as whiteness loss to the extreme of yellow appearance
5. **ecological aspects:** most of the FWAs are water soluble and may end in the environment after disposition of the material. Exposition to direct sunlight initiates a photochemical process that breaks down the molecules to pieces that are biodegradable

The influence of different factors on whiteness can be summarized on the reflectance spectrum as shown below:



Special attention must be paid to the absorption of the FWA since its extension controls the position of the fluorescence maximum and thus the UV metamerism of the sample.

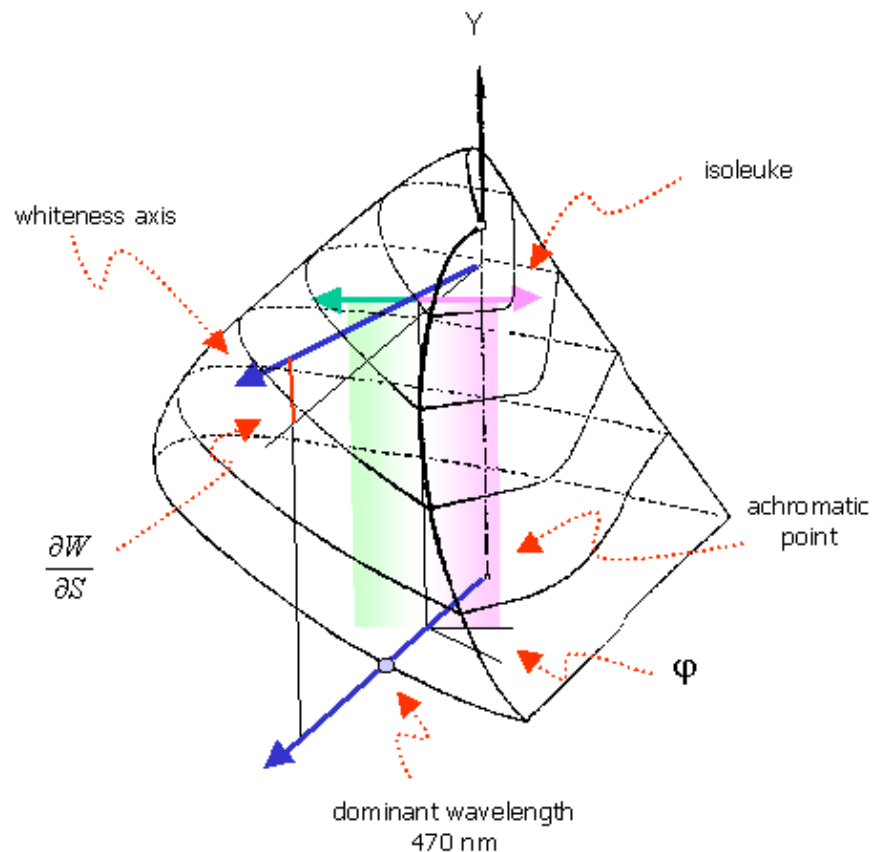
Part II- Measuring whiteness

Chapter 4. - Where are objects showing whiteness located?

Samples showing whiteness will be located in the blue region of the CIE chromaticity chart (see below) and will fulfill both following conditions:

1. **luminosity**: values over 70% will be considered as white, below this value samples will be considered as more or less grey
2. **chroma and hue**: definitely hue must be situated between the dominant wavelengths 465 and 475 nm; the limit value of the chroma for samples to be recognized as white, will depend strongly on the luminosity value, highly saturated samples will be recognized as bluish instead of white.

The region for samples exhibiting whiteness is thus clearly delineated in terms of luminosity, saturation and hue.



The whiteness space can be characterized further through following parameters:

- **whiteness axis**: this axis starts on the achromatic point towards the dominant wavelength of 470 nm; this axis defines whiteness perceived as neutral by the human observer and defines the basis

for a preferred white.

- **whiteness increase:** the values for whiteness can be increased by increasing luminosity Y and/or increasing blue saturation. It is clear that the independent increase of just one of these two parameters will result in “deficient” whites, for example an increase of saturation cannot be continued indefinitely since at certain point there will be agreement among observers of the sample turning blue and not longer white. The parameter defining whiteness increase for unit of saturation is denoted as (dW/dS) and determines the metric of the formula used for whiteness evaluation
- **shade deviation:** the regions on each side of the whiteness axis contain samples perceived as being white but showing certain shade (reddish or greenish) as compared with neutral whites. The axis for the shade deviation is not perpendicular to whiteness axis because of preference of the observer for reddish or greenish whites, the angle of inclination (denoted as ϕ) specializes a given formula for regional preferences
- **isoleukae:** lines sharing the same whiteness value (regardless of shade deviation) are called “isoleukae”

An interesting detail is illustrated by those samples with very high values of luminosity; provided that the amount of additive color mixing is high enough, some samples can leave the CIE color solid and occupy a point exterior to it. While the colorimetric description does not suffer (provided the tri-stimulus values have been calculated correctly), this fact illustrates the need to separate additive and subtractive color mixing process while quantifying fluorescent samples.

The term “fluorence” has been coined for this type of samples; fluorence starts at the point at which the sample crosses the envelope of the Roesch color solid due to the additional luminosity acquired through fluorescence. Fluorent samples catch immediately the attention of the observer because of their higher luminosity as compared with the surroundings.

4.1. – Critical comments about whiteness formulas

It is clear from the picture above that objects exhibiting whiteness form a subset within the color solid that is governed just by psychochromatic rules. From this point of view whites are special cases of colored objects and are defined, as any other color, by three numbers in any of the color order systems.

Earlier whiteness formulas tried to characterized white through just one value (denoted “whiteness”), this attempt being also due to lack of instrumentation; one-dimensional formulas were replaced by two-dimensional formulas after much effort invested in understanding the concept of neutral whites and shade deviation specially after the introduction of FWAs; their use is however limited by the lack of proper instruments. This difficulty, being now solved by the new generation of instruments, will open the development of three-dimensional formulas that will be fully capable of describing whiteness perception phenomena.

Chapter 5. - One-dimensional whiteness formulas

First attempts to describe whiteness were extensions of yellowness formulas modified according to measurements done with different filters modeled after the color receptors of the eye.

With the introduction of FWAs it was clearly recognized that samples showing whiteness are situated in the blue area of the chromaticity chart and linear relationships of the type:

$$W = \varepsilon \cdot Y + \rho \cdot x + \sigma \cdot y + k_3$$

were tried to describe whiteness. It was established from the beginning that whiteness can be represented by a linear relationship of the form $W = f(X, Y, Z)$, the formula given above is one of many possible ones; any color space could be used such as (Y, x, y) , (L, a, b) or (B, G, A) ; the coefficients must be found empirically, for example through a regression or correlation with visual assessment values.

One-dimensional formulas attempt to describe whiteness by just one number; the reference to a preferred white is thus already built-in in the numerical parameters. This is a serious drawback of the formulas, because they do not recognize the existence of cultural dependence of preferred whites.

5.1. - Berger whiteness formula

This formula was developed by Mrs. A. Berger (formerly employee of Bayer AG, Germany) and presented in 1959.

Whiteness values calculated after the formula of Berger was very popular during the sixties until beginning of the eighties mainly in the paper and also textile areas.

The general form is:

$$W_{Berger} = Y + a \cdot Z - b \cdot X$$

where the numerical parameters are defined as:

	a	b
2° observer	3.440	3.895
10° observer	3.448	3.904

In general terms, the formula has a preference for greenish whites; in other words white samples having a greenish shade (compared to neutral white ones) will possess higher values for Berger whiteness.

5.2. - Whiteness index (ASTM)

Norm E-313 gives an extensive review of aspects and formulas to assess

whiteness and appearance of white and near-white materials.

Interesting in the norm is the definition of a "blue directional reflectance factor" B, this is set identical with the CIE tri-stimulus function Z; in many cases the factor B has been used as a measure of whiteness.

Whiteness is defined as "the attribute by which an object color is judged to approach some preferred white"; crucial here is the recognition of the existence of a preferred white.

The ASTM-whiteness index is defined as:

$$WI = 3.388 \cdot Z - 3 \cdot Y$$

where Z and Y are the tri-stimulus values.

Important to mention are following points:

- the formula requires the measurement with a source equivalent to illuminant C
- instrument can be a three-filter colorimeter or spectrophotometer type with geometry 45°/0°
- if fluorescent dyes are present or their presence is suspected, the whole wavelength region from UV to NIR must be included and reported with the results.

5.3. - Stensby whiteness formula

This formula was developed by Mr. P. Stensby (formerly employee of J.R. Geigy AG, U.S.A.) and presented in 1968.

Whiteness values calculated after the formula of Stensby found ample application in the detergent area, especially in the United States where the use of Hunterlab system is widespread; today it has been replaced by newly two-dimensional formulas and it is rarely seen.

The general form is:

$$W_{Stensby} = L + 3 \cdot a - 3 \cdot b$$

where (L, a, b) are Hunter coordinates given by:

$$L = 100 \cdot \sqrt{\frac{Y}{Y_n}}$$

$$a = 175 \cdot \sqrt{\frac{0.0102 \cdot X_n}{Y/Y_n}} \cdot \left(\frac{X}{X_n} - \frac{Y}{Y_n} \right)$$

$$b = 70 \cdot \sqrt{\frac{0.00847 \cdot Z_n}{Y/Y_n}} \cdot \left(\frac{Y}{Y_n} - \frac{Z}{Z_n} \right)$$

Stensby whiteness values have a preference for red shades i.e. red-shaded whites will show higher values on the Stensby scale.

5.4. - Taube whiteness formula

The origin of this formula is not very clear, although it appears to have been developed by Hunter, it is attributed to Mr. Taube (formerly employee of BASF AG, Germany). It was mentioned in the literature before 1960. It has found ample application in the plastic sector.

The general form is:

$$W_{Taube} = 4 \cdot Z - 3 \cdot Y$$

Chapter 6. - Two-dimensional whiteness formulas

The introduction of a second dimension resolves the problem posed by the existence of multiple (culture dependent) preferred whites; each white sample is characterized by a whiteness number and a tint or shade deviation value calculated with formulas of following form:

$$W = Y + P \cdot (x_0 - x) + Q \cdot (y_0 - y)$$

and

$$T = m \cdot (x_0 - x) - n \cdot (y_0 - y)$$

Whiteness numbers are referred to a neutral white characterized with the dominant wavelength of 472 nm; the perfect diffuser is assigned the whiteness value of 100.

Within this context whiteness of a sample is given by:

- **Whiteness:** the distance from the achromatic point into the blue region along the dominant wavelength of 472 nm
- **Tint or shade deviation value:** the distance from the axis of neutral whites defined by the dominant wavelength of 472 nm. Depending on the contribution weight of the tint to whiteness, the distance may be not Euclidian (in general a slight preference for greenish whites is set in the formula)

Although the question about the proper contribution of luminosity to final whiteness as well as the preference of greenish-reddish shade deviation remained for many years unclear, there is today formal agreement for a direct contribution of the value Y to whiteness and a preference for greenish whites with an angle φ of 15°; these values apply for the two formulas generally used today.

6.1. - Method of Ganz and Griesser

Dr. E. Ganz (formerly employee of Ciba AG, Switzerland) belongs to the pioneer group on study of whiteness, as well as Mr. R. Griesser (formerly employee of J.R. Geigy, Switzerland). Their formula is the first one that is referred to a neutral white; further, and to take differences in preferred whites the second dimension of the tint or shade deviation is introduced.

Formulas have the general form:

$$W_{Ganz} = Y + P \cdot x + Q \cdot y + C$$

and

$$T_{Ganz-Griesser} = m \cdot x + n \cdot y + k$$

where the (nominal) coefficients are given for D₆₅/10° as:

$$\begin{aligned} P &= -1868.322 \\ Q &= -3695.690 \\ C &= 1809.441 \\ m &= -1001.223 \\ n &= 748.366 \\ k &= 68.261 \end{aligned}$$

Additionally:

- (dW/dS) is assigned a value for 4000
- **Tint >0**: white has a greenish shade
- **Tint <0**: white has a reddish shade
- samples differing in whiteness values less than 5 Ganz units appear undistinguishable to the human eye
- samples differing in tint values less than 0.5 Ganz-Griesser units appear undistinguishable to the human eye

Due to inadequacies in the instruments for measuring whiteness, Mr. Griesser propagated a method where the coefficients of formulas are determined through a regression procedure using a set of fluorescent standards; the coefficients of the formula get thus instrument specific values and cannot be generalized or transferred to a different one. The advantage lies in a consistent reproducibility of the tint values; on the other hand producing a norm that involves fitting and determination of instrument-specific values has not found much acceptance.

6.2. – CIE whiteness formula

The CIE issued whiteness and tint formulas of the form:

$$W_{CIE} = Y + 800 \cdot (x_0 - x) + 1700 \cdot (y_0 - y)$$

and

$$T_{CIE} = 900 \cdot (x_0 - x) - 650 \cdot (y_0 - y)$$

where (x_0, y_0) are the coordinates of the achromatic point for the given illuminant.

The values of the coefficients are (strictly) valid for D₆₅/10° conditions; however the formula has been used also with other illuminants.

Values of the tint have following meaning:

- (dW/dS) is assigned a value for 1700
- **Tint >0**: white has a greenish shade
- **Tint <0**: white has a reddish shade

The formula is quite widespread and has been adopted by many standardizing institutions like ISO, AATCC, ASTM, DIN, etc.

Chapter 7. - Instrumental assessment

As stated above, fluorescence depends on the intensity and spectral profile of the exciting light, from which derives the statement: "fluorescent samples must be measured with the same illuminant used during visual assessment".

This represents a strong limitation to the measurement made with a particular instrument and to universal validity of the results. It is clear that fluorescent samples cannot in general be measured with instruments designed for measurement of non-fluorescent samples.

Currently three methods are normally used:

Two-monochromator method

With this configuration the sample is illuminated with a tunable monochromatic light (coming from one monochromator), at each wavelength the reflected light is probed by a second monochromator in the whole wavelength region. The result is a two-dimensional excitation-emission matrix that contains enough information to calculate the reflectance and fluorescence spectra under any illumination condition.

This method is the only one able to produce correct results for any fluorescent sample, but only recently commercially available instruments have appeared; due to the high-level training needed for the personnel and the high cost of the instruments, there is certain reluctance to acquire this type of instrument to be used in industrial quality control or production areas.

One-monochromator instruments

Of the two possible configurations:

- monochromatic illumination-polychromatic detection
- polychromatic illumination-monochromatic detection

the latter one is the usually used one (notice that both configurations will not give the same result for fluorescent samples).

Basically proper results with this configuration are obtained only and only if the light source is calibrated exactly to correspond to one illuminant; this is in general not the case (especially for Xenon flash lamps), whiteness values are only conditionally correct and the inter-instrument correlation fails specially for tint values.

One-monochromator/multi-filter instruments

New-generation instruments have more than one lamp to illuminate the sample; by using specially designed conditions it is possible to separate fluorescence from reflectance providing thus with enough information to achieve following goals:

- separation of fluorescence and reflectance allows the correct calculation of tri-stimulus values
- fluorescence intensities can be calibrated to illuminants or conditions

- other than daylight
- calculation of tri-stimulus values at varying intensities of UV are possible giving information about whiteness values for indoor conditions
- reflectance only factors allow quantification of the impact of different shading agents and control metamerism effects during production
- separation of whiteness components allows the design of control algorithms for continuous measurements and matching tasks

7.1. - Adjusting the UV to daylight conditions

Following the statement that samples must be measured with a light source that corresponds to an illuminant, light sources of instruments for whiteness assessment should correspond to the spectral profile of daylight, down to 300 nm in the UV region.

This is strong limitation from the instrumental point of view, because standard light sources, like unfiltered QHT lamps or other incandescent sources do not produce enough UV levels to approach the level encountered in daylight illuminant.

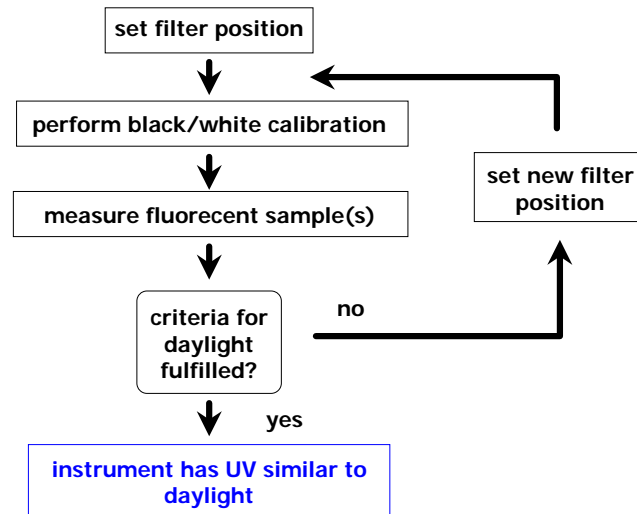
For this reason only instruments equipped with Xenon flash lamps can be used for measuring whiteness, the flash lamp must produce a level of UV, that is higher than the one encountered in daylight; using a movable filter and a set of calibrated fluorescent samples it is possible to set the UV level to correspond to daylight. A further advantage of this system is that the UV level can be adjusted on a periodical basis, the reason being that the amount of UV light deteriorates continuously with lamp operation.

The software provided to operate the instrument must be able to conduct the adjusting procedure. Many types of adjusting devices are found with different instruments:

- **manual adjustment:** the filter can be set manually by using a micrometer device; a disadvantage is that the software has no way to control the setting or to detect an accidental loss of adjustment
- **motor-driven filters:** the software controls the movements of the filter and is able in some cases to conduct the adjustment automatically
- **Numerical UV Control (NUVC):** this type of instrument is equipped with two lamps: one with UV intensity (normally close to daylight) and one with no UV intensity (using a 400 nm cut-off filter); setting for the proper UV level is made mathematically by the software; no moving parts are involved
- **multi-filter instruments:** using different filters (at least two that alter the profile of exciting light) it is possible to determine the amount and profile of the fluorescence and separate it from the passive reflectance of the substrate. Main advantage of this type of instruments is the fact that, since they determine directly fluorescence, they can be calibrated in terms of fluorescence intensity besides a calibration based on whiteness numbers; fluorescence calibration opens the possibility to maintain in one

instrument calibrations for different illuminant loosening in this way the strict demand of illumination with the same spectral profile as the observation of the fluorescent sample. The technique is being applied successfully with FWAs

UV-calibration is carried out by measuring a set of one or more fluorescent standards i.e. samples with values traceable back to an internationally recognized standardization organization, and moving the UV filter until measured values match with those in the certificate, according to the following scheme:



It is important to notice that moving the UV filter alters the overall spectral distribution of the light source; a new calibration for black/white after any filter reposition is mandatory to obtain reliable results.

Instruments equipped with two lamps perform the procedure described mathematically since no movable filters are present, this offer the advantage to perform and maintain calibration automatically without intervention of the operator.

7.2. - Calibration standards

Mandatory condition to achieve accuracy of results is the proper calibration with certified standards. Instruments must be maintained on a periodical basis (especially when working under unstable conditions) as well the standards used for calibration.

About standards

In general there are three levels of hierarchy to be observed while issuing and using standards:

- **Primary standards:** these are physical standards with certified reflectance values measured on an absolute basis by a certified

institution (normally a National Institute). Primary standards are used for issuing secondary standards.

- **Secondary standards:** these are physical standards with reflectance values that can be traced back to a given primary standard; its values must be checked periodically against the ones of the primary standard. Secondary standards should not be used for routine work, but to produce working standards to be used in daily work
- **Working standards:** these are physical standards with reflectance values traceable back to certain secondary standard that is stored at a central place. On a periodical basis their reflectance values are checked and re-issued using the corresponding secondary standard. Working standards are physically made from materials that are stable and easy to clean, nevertheless they must be treated with care. If cleaned they must be immediately recalibrated in order to maintain the standard chain.

The observation of this hierarchical chain of standards is a condition to establish a quality assurance system. It must be remarked that production laboratories are situated at the third level of the chain; working standards must be checked and recalibrated by a central lab.

STFI standards

The STFI, Sweden delivers periodically paper samples as secondary standards to be used to calibrate instruments. Following samples are provided:

- **non-fluorescent paper sample:** containing certified reflectance values along with colorimetric data. Data can be used to produce a working standard for daily use
- **fluorescent paper sample:** containing certified CIE whiteness for $D_{65}/10^\circ$ conditions. This sample is used to set the UV level of instruments to daylight conditions; recently samples for $C/2^\circ$ conditions are also offered as calibration for whiteness under "indoor" conditions

TITV standards

The institute TITV, Germany offers a set of five textile samples for calibration purposes, described as follows:

- **non-fluorescent textile sample:** containing certified reflectance values along with colorimetric data. Data can be used to produce a working standard for daily use
- **fluorescent textile samples:** containing certified reflectance values, Ganz and CIE whiteness for $D_{65}/10^\circ$ conditions. Samples are used to set the UV level of instruments to daylight conditions

These samples are used for adjusting the UV filter to D_{65} conditions using the

procedure of Ganz-Griesser. Special care is given during manufacturing to assure that all samples have the same base white; this is an important point for those instruments using the numerical UV control (NUVC).

Recently the TITV has started offering samples based on polyester material that shows improved time stability and reproducibility.

Hohensteiner Institute standards

The Hohensteiner Institute, Germany offers a set of four textile samples with certified Ganz and CIE whiteness values for setting UV levels to D_{65} conditions. These are four textile samples with the first one non-fluorescent, and the other three with increasing amounts of fluorescence. They are delivered with certified numbers for Ganz and CIE whiteness and are used for adjustment of the UV filter using the procedure of Ganz-Griesser. Since only whiteness data is provided, an external system defining reflectance levels must be used to complete the calibration system.

Recently the Hohensteiner Institute has started a series with certified reflectance values for certain instruments.

7.3. – Triplet effect

Instruments equipped with Xenon flash lamps produce a large amount of light energy within a very short time interval; the intensity is high enough with certain FWAs to populate the triplet state through the excited single state. This process leads to a triplet-triplet absorption that lies in the region of 540 nm and mimics the absorption of a shading agent; this results in increased whiteness values. Most modern instruments can produce (on demand) a “soft” flash to avoid producing false results, but still they may introduce an error of the order of 3 to 5 CIE whiteness points.

In general only FWA for plastic matrices (remarkable polyester) show tendency to populate the triplet state, ionic stilbene FWAs do not show this phenomenon.

The effect can just be detected with instruments. The triplet effect is not observed during visual assessment because illumination levels, even under direct sunlight, are too low to achieve a population of the triplet state high enough to notice the absorption. It has thus no consequences on the visual aspect of the object.

Part III. - Applications

Chapter 8. - Achieving high whiteness values

The achievement of high whiteness values is a carefully orchestrated interplay of all three whiteness components and the opacity or the volume scattering of the sample. The latter is important because it controls the level of penetration of light into the sample, a factor that has a major impact onto the appearance of the sample; in fact the volume scattering controls:

- **opacity:** if the sample is layered (textile, paper, etc) it is important to control the volume scattering within the sheet. Lower opacity values mean a deeper penetration into the material and the detected light comes from deeper regions below the surface giving a translucent appearance readily detected by the human eye (but difficult to quantify instrumentally)
- **changes of base white:** a more transparent material means a lowering in the measured base white as a consequence of light losses through side-wards channels
- **changes of shaded white:** a deeper penetration means a higher thickness and the absorption of the shading will be overvalued
- **changes of fluorescent white:** a deeper penetration means a higher number of FWA molecules excited and automatically a higher level of fluorescence

Doubtless the most important point is to start with the proper level of base white; the optical properties of the substrate will dictate ultimately the behavior of shading dyes and fluorescence production. It is extremely important to study and determine carefully the optical properties of the substrate material in order to initiate an exploratory work leading to high levels of whiteness.

8.1. – Tools for the evaluation whiteness

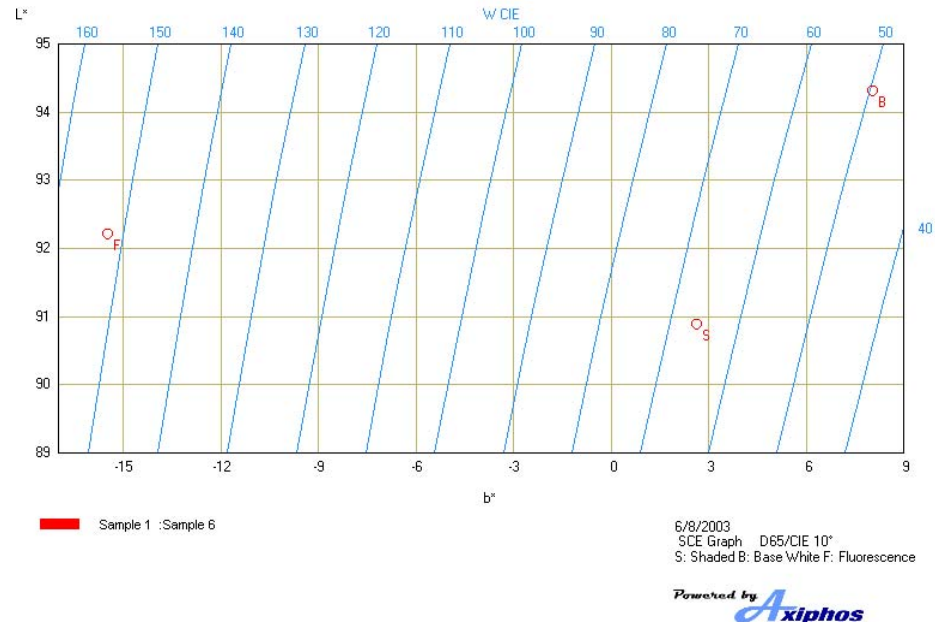
Studies of whiteness behavior require a separation of whiteness phenomena into its components and proper ways of representation of results.

Results have an inherent tri-dimensional character and this poses in general some problems choosing appropriate parameters for an overall characterization:

- **classical colorimetry:** triples like (X, Y, Z) or (Y, x, y) do not give much a pictorial information and in this respect perception-based parameters provide more information; two-dimensional quantities like (W_{GG}, T_{GG}) or (W_{CIE}, T_{CIE}) lack the third dimension for fully characterization
- **perception-based systems:** (L^*, a^*, b^*) has the advantage to appreciate the perceived color as expressed by the numbers but whiteness axis is not parallel to any of the three axis; help can be provided by tracing the neutral white axis on the (a^*, b^*) plane that provides information about the shade deviation of the sample, but a

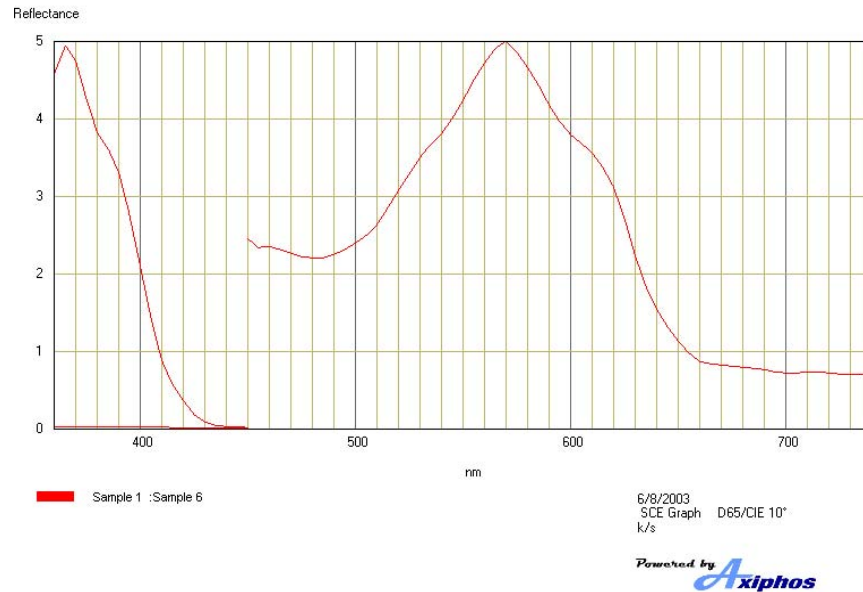
quantitative correlation with whiteness values is difficult to establish

- projection plots:** expressing the CIE whiteness formulas in (L^*, a^*, b^*) system results in tints that are independent on the value of b^* and whiteness values that are independent on the value of a^* , in other words whiteness values can be projected on a plane (L^*, b^*) (see picture below); some care must be exercised while using this diagram because samples may have the same value of whiteness but differ noticeably in their shade deviations and are thus perceived as totally different whites. The diagram is easy to understand and gives much information about the relationship between luminosity and whiteness; in the picture below the contribution of the shading agent to whiteness at expenses of luminosity is clearly seen, as well as the large whiteness increase due to fluorescence. The shortcoming of the two-dimensionality of the CIE whiteness is also readily appreciated: each of the isoleukae describe samples with the same CIE whiteness, but they differ visually evidently if they differ in luminosity

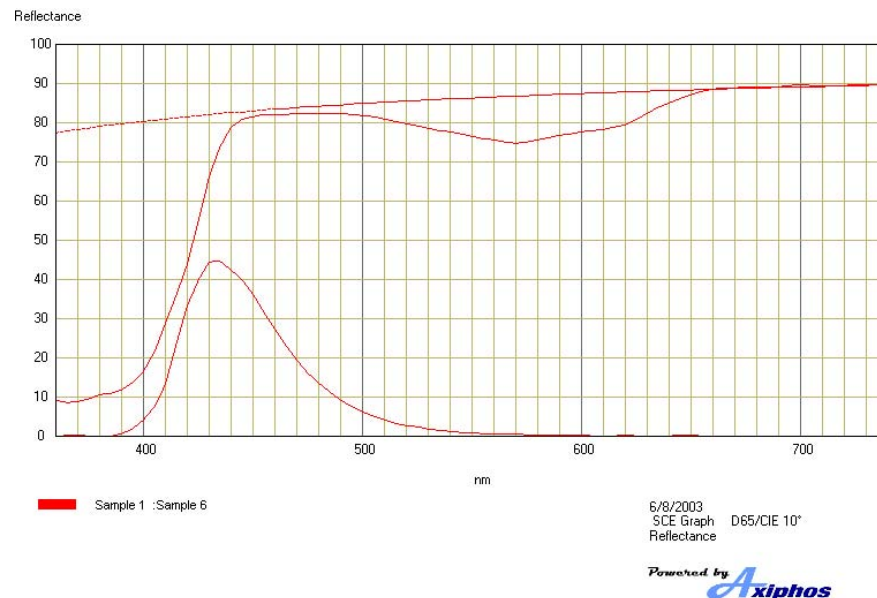


- Kubelka-Munk spectrum:** especially when dealing with shading agents it is preferably to switch to Kubelka-Munk (k/s) diagrams because of the near-linearity of the (k/s) -values with concentration of the shading agents (see picture below). Since quantities of shading dyes are quite small its impact on the reflectance spectrum is sometimes not clear, specially when comparing samples; furthermore on this type of diagram it is easier to count the peaks that may give information about nature and number of the present shading dyes. Another useful information comes from the corresponding (k/s) -values of the FWA: the difference to the substrate is directly proportional to the amount of FWA present

(strictly to all absorbing substances in that region!) that provides information about FWA concentration, also the profile gives sometimes enough information on the degree of agglomeration of the FWA and to decide if two FWA are of identical nature.



- Reflectance/fluorescence spectrum:** certainly the reflectance spectrum contains the full information about the optical behavior of the sample. As shown in the picture below the information is completed with the fluorescence profile (corrected to the UV content of a given illuminant). The reflectance of the corresponding substrate can be modeled providing valuable information for color matching tasks



8.2. - The importance of shading

In general the human eye is more sensitive to changes in the shade rather than of the chroma, in the present case changes in the shade deviation are seen more readily than of whiteness.

Most of the objects of daily use are seen under continuously changing illumination conditions, mainly between daylight conditions (with varying amounts of UV for indoor conditions, assumed close to illuminant C) and artificial lighting (in many cases close to illuminant A).

Taking these two illuminants as opposite extremes of illumination conditions, one must conclude that materials are probed with two different spectral distributions, one emphasizing the blue region (daylight) and the other the orange-red region (illuminant A); in other words the whole spectrum of the visible region is involved, such that small differences in spectral values of the sample against the standard may result in large metameric effects. In fact the shaded white has a relative higher importance for illuminant A than for D_{65} , on the other hand fluorescence is more affected by daylight.

The primary goal of shading is then not (only) to increase whiteness, but to control the shade of the underlying substrate and its influence onto the final appearance of the material. Two factors should be taken into consideration:

1. **shade of the substrate:** while ideal grays and whites show a neutral shade that is not affected by changes of the illuminant, natural (yellowish) materials show in general a reddish shade that is quickly compensated by the fluorescence, but at the expense of introducing a strong dependence on the amount of UV of the illuminant. Choosing number, nature and quantities of shading agents should focus on ways to reduce changes of shade upon changes in illuminant (invariant shade method) rather than increasing whiteness values by any means
2. **production stability:** the emergence of efficient continuous control methods makes more evident than ever the need for stable, robust recipes. A stability factor can be assigned to each recipe that gives information on its robustness (as production cost indicator); shading agents should be chosen within a general cost structure concept rather than on individual dye costs.

8.3. - Evaluation of impact of fluorescence on metameric effects

The contribution of fluorescence to final whiteness is a variable quantity that depends solely on the amount of UV radiation at disposition of the FWA. The position of the starting point (no fluorescence i.e. shaded whiteness) is determined by the combination of whiteness of substrate and the absorption from the shading agent and the FWA.

The nature of the FWA gives the direction of whiteness gain upon increase of fluorescence; while most of the FWA have fluorescence profiles that shift whiteness parallel to whiteness axis, there are departures especially at high FWA concentrations. The latter appears as a shift of the fluorescence maximum as its intensity goes up. In these cases the amount of fluorescence

results in a shift of shade deviation that can cross the neutral axis and change for example from green to red just from variation in the UV content of illumination.

A change in the illuminant (for example from daylight to incandescent) changes in general the whiteness and shade deviation of the shaded white along with a probably change in the behavior of the FWA; results can be however predicted and a case of strong UV metamerism avoided by proper design of a recipe.

As a matter of fact a high load of FWA results normally in a strong UV metamerism.

8.4. - Matching whiteness of pairs

The problem posed by matching a given whiteness is sometimes more formidable than it appears at first sight. Certainly matching for just one illuminant is in most cases not difficult to achieve, to reach a level where metameric effects have been reduced to acceptable levels demands a systematic approach and most certainly an exact description of the whiteness components of the sample to be matched. In general each of the whiteness components must match (within metameric limits) in order to obtain an acceptable agreement of the samples.

Base white

Starting point for the matching job is to establish exactly the properties of the base white of the goal sample; not only the bleach level must be characterized but also the level of the opacity (for layered material) or of the volume scattering (for bulk samples).

Achieving a close match for these properties build a good base to complete the recipe, but normally it is not possible to match them to a satisfactory level such that a compromise (normally with the shading agent) must be met in order to continue.

The absorption from the FWA must be considered also in order to obtain a stable final shade, in fact within the definition of base white, it contains the absorption of the FWA since it contributes to the overall yellowness of the substrate; this point is especially important when a different FWA is used (in most of the cases the FWA of the reference to be matched is not known) that may have different absorbance or, if the FWA is the same, different concentration must be used to achieve the same fluorescence because of poor performance of the build-up on the particular substrate.

Shaded white

Remembering that the shading agent not only affects the natural metameric potential of the substrate but also has an impact onto the opacity, caution must be exercised to select the right dye in the proper proportion. Furthermore production stability must be also taken into consideration in order to produce a robust recipe. The absorption from the FWA must be considered also in order to obtain a stable final shade.

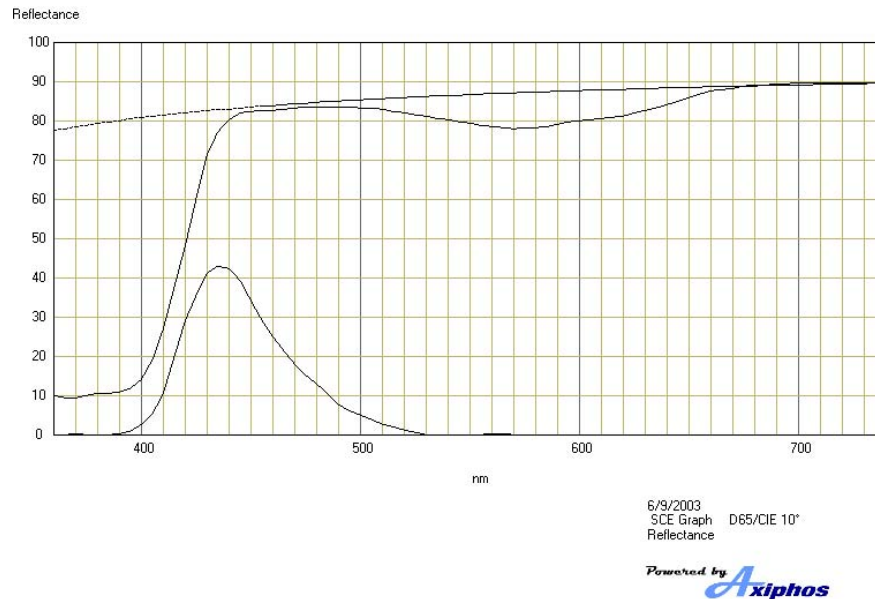
Fluorescent white

Selecting and adding the proper amount of FWA is the easier part if both

preceding steps have been completed properly. In general a feedback is required to get the final recipe that fulfills whiteness, tint, opacity and metamerism boundary conditions

A worked example

The reflectance spectrum (D_{65} conditions) shown below corresponds to a sample that should be matched for production using different chemicals and set as reference, however using the same substrate.

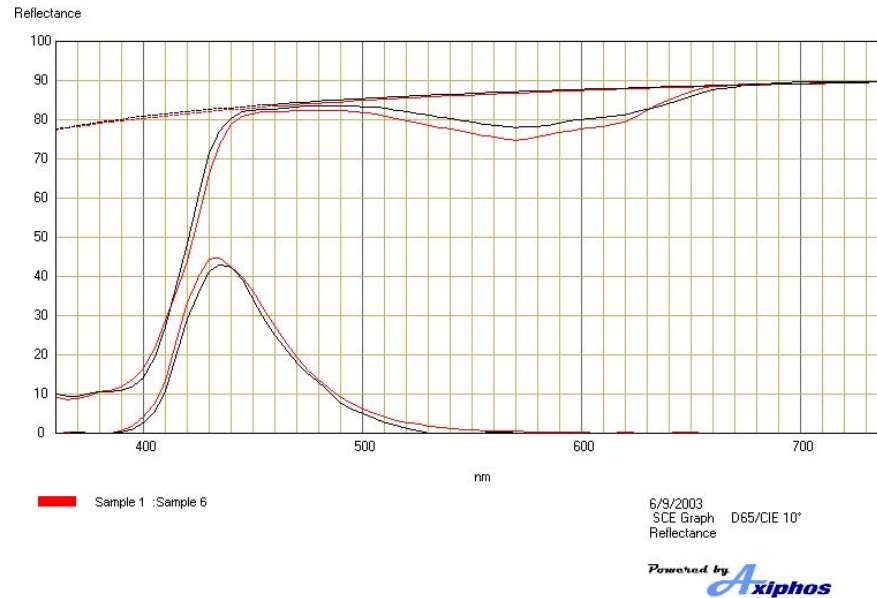


It shows a bleached substrate with probably two shading agents and extended absorption of the FWA.

Using the materials at disposition no perfect match can be found because their spectral characteristics do not corresponds exactly with the ones shown in the reference spectrum, such that a best approximation could be found that leads to an acceptable match. The problems are twofold and derive from following facts:

- chemical constitution of the FWA is different from that of the reference and has a violet shade
- there is no shading agent with extended absorption into the higher wavelength region such that obtaining a congruent curve for shading is not possible

Within these limitations is unavoidable that the matched sample will show certain extent of metamerism that must be controlled to obtain an acceptable match.



The best match is shown in the picture above with following values:

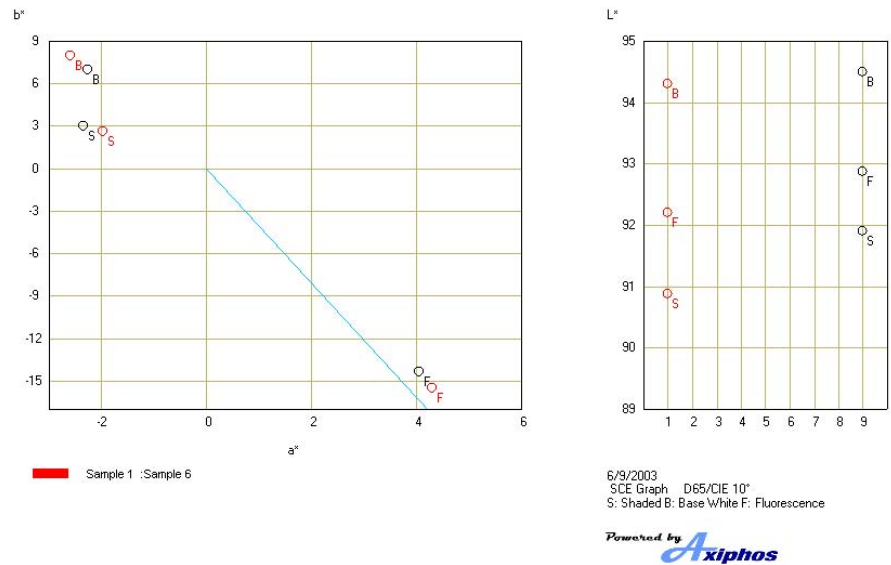
Results for D₆₅

	Sample			Reference		
	W _{CIE}	T _{CIE}	(GG)	W _{CIE}	T _{CIE}	(GG)
base white	49	1.5	(GG)	54	1.3	(G5)
shaded	66	2.4	(GG)	61	2.9	(GG)
with FWA	134	-1.5	(RR)	135	-2.2	(RR)
total	152	-0.8	(R3)	148	-0.9	(R4)
	Y=81.2			Y=82.7		

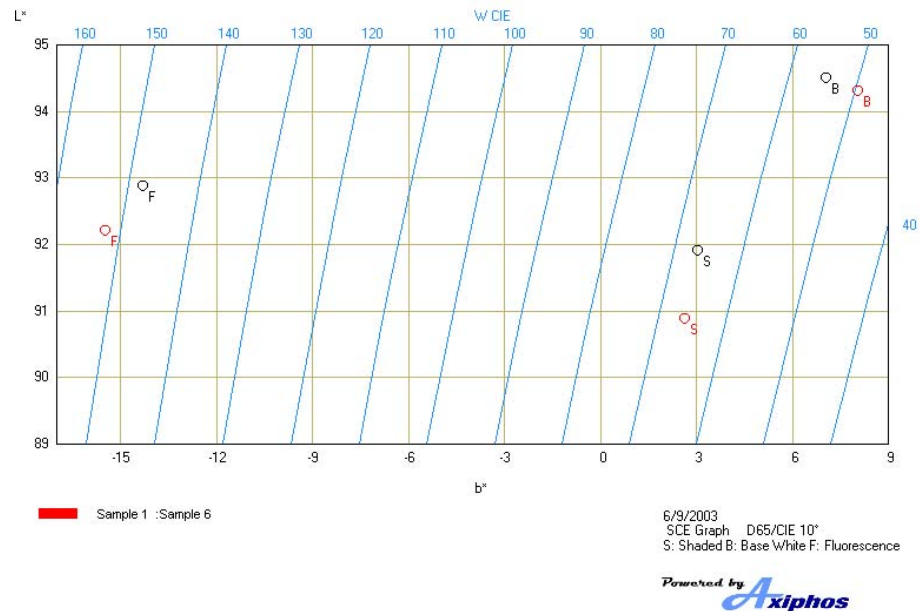
Results for A

	Sample			Reference		
	W _{CIE}	T _{CIE}	(RR)	W _{CIE}	T _{CIE}	(RR)
base white	71	-2.9	(RR)	74	-2.5	(RR)
shaded	76	-2.5	(RR)	77	-1.0	(R4)
with FWA	100	-0.8	(R3)	101	-0.9	(R3)
total	107	-0.3	(R1)	106	0.7	(G3)
	Y=78.8			Y=80.9		

In order to match the shade deviation accentuated by the different nature of the FWA, the substrate has to be over shaded but in a controlled way not to deteriorate too much the value of the luminosity as can be seen on the following (L*,a*,b*) diagram:



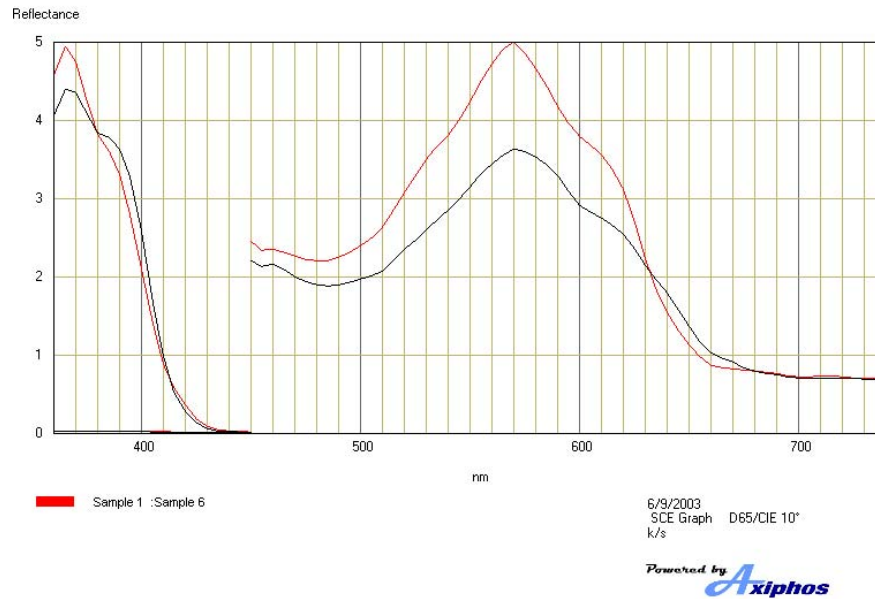
The interrelationship between whiteness and luminosity is better seen on the following projection plot:



Notice the loss of luminosity introduced by the higher amount of shading, reaching however about the same level of whiteness; the action on the shade deviation is clearly visible on the (L^*, a^*, b^*) diagram, the position of the final attained (a^*, b^*) depends strongly on the position of the shaded white since fluorescence will shift the final points along different paths due to the different nature of the FWAs. Since the eye is very sensible to small changes in shade must care must be applied to maintain shade within

acceptable limits.

The different nature of the FWAs and the resulting shading is shown in the following Kubelka-Munk diagram:



The difference of FWAs is clearly seen in the profiles below 400 nm while the compensation for this difference and the remedy for the inability to cover the region above 630 nm by the shading agents is shown in the upper wavelength region (zoomed 118 fold to increase visibility of details).

Notice that the difference in shading is mainly responsible for the departure of values for illuminant A.

Appendix (Books, reviews and norms)

Internet resource

Whiteness Homepage

<http://mitglied.lycos.de/whiteness>

Selected literature

Books

A.K. Sarkar

Fluorescent Whitening Agents

Marrow Publishing Co. Watford 1971

ISBN 0-900-54121-2

T. Rubel

Optical Brighteners: Technology and Applications

1972

R. Anliker and G. Müller (Eds.)

Fluorescent Whitening Agents

Georg Thieme Publishers, Stuttgart, 1975

ISBN 3-13-517101-9

R. Williamson

Fluorescent brightening agents

Textile Science and Technology Vol. 4

Elsevier, Amsterdam, 1980

ISBN 0-444-41914-4

Milos Zahradnik

The Production and application of fluorescent brightening agents

Wiley, Chichester, 1982

ISBN 0-471-10125-7

Arno Cahn

Bleachers and Brighteners

Academic American Encyclopedia, Grolier Inc., Danbury, Connecticut, 1995,

Volume 3

P.G. Engeldrum

Psychometric Scaling - a Toolkit for Imaging Systems Development

Imcotek Press, Winchester 2000

M.G. Gore (Ed.)

Spectrophotometry and spectrofluorimetry : a practical approach

Oxford University Press, 2000

ISBN 0-19-963812-8

Bruce Hapke
Introduction to the Theory of Reflectance and Emittance Spectroscopy
Cambridge Univ. Press, Cambridge, 2001
ISBN: 0-5213078 99

Bernard Valeur
Molecular Fluorescence: Principles and Applications
John Wiley and Sons; New York, 2001
ISBN: 352729919X

Reviews

H. Gold, S. Petersen and O. Bayer
"Fluorescent Brightening Agents of the Triazole Series"
in Gore et al. (Eds) *Recent Progress in Chemistry of Natural and Synthetic Colouring Matters*, pp. 605 ff, Academic Press, New York, **1962**

R. Zweidler and H. Häusermann
"Optical Brighteners"
in *Kirk-Othmer Encyclopedia of Chemical Technology*
Vol. 3, Second Edition, pp. 737-750, J.Wiley & Sons, New York, **1964**

H. Gold
"Fluorescent Brightening Agents"
In K.Venkataraman (Ed.) *The Chemistry of synthetic dyes*, Vol. V pp- 536-680
Academic Press, New York **1971**

R. Anliker and G. Müller
"Fluorescent Whitening Agents"
In F. Coulson and F. Korte (Eds.) *Environmental Quality and Safety, Suppl. Vol. IV: Fluorescent Whitening Agents*
Academic Press, New York **1975**

E. Siegel
"Organic Dyes and Optical Brightening Agents"
Int. Rev. Sci. Org. Chem. Ser. Two **1976**, vol. 2, 259-297

P. Stensby
„Fluorescent Whitening Agents“
in W.G . Cuttler (Ed.) *Detergency*, Part III, pp. 730-806, Marcel Dekker, New York, **1981**

R. Levene and M. Lewin
"The Fluorescent Whitening of Textiles"
In M. Lewin and S.B. Sello (Eds.) *Handbook of Fiber Science and Technology Vol. 1*, Part B, pp.257-304
Marcel Dekker, New York **1984**

A.E. Siegrist, H. Hefti, H.R. Meyer and E. Schmidt

"Fluorescent Whitening Agents 1973-1985"
Rev. Prog. Color. Relat. Top. **1987**, 17, 39-55

H. Zollinger
"Fluorescent Brighteners"
in *Color Chemistry*, VCH Verlagges., Weinheim, **1987**, pp. 203-213

A. Mercer
"Fluorescent Brightening Agents"
In J. Shore (Ed.) *Colorants and Auxiliaries: Organic Chemistry and Application Properties. Vol. 2. Auxiliaries* Chapter 11, pp. 470-511, Society of Dyers and Colourists, Bradford, **1990**

A.E. Siegrist, C. Eckhardt, J. Kaschig and E. Schmidt
"Optical Brighteners"
in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed. Vol. A18, pp. 153-176, **1991**

H.J. McElhone
Fluorescent Whitening Agents
in *Kirk-Oethmer Encyclopedia of Chemical Technology*, Wiley, New York, **1994**

J. Leland, N. Johnson and A. Arecchi
„Principles of Bispectral Fluorescence Colorimetry“
in A.V.Arecchi(Ed.)*Photometric Engineering of Sources and Systems*, 29-30 July **1997**, 3140, 76-87, San Diego, USA

K.J. Smith
"Evaluation of Whiteness and Yellowness"
in *Color Physics for Industry*, 2nd Edition, pp. 185, Society of Dyers and Colourists, **1997**

M. Holmberg
"Dyes and Fluorescent Whitening Agents"
in *Papermaking Science and Technology 4. Papermaking Chemistry*, J. Gullichsen, H. Paulapuro and H. Neimo (Eds.), Chapter 14, pp. 303-320, Fapet Oy, Helsinki, Finland, **1999**

R. Röchel, M. Behe, B. Torp and H. Laatsch
„Usefulness of optical brighteners in medical mycology“
Rev. Iberoam. Micol. **2001**, 18, 147-149

Reports

A.S. Richardson
Optical Bleaching Agents
FIAT Final Report 1302, **1947**

EMPA
Instrumentelle Weissbewertung in der Textilindustrie

KWF-Projekt-Nr. 222.1, Eidgenössische Materialprüfungs- und Forschungsanstalt (EMPA), St.Gallen, Switzerland, **1995**

E.J. van de Plassche, P.H.F. Bont and J.M. Hesse
Exploratory Report on Fluorescent Whitening Agents (FWAs)
RIVM Rapport 601503013, **1999**

Sergio González
Evaluation of Bispectral Spectrophotometry for Accurate Colorimetry of Printing Materials
Ms.Sc Thesis, Rochester Institute of Technology, Rochester, N.Y., USA **2000**

Tarja Shakespeare
Colorant Modeling for On-Line Paper Coloring: Evaluation of Models and an Extension to Kubelka-Munk Model
Diss. Tampere University of Technology, **2000**

Related norms

ASTM

Standards on Color and Appearance measurement

Publication Code Number (PCN): 03-512096-14
ASTM, 100 Barr Harbor Drive, West Conshohocken
PA 19428-2959, U.S.A.

On color

ASTM

E308-99: Standard Practice for Computing the Colors of Objects by Using the CIE System

CIE

CIE 15.2-1986: Colorimetry, 2nd Edition (ISBN 3 900 734 00 3)

ISO

ISO 105-J01: 1997 Part J01: General principles for measurement of surface colour

ISO/CIE 10526:1991: CIE standard colorimetric illuminants

ISO/CIE 10527:1991: CIE standard colorimetric observers

On whiteness

ASTM

D985-97: Standard Test Method for Brightness of Pulp, Paper and Paperboard (Directional Reflectance at 457 nm)

D332-87 (1991): Test method for relative tinting strength of white pigments by visual observation

D985-93: Standard test method for brightness of pulp, paper, and paperboard (directional reflectance at 457 nm)

D1925: Test method for yellowness index in plastics

D2745-93: Test method for relative tinting strength of white pigments by reflectance measurements

E259-98: Standard Practice for Preparation of Pressed Powder White Reflectance Factor Transfer Standards for Hemispherical Geometry and Bi-Directional Geometries

E308-95: Standard Practice for Computing the Colors of Objects by Using the CIE System

E313-98: Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates

E991-98: Standard Practice for Color Measurement of Fluorescent Specimens

E1247-92: Standard test method for identifying fluorescence in object-color specimens by spectrophotometry

AATCC

Test Method 110-1995: Whiteness of Textiles

ISO

ISO 105-J02: 1997 Part J02: Instrumental assessment of relative whiteness

ISO 2470:1996 Pulp and Paper -- Measurement of diffuse blue reflectance factor (ISO brightness)

ISO 3688:1996 Pulps -- Measurement of diffuse blue reflectance factor (ISO brightness)

JIS

JIS 1064: Identification of fluorescent brightening agent classes on textiles

Tappi

T 452 om-92: Brightness of pulp, paper, and paperboard (directional reflectance at 457 nm)

T 525 om-92: Diffuse brightness of pulp (d/0°)

T 534 om-92: Brightness of clay and other mineral pigments (d/0° diffuse)

T 646 om-92: Brightness of clay and other mineral pigments (45°/0° directional)

T 560 pm-96: CIE whiteness and tint of paper and paperboard (using d/0°, diffuse illumination and normal viewing)

T 562 pm-96: CIE whiteness and tint of paper and paperboard (using 45°/0°, directional illumination and normal viewing)

TIS 0804-01: Light sources for evaluating paper including those containing fluorescent whitening agents

TIS 0804-05: Indices for whiteness, yellowness, blue reflectance factor and luminous (green) reflectance factor

Selected literature (1990-2002)

- H. Uchida
„A Study on the CIE Whiteness Formula“
J. Color Sci. Jpn. **1990**, 14(2), 106-113
- B.D. Jordan and G.H. Snow
„The Whiteness of Paper - Colorimetry and Visual Ranking“
Tappi J. **1991**, 74, 93-101
- R. Griesser
„Whiteness not Brightness: A New Way of Measuring and Controlling
Production of Paper“
Appita **1993**, 46(6), 439-444
- A.C. Jackson
„The Environmental Benefits of Modern Developments in Dyestuffs and
OBAs“
Paper 05 at Chemistry of Papermaking Conference, 27-28 Jan. 1993,
Wilmslow, UK, 12 pp. (PBA Abstract 2616, **1993**)
- J.A. Bristow
„The Calibration of Instruments for the Measurement of Paper Whiteness“
Color Res. Appl. **1994**, 19(6), 475-483
- J.A. Bristow
„What is ISO Brightness?“
Tappi J. **1994**, 77(May), 174-178
- R.M. Christie
„Pigments, Dyes and Fluorescent Brightening Agents for Plastics“
Polymer International **1994**, 24, 351
- R. Griesser
„Assessment of Whiteness and Tint of Fluorescent Substrates with Good
Inter-Instrument Correlation“
Color Res. Appl. **1994**, 19(6), 446-460
- D. Gundlach and H. Terstiege
„Problems in Measurement of Fluorescent Materials“
Color Res. Appl. **1994**, 29, 260-266
- P.L. Moriarty
„Optical Brighteners for Polyester“
Book Pap. – Int. Conf. Exhib. AATCC **1994**, 297-300
- J.A. Bristow
„Optical Properties of Pulp and Paper - New Standardization Proposals“

Tappi J. **1995**, 78(December), 45-47

E. Ganz and H.K.A. Pauli

"Whiteness and Tint Formulas of the CIE: Approximations in the L*a*b* Color Space"

Appl. Optics **1995**, 34, 2998-2999

D.D. Malthouse and S.J. Popson

"A New Way of Measuring the Effect of Fluorescent Whitening Agents"

Appita **1995**, 48(1), 56-58

W. Erb and M.P. Kryster

"Weighting Function for the Calculation of ISO Brightness"

TAPPI Journal **1994**, 79, 279-28

R. Griesser

"CIE Whiteness and Tint: Possible Improvements"

Appita **1996**, 49(2), 105-112

J.B. Kramer, S. Canonica, J. Hoigné and J. Kaschig

"Degradation of Fluorescent Whitening Agents in Sunlit Natural Waters"

Environ. Sci. Technol. **1996**, 30, 2227-2234

C. Puebla and R. Griesser

"Whiteness: Concepts and Instrumental Assessment"

Paper Industry China **1996**, 163-164

J. Rieker, R. Griesser and C. Puebla

"Can the CIE-Whiteness Formula Be Improved for Better Correlation?"

Textilveredlung **1996**, 31, 64

J. Kaschig

"The Photochemistry of Fluorescent Whitening Agents – Impact on Light Fastness and Environmental Fate"

'96 International Seminar on Surfactants and Detergents, September 22 - 25,

1996, Nanjing, P.R.China

Claudio Puebla and Zhang Gui Min

"An Overview on Whiteness Measurement and Application"

'96 International Seminar on Surfactants and Detergents, September 22 - 25,

1996, Nanjing, P.R. China

C. Puebla

"Predicting Whiteness from First Principles. A Further Step Towards Recipeing White Paper."

29th Pulp and Paper Annual Meeting, ABTCP, November 4 - 8, **1996**, Sao Paulo, Brazil

- J.C. Zwinkels and W. Erb
„Comparison of Absolute d/0 Diffuse Reflectance Factor Scales of the NRC and the PTB“
Metrologia **1997**, 34, 357-363
- J.C. Zwinkels, D.S. Gignac, M. Nevins, I. Powell and A. Brewsher
„Design and Tetsing of a Two-Monochromator Reference Spectrofluorimeter for High-Accuracy Total Radiance Factor Measurements“
Appl. Optics. **1997**, 36(4), 892-902
- A. Tindal
"Producing and Measuring Whiteness"
PITA Annual Conference "Chemicals in Papermaking", October **1997**, Manchester, UK
- V.R. Kanetkar, G. Shankarling and J. Malanker
"Heterocyclic Fluorescent Brightening Agents - An Overview"
Colourage **1998**, September, 35-42
- G. Thurman
"Color Calibration Standards (D₆₅) Change"
TAPPI Journal **1998**, 81(May), 94
- J. Kaschig, M. Schaumann and B. Schultz
"The Photochemistry of Fluorescent Whitening Agents: Impact on Light Fastness"
Proceedings of the 4th World Conference on Detergents, AOCS Press, **1998**, pp. 323
- J. Kaschig and C. Puebla
"Exhaustion and Leveling Properties of Fluorescent Whitening Agents in Typical Asian Laundry Processes"
'98 International Seminar on Surfactants and Detergents, September 23 - 25, **1998**, Hangzhou, P.R. China
- T. Akatsu, E. Toriumi, M. Ayama, K. Mukai and S. Kanaya
„Effect of Color Temperature of Fluorescent Lamp on the Whiteness Perception“
24th Session of the CIE, Warsaw June 24-30, **1999**
- A. Bristow
„ISO Brightness: a More Complete Definition“
TAPPI Journal **1999**, 82(10), 54-56, 985
- I. Katayama, M. Iiyama and K. Masumil
„Effect of Spectral Distribution of an Illuminant on Perceived Whiteness“
J. Illum. Engng. Inst. Japan. **1999**, 83(11) 847-853

- T. Shakespeare and J. Shakespeare
„Problems in Colour Measurements of Fluorescent Paper Grades“
Anal. Chimica Acta **1999**, 380(2-3), 227-242
- J. Kaschig and C. Puebla
"Whiteness Risk Management"
5th World Surfactants Congress, May 29 - June 2, **2000**, Fortezza de Basio,
Italy
- A.V. Makarenko and I.A. Shaykevich
"Whiteness of Paper"
Color Res. Appl. **2000**, 25, 170-176
- B. Mensak
"Exact Whiteness Numbers with Spectralphotometers"
Maschen Industrie **2000**, 3, 40-42
- K. Mukai, T. Takeuchi, M. Ayama and S. Kanaya
"An Objective Method for Quantifying Whiteness Perception by Applying
CIECAM97s"
2000 Annual Conference of the Illuminating Engineering Institute of Japan,
August 24-25, **2000**, Kanagawa Institute of Technology, Atsugi-City, Japan
- R. Olmedo
"Whiteness Retention under High Levels of Solar Radiation"
JOCS/AOCS World Congress, October 22 - 27, **2000**, Kyoto, Japan
- J.F. Suthers
"An Overview of Optical Brighteners for Co polyester"
Extrusion Paper Coating Applications ANTEC 2000: Color and Appearance,
May 8, **2000**, Orlando, USA
- J.R. Aspland
„The Emission and Absorption Spectra of Polyester Fabrics Dyed with
Fluorescent Disperse Dyes, Treated with Fluorescent Brighteners“
Textiles 2001, Greenville, SC, USA October 21-24, **2001**
- M. Ayama, M. Eloholma, M. Hyvärinen, T. Eda, D. Kon, K. Mukai, S. Kanaya
and L. Halonen
„Whiteness Perception in Japanese and Finnish Under Cool and Warm
Fluorescent Lamps“
AIC Color 2001, Rochester, NY, USA June 24-29, **2001**
- J. Bemska
„Influence of Fiber Materials on the Course of Occurrence of Fluorescence“
Fibres & Textiles in Eastern Europe **2001**, 2(33), 130-134

- M. Blanco, L. Jiménez and L. Valverde
„Degradation of a Stilbene Type Fluorescent Whitening Agent Against Hypochlorite Bleaching“
Textile Research Journal **2001**, 71(2), 130-134
- A.K. Gaigalas, L. Li, O. Henderson, R. Vogt, J. Barr, G. Marti, J. Weaver and A. Schwartz
„The Development of Fluorescence Intensity Standards“
J. Res. Natl. Inst. Stand. Technol. **2001**, 106, 381-89
- S. Kanaya, M. Ayama, L. Halonen, M. Eloholma and K. Mukai
„A Comparative Study of Whiteness Perception in Japan and Finland“
CIE 2001 Lighting Congress, Istanbul, Turkey, September 12-14, **2001**
- I. Katayama, K. Masumi and T. Aoki
"Study on the Relation Between Chromatic Strength and the Perceived Whiteness"
Annual Conference of IEI-J, September 6 - 7, **2001**, Yamaguchi University, Ube, Japan
- J. Kaschig and C. Puebla
"Level Brightening Effects of Fluorescent Whitening Agents in Low Temperature Laundry Processes - A Kinetic Model"
92nd AOCs Annual Meeting, May 13 - 16, **2001**, Minneapolis, USA
- D. Kon, M. Ayama, S. Kanaya, K. Mukai, M. Eloholma and L. Halonen
"Comparison of Whiteness Perception"
Annual Conference of IEI-J, September 6 - 7, **2001**, Yamaguchi University, Ube, Japan
- Y.M. Lam, J.H. Xin and K.M. Sin
„Study of the Influence of Various D65 simulators on Colour Matching“
Color Technol. **2001**, 117(5), 251-256
- K. Suganuma
„Effect of Content of Fluorescent Brightening Agent on Colour Change of Dyed Cotton Fabric“
Color Technol. **2001**, 117(5), 289-292
- S. Veleva, E. Valcheva, I. Valchev and Gr. Radeva
„Application of an exponential kinetic equation to the interaction of optical brighteners with pulp“
React. Kinet. Catal. Lett. **2001**, 72(2), 355-364
- E. Bobu and F. Ciolacu
„Increasing Efficiency of Optical Brighteners in Papermaking by Controlling Interactions with Other Chemicals“

Proc. 15th PTS-Symposium: Chemical Technology in Papermaking, September 17-19, **2002**, Munich, Germany

R. Connelly

„Measuring Fluorescent Whitened Materials: Problems, Status, and Recommendations“

Fourth Oxford Conference on Spectrometry, June 9-13, **2002**, Davidson College, Davidson, NC, USA

H. Epps

„Mono- and Bi-Spectral Colorimetry of Fluorescent Materials“

AATCC's International Conference and Exhibition, October 3, **2002**, Charlotte, NC, USA

He Guoxing and Zhang Zhenyang

„New Whiteness Formula in the CIELUV Color Uniform Space“

Proc. SPIE **2002**, 4922, 163-166

S. Kaufmann and H. König

„Differences while determining the color of fluorescent surfaces using the sphere geometry“

Melliand Textilberichte **2002**, 9, 656-659

He, Guoxing and Zhang, Zhengyang

„New whiteness formula in the CIELUV uniform color space“

Proc. SPIE Vol. 4922: „Color Science and Imaging Technologies“, Dazun Zhao, Ming R. Luo and Kiyoharu Aizawa (Eds.) p. 163-166, **2002**

R. Jäger and K.P. Kreuzer

„Shading Systems for White Paper“

Proc. 15th PTS-Symposium: Chemical Technology in Papermaking, Munich September 17-19, **2002**

L. Ohlsson

„Fluorescent Whitening Agents and Shading Colorants in Production of White Paper and Board“

XIV International Papermaking Conference: Progress in Papermaking and Paper Converting in Central and Eastern Europe, PROGRESS'02, 24 - 27

September **2002**, Gdansk, Poland

R.F. Willis

„The Color Measurement of Textiles Which Contain FWAs“

AATCC's International Conference and Exhibition, October 3, **2002**, Charlotte, NC, USA

Glossary

Additive color mixing

See Color mixing

AATCC

American Association of Textile and Colorist Chemists

<http://www.aatcc.org>

ASTM

American Society for Testing and Materials

<http://www.astm.org>

Axiphos GmbH

<http://www.axiphos.com>

Base white

Contribution of the substrate to the total perceived whiteness

Bleach

Destruction (normally involving chemicals like Chlorine or Oxygen) of light absorbing molecules responsible for yellowness in substrates

Build-up

Gain of whiteness for each additional amount of FWA

Chroma

Distance of the color from the achromatic point, also known as saturation

CIE

Commission Internationale de l'Éclairage

<http://www.cie.co.at>

Color compensation

Color change through the action of a different color (see additive and subtractive mixing)

Color mixing

There are two ways of mixing colors: additive mixing adds light intensities from colored sources increasing thus the luminosity value, while subtractive mixing modulates the light from a single source with through absorption of dyes on a substrate and lowers the overall luminosity

Colorimeter

Color measuring instrument having three filters that simulate tri-stimulus functions for a given illuminant. Colorimeters report strictly color coordinates only just for a given illuminant/observer

CRI

Color Rendering Index: level of approximation of a given light source to defined illuminant. The closer to value 100, the less are the metameric effects seen with a set of samples when changing from the light source to illuminant

D₆₅

Illuminant D₆₅ of CIE: corresponds to spectral distribution of an average daylight

Daylight

Homologous to CIE D₆₅ illuminant

Fluorescence

Emission of light by molecules that have been in general excited by absorption of light; the process of emission follows in the range of picoseconds after absorption

Fluorescent white

Contribution of the fluorescence (from FWA) to the total perceived whiteness

Fluorescent Whitening Agents

Fluorescent Whitening Agents (FWA) are chemical substances that upon excitation in the UV region (below 400 nm) produce blue fluorescence (peak at 445 nm) that is used to compensate the yellowness of a given substrate. They are normally yellow colored that changes the behavior of the substrate on which they are applied

FWA

Fluorescent Whitening Agents

Geometry

Spatial configuration of instrument for illumination and observation of a sample

Greening effect

Shift of the whiteness to greenish shades as result of FWA overload or molecular agglomeration; normally a strong decrease of whiteness is also observed

Hohensteiner Institute

<http://www.hohenstein.de>

Hue

Describes the position of a color as an angle value

Illuminant A

Radiation from a black body at 2856 K

Invariant shading method

Method of selection of shading dyes to find a recipe leading to a shaded substrate with minimal shade changes under different illuminants

ISO

International Standardization Organization

<http://www.iso.ch>

JIS

Japan Industrial Standards Committee

<http://www.jisc.org>

Light fastness

Resistance of a dye to degradation upon exposure to light

Luminosity

Relative intensity of the color as valued by Y

Metameric effects

Samples showing some type of metamerism. In general there are metamerism towards changes of illuminant, towards changes of persons conducting the color assessment (observer metamerism), metamerism towards changes in the UV content (UV metamerism)

Metamerism

Denotes the phenomena shown by certain object pairs that appear to match in color under a certain illuminant, but depart when the illuminant is changed

Monochromatic light

Light with only one wavelength

Monochromator

Device that filtrates one single wavelength from a light source; in general a monochromator is tunable to sweep a certain wavelength range

Munsell

Munsell color system: three-dimensional arrangement of colors developed by artist Albert Munsell

Opacity

Also known as hiding power; reports the amount of light that is lost during the passage through a medium (opposite of translucency that reports the amount of light that passes through a medium)

Perfect diffuser

Non-glossy material presenting 100% reflectance at all wavelengths

Phosphorescence

Emission of light by molecules that have been in general excited by absorption of light; the process of emission follows after milliseconds and can last for hours

Polychromatic light

Light containing many wavelengths at once, this type of light is characterized by its spectral intensity distribution

QHT

Quartz Halogen Tungsten incandescent lamp; the quartz bulb let more UV through than normal incandescent sources (but not high enough to match the amount of daylight). The added halogen prolongs the working life of the Tungsten incandescent coil

Quantum yield

Quantum yield is defined as the ratio of emitted energy to absorbed energy; care must be exercised with the definition of absorbed energy, molecular absorption yields a molecular quantum yield that could be regarded as characteristic of the given compound; if total absorption is used the quantum yield is referred to the molecule in its application environment

Quencher

Chemical added to eliminate fluorescence; passive quenchers are UV absorbers that "steal" the UV weakening the fluorescence production of the FWA, active quenchers interact actively with the FWA deactivating the fluorescence process

Radiometer

Instrument that measures the relative intensity distribution of light in certain

spectral region

Shaded white

Contribution of the shading agent to the total perceived whiteness

Shading agent

Blue or violet dye added to the substrate to increase whiteness perception

Spectrophotometer

Instrument that measures the relative intensity distribution of light in certain spectral region in comparison with a given standard distribution

STFI

Swedish Pulp and Paper Institute

<http://www.stfi.se>

Subtractive color mixing

See Color mixing

Tappi

Technical Association of the Pulp and Paper Industry (TAPPI)

<http://www.tappi.org>

TITV

Textilforschungsinstitut Thüringen-Vogtland

<http://www.titv-greiz.de>

Tri-stimulus

Response of eye color receptors to red (X), green (Y) and blue (Z) excitation

UV light

Light with wavelengths below 400 nm

Wash fastness

Resistance of the dye to be washed out

Whiteness

Property of an object by which it appears white to the human observer

Xenon flash lamp

This type of lamps emit high intensity light in the region 300 to 800 nm (and

beyond); they emit high intensities in the UV region needed to match the amount present in daylight

Yellowness

Attribute by which an object color is judged to depart from a preferred white toward yellow

Index

AATCC	57	Munsell	59
ASTM	57	Near-white	13
ASTM whiteness	26	NUVC	33
Base white	18	Opacity	37
BASF	14,28	Passive diffuser	6
Berger	26	Pigments	13
Bi-spectral instrument	32	Polychromatic illumination	32
Brightness	15	Primary standard	34
Calibration standard	34	Projection plot	38
Chroma	5,24	QHT	60
CIE	56	Quantum yield	20,60
CIE whiteness	30	Quencher	60
Color mixing	16	Reflectance spectrum	39
Color rendering index	8, 58	Scattering	13
Colorimeter	10	Secondary standard	34
Daylight (D ₆₅)	7	Self luminous	7
Fluorescence	20	Shade deviation	29
Fluorescent white	18	Shaded white	18
Fluorence	25	Shading	21,41
FWA	20	Spectrometer	10
Ganz	29	Stensby	26
Geometry	9	STFI	61
Greening effect	20	STFI standards	35
Griesser	29	Substrate	19
Hohensteiner Institute	58	Tappi	
Hohensteiner standards	35	Tappi brightness	15
Hue	5,24	TITV	61
Illuminant	7	TITV standards	35
Index of refraction	23	Triplet effect	36
Indoor conditions	40	Tri-stimulus	16
Instrumentation	32	Two-monochromator	32
Invariant shading	22,40,59	UV calibration	34
ISO	59	UV lamps	8
ISO brightness	15	Visual assessment	8
Isoleukae	25	Wash fastness	21
JIS	59	White	11
Kubelka-Munk	38	Whiteness	12
(L*,a*,b*)	18	Whiteness axis	25
Light fastness	21	Whiteness CIE	30
Light sources	7	Whiteness index	26
Luminosity	5,24	Working standard	35
Matching whiteness	42	Yellowness	61
Metamerism	22	Yellowness index	14
Multi-filter instrument	33		