# DETERMINATION OF OPTICAL CHARACTERISTICS OF MATERIALS FOR COMPUTER COLORANT ANALYSIS

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## ABSTRACT:

The huge information associated with color can give us tremendous benefit only by proper application of color theory as well as measurement of color quantitatively in terms of reflectance, transmittance and absorption. In coloring industries, the overall goal of color theory and measurement is how colors are produced from many different combinations of colorants in order to match the color of materials. Among the various theoretical models, Kubelka-Munk (K-M) is one of the most useful and applicable theoretical approach or model for colorants mixing particularly, when colorants exhibit properties of light absorbing and scattering. With this model, optical properties of colorants under diffuse illumination can be predicted from effective absorption and scattering coefficients of the material. The author has applied Kubelka-Munk theory to develop mixing laws for two types of samples. The first type of sample is opaque absorbing and scattering material. The second is translucent or semi-transparent plastics with appreciable scattering. For opaque system, the ratio of absorption 'K' to scattering 'S' also known as K/S is used to characterize colorants. This leads to the expression 'Single constant Kubelka-Munk theory'. Similarly, for plastics, individual absorption and scattering properties of each colorant is necessary for scalability and additivity. This leads to the expression 'Two constant Kubelka-Munk theory'. Various forms of Kubelka-Munk theory are also applied for comparison of optical properties. Least- squares techniques are used to estimate absorption and scattering coefficients for all colorants in the application of two constant theory. Dichromatic reflection model was also studied. Finally, the prediction of spectral reflectance for a mixture of colorants are calculated which have been characterized by absorption K and scattering S coefficients.

**Keywords:** Reflectance, Transmittance, Colorants, Scattering Coefficient, Absorption Coefficient, Kubelka-Munk, Least-squares

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This thesis is the product of more than half year of work, procrastination, applying theoretical models and techniques, and a colossal amount of external assistance from CPS Color. The results in this thesis are the most significant since it enhanced my productivity and my sincere effort on work. This work was contributed not only by me but by Tuomas Backman and Janne Karila of CPS COLOR and others interested in this work also. Any errors or shortcomings here are my responsibility alone. Especially, I would like to thank CPS COLOR for providing fund to conduct this research.

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This thesis is dedicated to my parents whose example and inspirations make me work hard.

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# CHAPTER ONE

## 1. INTRODUCTION:

Color is extremely important in the modern and informative world. Color can tell us lots of information because it is another form of data. Persons with normally functioning visual system obtain perhaps the largest amount of information about their surroundings from vision and color plays important part in this flow of communication [1]. It comes from the fact that the human eye can perceive more than ten millions different colors and it is really a huge and potential amount of data [5]. So, the importance of color and its influence on modern life has been increasing day by day with the growing impact of information technology .Today's no industry , no business or individual can afford to be color unaware. Hence, industries especially working on product development must have to make a color decision carefully to get benefit. For such wise decision, proper application of color theory and measurement of color is highly essential.

In industries, coloring process is quite complex due to non linear and complex nature of colorants, as well as defining color of colored object because it is more than just the property of objects. It is commonly stated that color vision is the result of the nature of physical world, the physiological response of retina in the eye to light and neural processing of the retinal response by the brain [10]. In this sense, color of an object depends on many factors such as lighting, size of sample, background and surrounding colors and much more importantly, the observer [2]. This important factor makes color a subjective matter. Obviously, doing analysis or dealing with subjective matter is more difficult than other branches of science and engineering which deal pure objective phenomenon such as amplitude of a signal, period and time. However, with the advancement of technology, various color theories, measurement methods and computer have made this subjective matter almost fully understandable [3] and without any doubt, it is quite possible to approach with greater precision to judgments taken by an observer on color.

In industries, many common materials are colored with pigments and dyes and they are capable to absorb, transmit and scatter the light. Thus, it is necessary to apply appropriate theory to know what color the mixture of colorants give in order to match the color of materials [15]. Among the various theoretical models, Kubelka-Munk (K-M) is one of the most useful and applicable theoretical approach for colorants mixing particularly, when colorants exhibit properties of light absorbing and scattering [16]. In many cases, the final product is the composition of different colorants having different light absorbing and scattering properties (also known as optical properties).To determine the simultaneous effect of absorption and scattering of light by different colorants, we need color mixing laws and the K-M theory provides us approximate mixing equations[2]. Therefore, the K-M theory, which describes the reflection and transmission of light within the colorants layer, is of great importance in many industrial applications such as pigmented polymers, paints, paper and textile where the color and appearance of final product is relevant [16].

The Kubelka-Munk theory is a two flux (upward and downward light in the colorant layer) radiative transfer approach which deals with the combined effect of absorption and scattering processes [18]. The application of K-M theory varies depending upon whether the application is for the prediction of the color of opaque materials or semitransparent (translucent) materials. In general, the K-M theory characterizes colorants according to two coefficients, K and S, the absorption and scattering coefficients respectively[25].These coefficients are known as the most fundamental optical properties of pigment colored materials. The coefficient K describes absorption of diffuse flux by the colored material, while the coefficient S describes the net scattering of flux from the surface layer. The application of K-M equation requires that one experimentally determine the unit scattering and absorption coefficients of the colorant commonly known as the optical data file. These optical data are then used to predict the reflectance spectra of mixtures of colorants [23].

## PROBLEM INTRODUCTION:

In industries, coloring process is complex. So, in practice, many coloring industries are facing problem how to predict the proportion of the three or more colorants required to produce a color match for an object showing the same color as a given reference object or standard. This complexity occurs when the colorants scatter and absorb light because the light scattering properties of colorant layers deposited on the substrate such as paint or plastic materials are difficult to describe in quantitative terms[2,6,23, 25,].

The traditional way or old style to formulate colorants for matching the color in industries is by using knowledge of experienced personal working in the laboratory. We generally say this approach as error and trial and to go on this road, industries must have time as well as patience. It also seems impractical as well as unscientific for today’s industries. By this reason, they are looking for the best theoretical model to solve their color matching problem. But, in practice, we don’t have yet any single theoretical model which can describe colorants formulation as a cook book. The reasons are first, computer colorant formulation is not an exact science rather it is an approximation and second, real dyes and pigments do not respond ideally with theory [3]. .Nevertheless, certain computer colorants formulation systems or theories do give a very high success rate. Industries are also trying to solve their colorant formulation problem by such systems.

Among these theories, perhaps the simplest one is the Kubelka-Munk theory which succeeds reasonably well in a number of applications and provides a quantitative description of the properties of light-scattering colorant layers, embracing their reflectance, transmittance, absorption, hiding power and their characteristics [6].

The author also has successfully implemented Kubelka-Munk theory in a satisfactory level to reproduce color by determining the optical properties of industrial materials or pigments.

## 1.2 CHAPTER INTRODUCTION:

The intent of chapter 2 is to provide a relatively simple concept of basic color theory. In sub section 2.1, the author has described the visual perception of process. Similarly, how light is associated with color of an object is described by elaborating light, color spectrum and standard illuminants and light sources. The next sub section of this chapter gives glimpse of interaction of light with materials or objects with description of terms reflection, refraction, transmission, scattering and absorption. From the stand point of color, the effect of objects on light is described by their spectral transmittance or reflectance in sub section 2.4.Again, basic terminology describing characteristic of color visually is explained in sub section 2.5.Finally this chapter ends by explaining standard observer and CIE system.

Chapter 3 is the main important part of the thesis where detail optical theory as well as various procedures to determine optical properties of colorant has described thoroughly. It contains nine subsections. First subsection describes historical background of well known theory ‘The Kubelka-Munk theory, second sub section describes reflectance theory of the Kubelka-Munk, third describes colorant mixing laws, fourth describes theory for semi-transparent layer, fifth describes inversion techniques from Kubelka-Munk for semitransparent layer, sixth describes Reflectance-Transmittance techniques from Kubelka-Munk for semitransparent layer, seventh describes Saunderson’s correction equation for partial reflection, eight describes determination of relative scattering and absorption coefficients and the last sub section nine describes determination of absorption and scattering coefficients by Least-squares.

Chapter 4 is associated with color measurement and sample preparation. Color measurement here, basically directs measurement of reflectance and transmittance of colorants or objects. The contents of this chapter are colorants, setting work environment, instrumental color measurement, measuring reflectance, measuring transmittance, tolerance and measurement accuracy.

Chapter 5 is concerned with the result of practical work of opaque samples and semi-transparent samples. The results are presented in graphical forms and easily understood to readers.

Chapter 6 is short and show the possibility of future work related with Kubelka –Munk and other optical theories.

The final chapter 7 is the conclusion.

# CHAPTER TWO

## 2. BASIC COLOR THEORY:

The origin and nature of color have been speculated on for hundreds of years [8]. The large number of color phenomena in the natural world such as color of rose, blue sky and so on, which we see everyday are the examples. But, in industrial application, we deal color as an objective matter through the application of color physics and color technology. So, the color of a manufactured object depends on three factors [3].

1) the nature of the prevailing illumination under which the colored surface is viewed
2) the interaction of the illuminating radiation with the colored species in the surface layers, particularly within the visible region of the electromagnetic spectrum
3) the ability of the radiation that is transmitted , reflected and scattered from the colored surface to induce the sensation of color in the human eye

In simple words, we need three things to experience color: a light source, an object and an observer. It is therefore necessary to understand these factors to deal with color theory and coloring process in industries.

### 2.1 VISUAL COLOR PERCEPTION PROCESS:

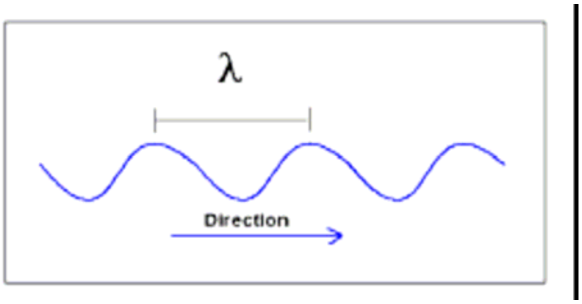
Color is a perception or sensation. It describes in general three subtly different aspects of reality. First, it denotes a property of an object. Second, it refers to a characteristic of light rays. And, third, it specifies a class of sensations in the brain. Therefore, in order to experience color, three things must be present: a light source, an object and an observer. On the basis of these factors, the color perception process occurs as follows:

When a beam of light from the source reaches the surface of the object, a portion of the light is reflected from the surface and triggers light-sensitive cells in the eye. The cells send signals to the brain where the color of the object is perceived. If the light is changed with the object, the perceived color of the object will change, but the eye-brain system attempts to compensate for the change in lighting. The more pronounced the change in lighting, the more pronounced the change in color will be.

The CIE (*Commission Internationale de l'Eclairage*) system of colorimetry attempts to simulate mathematically the perception of color and provide a standardized procedure for measuring and quantifying that perception. So, it can be concluded that all the three factors, the light, object and observer are governed by science and necessary to know about them fully to understand color [5,7,11].

## 2.2 LIGHT, COLOR SPECTRUM AND LIGHT SOURCES:

Without light there is no color [1]. Light sources therefore have key role in determining color of an object. Basically, light is a form of energy and can be thought of as a waveform because the energy content of radiation is usually expressed in terms of wavelength. So, light is similar to radio waves and other electromagnetic radiation. It is commonly denoted with the Greek letter $\lambda$ and measured in metric units. The following figure illustrates this concept.

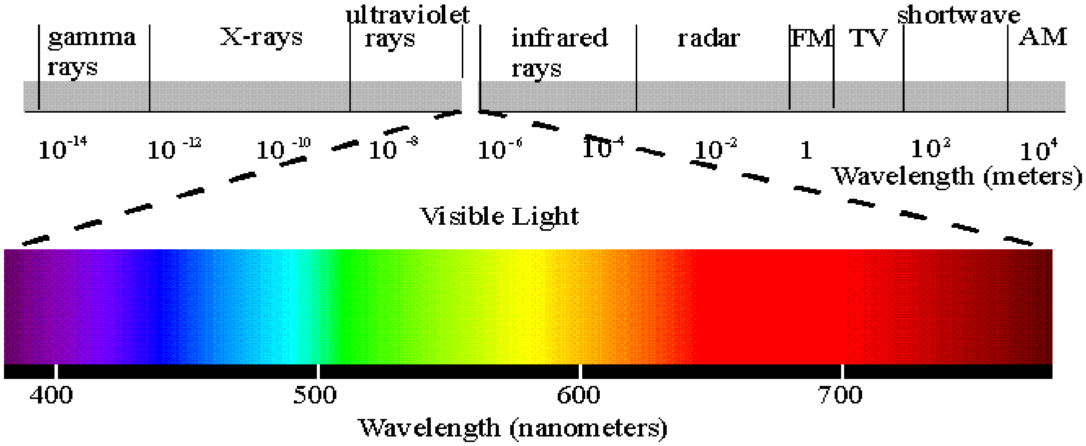


Light wave [9].

Figure 2.1

The wavelength of light is very small. For our convenience, we use the term nanometer (nm) to measure light wavelength. A nanometer represents one thousand millionth of a meter or $10^{-9}$ m. All electromagnetic waves having the shorter wavelength exhibits higher energy and vice versa [8, 9, 10].

The modern understanding of color was originated in the discovery of the spectral nature of light by Isaac Newton in the 1600s [1]. He successfully demonstrated that light consists of energy of different wavelength. Our eyes are sensitive to a band of wavelengths with the approximate range 400 to 700 nm. We define the range of wavelengths by visible spectrum. The visible spectrum represents only a small fraction of the full electromagnetic spectrum. Within the visible spectrum certain wavelengths give rise to certain visual sensations commonly described by hue. For example, the 700 nm end is red. Orange appears between 590 to 630 nm. Yellow falls over the range between 560 to 590 nm. Green light occurs next between 480 and 560 wavelengths. The shortest wavelengths, below about 480nm are perceived to be violet and blue. The following figure illustrates this concept more clearly [1,9,11].



**The electromagnetic spectrum**
**from "The Joy of Visual Perception: A Web Book"**
**http://www.yorku.ca/eye/**

Figure 2.2

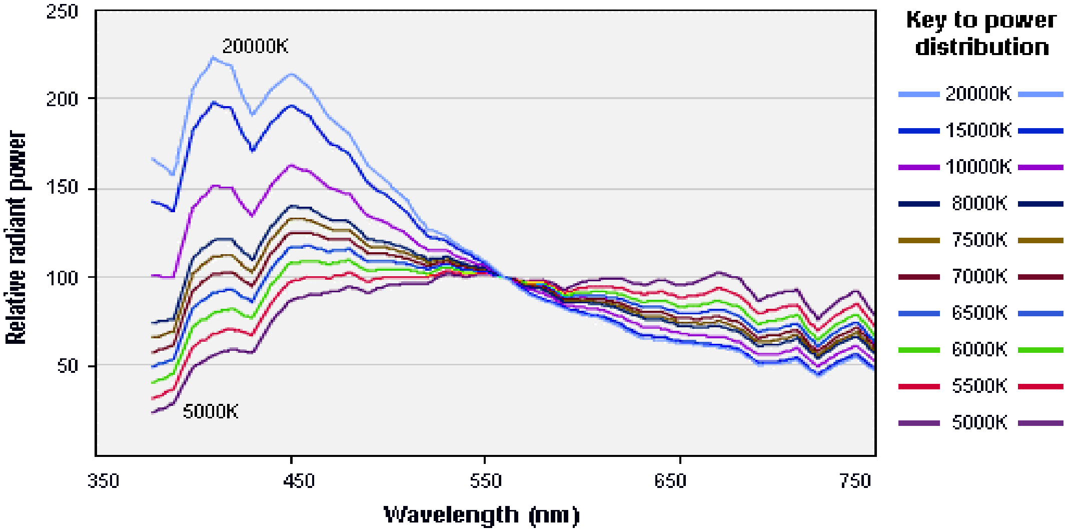
A light source in simple words is a physical emitter of radiation. Examples of light sources are the sun, an ordinary incandescent lamp, a fluorescent lamp, a metal halide and so on. Light sources generally exhibit characteristics of a blackbody radiator, a theoretical material that changes color predictably with temperature. Physical example of blackbody radiator is a carbon block. This implies that a block of carbon at a temperature of absolute zero (0 K on the Kelvin scale) would look black. If the block of carbon is heated, its color will change from black at 0K to red at about 1000K to yellow at about 2500K to white at about 4500K and to bluish white at about 6500K[7].

On the basis of above concept, manufacturers of light sources generally describe their light sources in terms of color temperature. In colorimetric calculations, a light source specified by color temperature is not sufficient. Further more, there are other light sources such as mercury vapor, sodium vapor and neon, do not contain or emit light of all wave lengths. Thus, it is necessary that light sources should be characterized by its spectral power distribution, the amount of power the source emits at each wavelength of the spectrum. Mathematically, spectral power distribution is defined by the definite integral of the spectral concentration $P_\lambda$ of radiant power in the visible spectrum.

$$P = \int_{\lambda_a}^{\lambda_b} P_\lambda d\lambda \qquad (2.1)$$

where, the quantity $P_\lambda d\lambda$ represents the radiant power in the wavelength interval of width $d\lambda$ centered at the wavelength $\lambda$. The range $[\lambda_{a,} \lambda_b]$ represents the visible spectrum [6].

For example, the figure 2.3 below illustrates ten different phases of day light power distribution. The power distribution of day light around 6500k is considered best to view color.



Source: Full Spectrum Solutions. 2003. The Benefits of Full Spectrum lighting…
http://www.lrc.rpi.edu/programs/NLPIP/lightingAnswers/fullSpectrum/comparisons.asp
Figure 2.3

But, unfortunately, the same power distribution can not be realized in electric lamps as given by day light because of the infinite variety and variance of natural daylight spectra. Again, each artificial light source has its own spectral power. Due to this variety of power distributions of light sources, we get color rendering effect [11]. This means, color of an object can look different if viewed under different light sources. Therefore, for the purposes of colorimetry, it is clear to us that standardizing the light sources are important and necessary.

### 2.2.1 STANDARD ILLUMINANT:

An illuminant is the specification for a potential light source. In other words, an illuminant is a mathematical description of a light source [3]. In this sense, all light sources can be described as an illuminant but not vice versa. Illuminants are normally specified in terms of the relative energy tabulated for each wavelength or wavelength band. There are several illuminants that are widely used by the color industry and these include A, C, D65, and TL84.Illuminants A and C were defined by the CIE (*CommissionInternationale de l'Eclairage*) in 1931 to represent tungsten light and natural daylight respectively. Illuminant C was found to be a poor representation of daylight, in that it contains insufficient energy at the shorter wavelengths and it has generally been replaced by a class of illuminants known as class D illuminants. For example, the illuminant D65 has a spectral energy distribution that closely matches that of a black-body at 6500K as well as closely resembles the relative spectral energy distribution of north-sky daylight and is accordingly important for color specification. The CIE recommends D65 be used whenever possible [6,7,9].

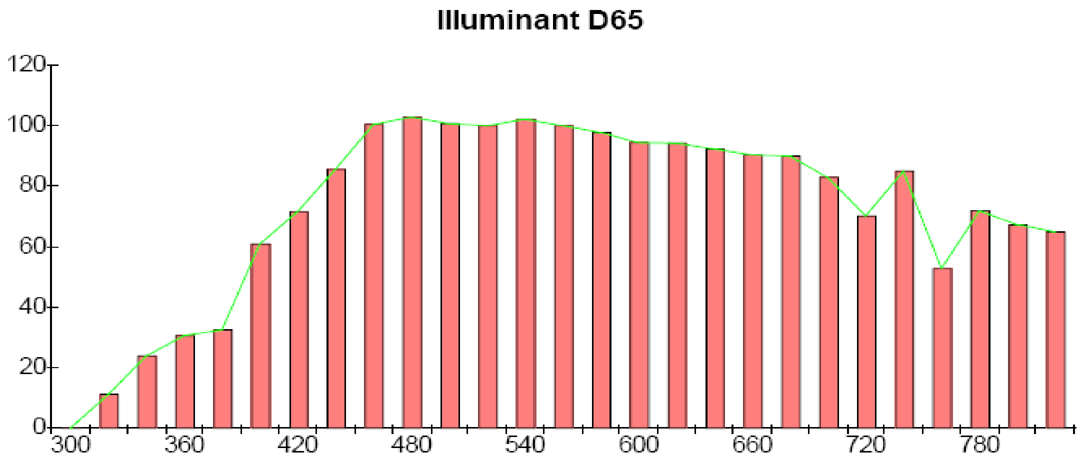


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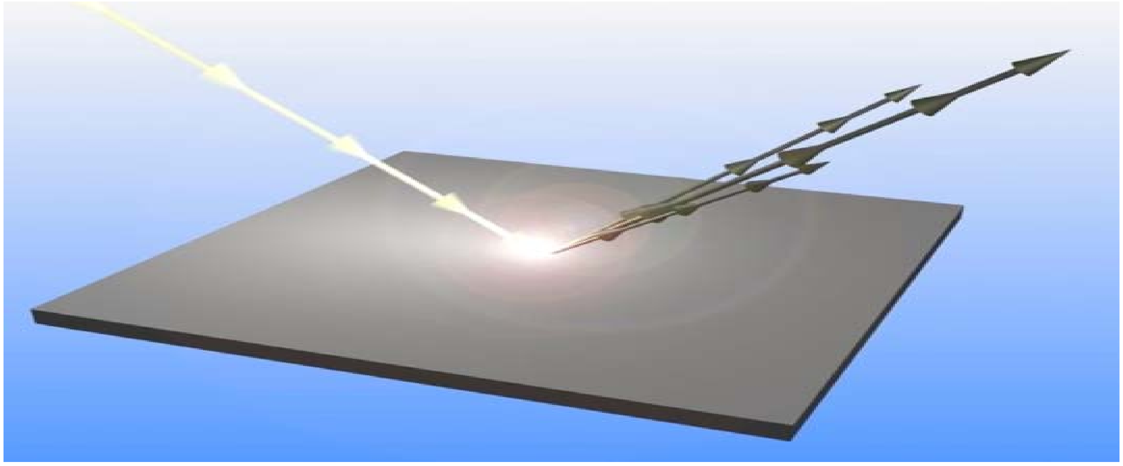
Figure 2.4

### 2.3 INTERACTION OF LIGHT WITH OBJECTS:

When light strikes an object, its path is modified by many ways. Some absorbs more light than others. Some transmit more than others. Some reflects more than others. The ability of an object to modify light is known as properties of the object [2]. We will discuss the important properties of the object for the purpose of coloring process in industries below.

### 2.3.1 REFLECTION:

Reflection is the process by which photons arriving at the surface of a material with a smooth surface change their direction of travel on impact and return [5]. The laws of reflection indicate that the angle of incidence (the angle at which the photons strike the surface) is equal to the angle of reflection. In the figure 2.5, we can see this phenomenon. Reflection is therefore, unequivocally predictable [8].



Reflection of Light [8]

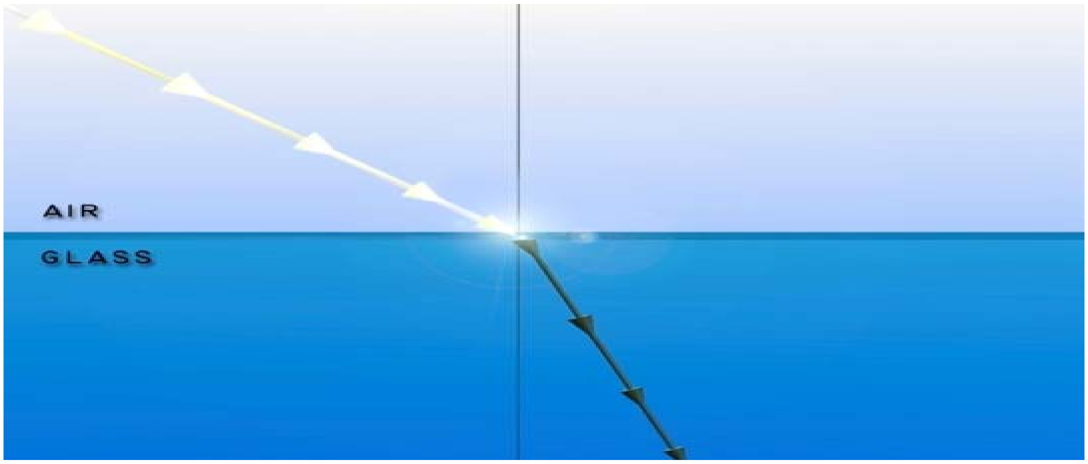
Figure 2.5

### 2.3.2 REFRACTION:

The term refraction is used to denote a change in the direction of the path of photons when they pass from one medium into another [5]. According to Snell's law, when light traveling through a medium of refractive index $n_1$ encounters and enters a medium of refractive index $n_2$ then the light beam is bent through an angle given by following equation:

$$\frac{Sini}{Sinr} = \frac{n_1}{n_2} \tag{2.2}$$

Where, $i$ is the angle of incidence and $r$ is the angle of refraction. The refraction angle depends on the wavelength. Refraction is, therefore an efficient technique for separating the components of a mixture of wavelengths [6]. By special arrangement, we can perceive the color of an individual component. Newton's well-known prism experiment is a good example of refraction.

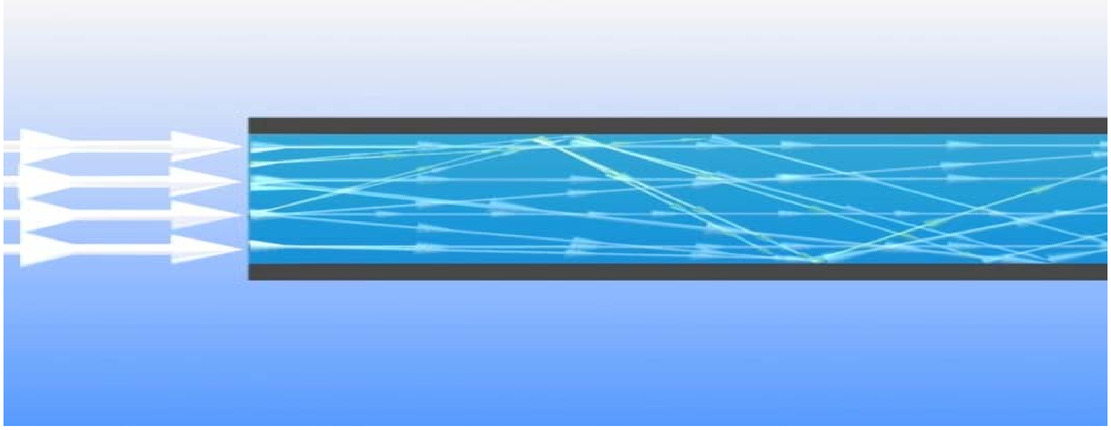


Refraction of light [8].

Figure 2.6

**2.3.3 TRANSMISSION**:

Light may pass or go completely through an object if it is transparent and colorless. In such case, we say light is transmitted. In the transmission process, a small amount of light is reflected from the two surfaces of the object due to the change in refractive index. At every boundary between two objects with different refractive indices, light beam changes its direction. For example, in materials with refractive index 1.5, the amount of light reflection is about 4 % at each boundary with air. This is in fact a considerable effect of medium on light and we should have to take account the boundary condition when determining optical properties of colored sample [2, 3, 6, 12].

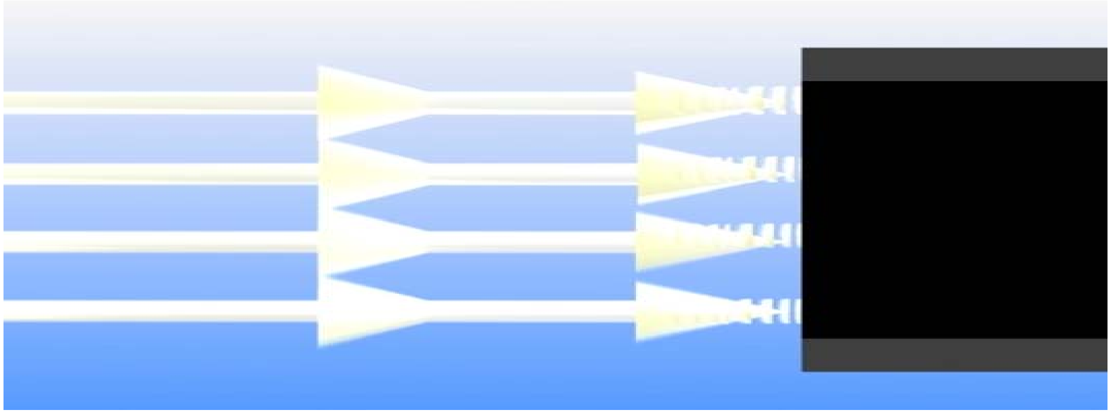


Transmission of Light [8]

Figure 2.7

### 2.3.4 ABSORPTION AND BEER-LAMBERT LAW:

Light can be absorbed by objects. It is a process that involves collision of the light with objects. In general, when the photons of light beam interact with atoms or molecules of objects, the radiation is lost as a visual stimulus due to change in energy level. There are number of mechanisms such as atomic vibration and rotation, ligand-field effect, molecular orbital and charge transfer that cause absorption of light [3]. In colorimetry, the light absorption property of objects as a function of wavelength is used to estimate their color [3].



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Absorption of Light [8]

Figure 2.8

Two laws known as Lambert and Beer, describe quantitatively the absorption process for transparent objects. Lambert's law is used to predict changes in color with changes in a materials thickness. Similarly, Beer's law is used to predict changes in color with changes in concentration [2].

Mathematically Lambert's law can be expressed in differential form

$$-\frac{dI}{dl} = kI \tag{2.2}$$

this on integrating suggests that the intensity $I$ decreases exponentially with thickness or path length.

$$I = I_o \exp(-kl) \tag{2.3}$$

In practice, we use logarithmic form

$$\ln(\frac{I}{I_o}) = (-kl) \tag{2.4}$$

where $k$ is known as an absorption coefficient.

By defining the transmittance $T = \frac{I}{I_o}$ and inverting the quantity inside the logarithmic expression to remove the negative sign, we obtain the normal form of the Lambert's Law expression:

$$\log(\frac{1}{T}) = k'l \tag{2.5}$$

The quantity $\log(\frac{1}{T})$ is known as the absorption. It increases linearly with thickness or path length.

Beer's law also gives the similar result of linear dependence of absorption A with concentration. In fact, the combined Beer-Lambert law is written as:

$$A = \log(\frac{1}{T}) = \varepsilon cl \tag{2.6}$$

where the proportionality constant $\varepsilon$ is known as the absorptivity [3]. We will also discuss further about these laws in chapter 5.

### 2.3.5 SCATTERING:

Light may be scattered when it interacts with objects. Scattering results when light falls on small particles. It allows us to determine type of material or object. For example, if only part of the light passing through the material is scattered and part is transmitted, the material is said to be translucent; if the scattering is so intense that no light passes through the material, it is said to be opaque[2].

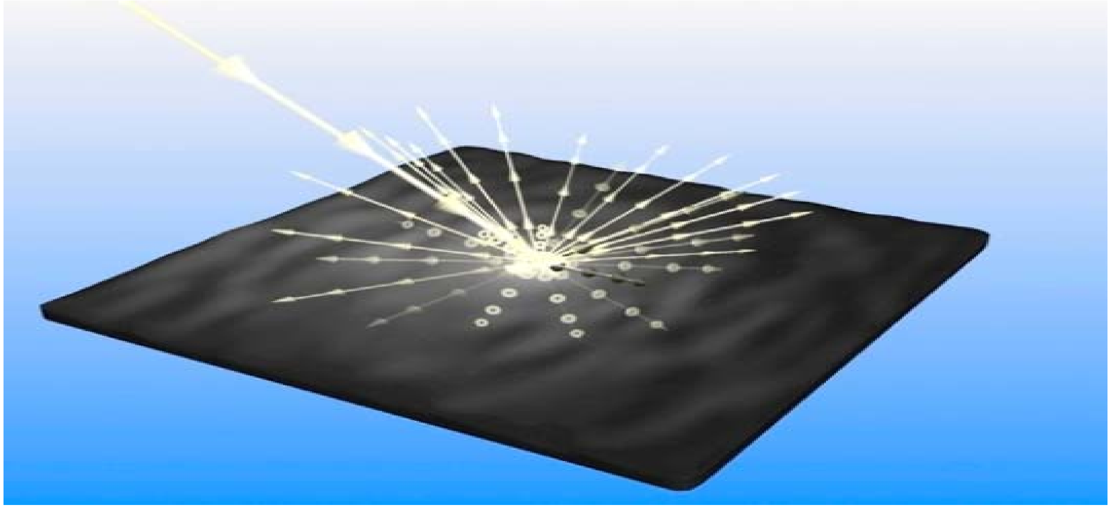
Scattering depends strongly on the size of the scattering particles. When the scattering particles are extremely small (to the order of 1000nm) the light is scattered according to a simple law proposed by Rayleigh in which short wavelength are scattered more than long wavelengths. For larger particles (to the order of 4000 nm and larger) the amount of scattering is according to Fresnel's equations: the amount of scattering depends upon the difference between the refractive index of the particle and of the medium in which it is dispersed and this difference is wavelength dependent [9].

$$R_s = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \qquad (2.7)$$

Where $R_s$ scattering of light, $n_1$ and $n_2$ are the refractive indices of the mediums [6].

For these reasons, pigments are most efficient as light scatters when their refractive index is quite different from that of resin with which they are to be used and their particle diameter is about equal to the wavelength of light. When pigments are of very small particle size and have about the same refractive index as resin with which they are used, they scatter so little light that they appear transparent. Scattering can therefore, be controlled by selection of pigments with appropriate differences in refractive index or by control of particle size [9]

Knowledge of the absorption and scattering properties of colorants as functions of wavelength allows us to predict there color and we have a number of theories to describe the complex optical properties of particles including the Kubelka-Munk theory.



Scattering of Light [8]

Figure 2.9

**2.4 SPECTRIAL CHARACTERISTICS OF MATERIALS**:

From the stand point of color, the effect of objects on light can be described by their spectral transmittance or reflectance depending upon the type of object or material [2]. For example; we use transmittance for transparent materials and reflectance for opaque materials. But, for semitransparent (translucent) materials, we use both reflectance and transmittance. Reflectance and transmittance curves describe the objects just like as the spectral power distribution curve describes light sources. These curves show the fraction of light reflected or transmitted at each wavelength from the objects.

In general, we can recognize colors of objects by their spectral characteristics because colored objects or materials always reflect or transmit light of their own hue and absorb that of complementary hues. We will discuss more rigorously about reflectance or transmittance and the other related terminology in chapter 5. However, here we define the basic terms.

### 2.4.1 REFLECTANCE AND REFLECTANCE FACTOR:

Reflectance is the ratio of reflected light to the incident light under specified geometric condition. Reflectance represents the basic quantity which characterizes the process of reflection [6]. In equation form, it is defined by

$$R_\lambda = \frac{J_x}{I_x} \tag{2.8}$$

where $R_\lambda$ is spectral reflectance, $J_x$ and $I_x$ are reflected and incident fluxes respectively. In practice, the need arises for making measurements of the reflecting properties of materials under different illuminating and viewing conditions and the quantity measured under any of these conditions is given by the generic term reflectance factor [6].

Hence, Reflectance factor is defined as the ratio of radiant or luminous flux reflected in a given cone ; whose apex is on the surface considered , to that reflected in the same direction by the perfect diffuser identically irradiated[1].

### 2.4.2 TRANSMITTANCE AND TRANSMITTANCE FACTOR:

Transmittance is the ratio of the transmitted light to the incident light under specified geometric condition [2]. Mathematically, we can write as follows:

$$T_\lambda = \frac{I}{I_o} \tag{2.9}$$

where, $T_\lambda$ is transmittance, $I_o$ is the incident light and $I_o$ the transmitted light.

Like as the reflectance, the transmittance is also measured under different illuminating and viewing conditions so the term transmittance factor is also defined in a similar fashion.

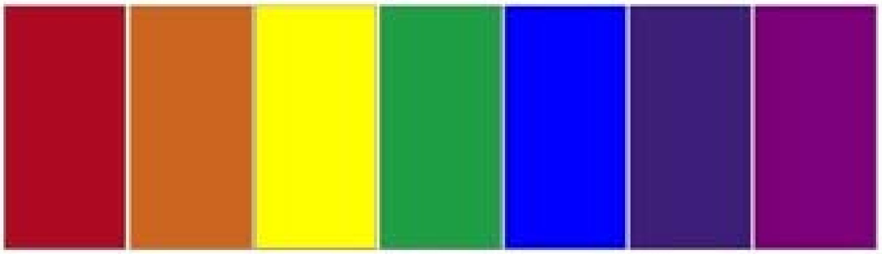
Transmittance factor is the ratio of radiant or luminous flux transmitted in a given cone ; whose apex is on the surface considered , to that transmitted in the same direction by the perfect diffuser identically irradiated[1]

## 2.5 VISUAL CHARACTERISTICS OF COLOR IN COLOR TECHNOLOGY:

In color technology, we consider some factors to determine the characteristics of color visually. These factors are hue, saturation, brightness and value.

### 2.5.1 HUE:

It is really the proper name for color. Hue is the property or attribute of color as it is perceived and determined by the wave length of light [8].It can be reflected or transmitted. Red, blue and yellow are examples of hues. White black and gray are called achromatic colors because they are devoid of hue. Achromatic color can only be described in terms of intensity and luminance which are light properties. Objects with hue are called chromatic [5,9,10].

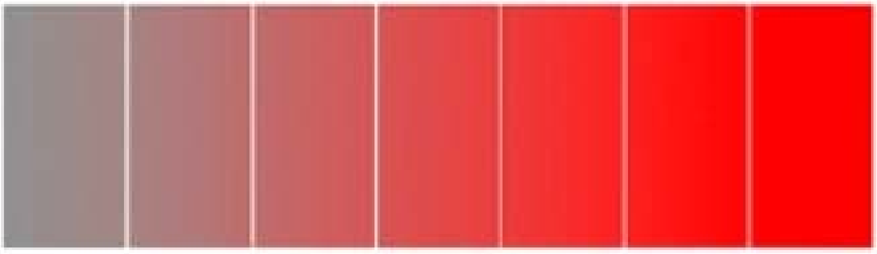


Hue [8]

Figure 2.4.1

### 2.5.2 SATURATION:

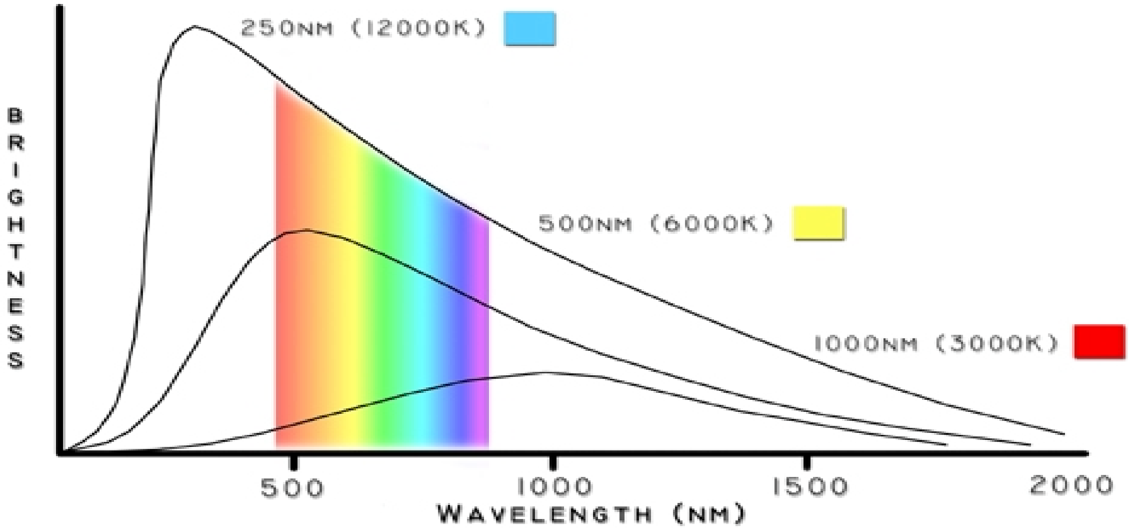
A hue can be pure depending on its mixture with gray. This property is called saturation. A saturation scale ranges from gray to the pure color. In other words, saturation is the vividness or dullness of a hue. It is also a perception of a hue's purity. Saturation is in effect, the perceived intensity of a hue. Saturated colors are perceived to have a no white color component. According to CIE, saturation is 'the colorfulness of an area judged in proportion to its brightness. Yellow is a color that is highly saturated as well as possessing the tendency to be bright perceptually. Determining the absorption and scattering properties of bright colorants from theory needs to follow special procedure [2,5,8].



Saturation [8]
Figure 2.4.2

**2.5.3 BRIGHTNESS**:

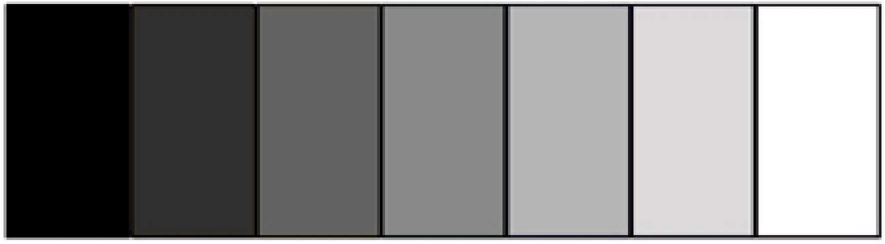
Brightness is the apparent intensity of light that ranges from a totally dark black or a luminous white. The word brightness is used to describe self luminous objects that emit light for example CRT tube. When a color is on a surface of an object its brightness characteristic is described by its value. Brightness is really a perceptual evaluation that indicates whether an object appears to emit more or less light [2, 5, 8].



Brightness [8]
Figure 2.4.3

### 2.5.4 VALUE:

Value is the deviation of a hue from white or black. It is an indication of how light or dark an object is. Value is also called lightness [8]



Value [8]

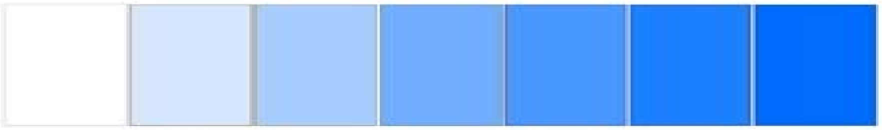
Figure 2.4.4

### 2.5.4 PIGMENT MIXTURE COLOR CHARACTERISTIC:

To describe a color, we use the terms hue, saturation and value but when dealings with pigments and dyes in coloring industries, we use different but related descriptions. These are tint, shade and tone.

Tint:

Tint primarily results from the addition of white to a pure hue. The consequence of adding white to a pure color is decreased saturation. Therefore, tint is a gradation of a color made by adding white to it to lessen its saturation. Tint strength is the ability of a paint or pigment to modify the color of paint or pigment of a different color. Tint strength is influenced by the particle size and particle size distribution of the pigment. The narrower the particle size distribution, and the closer the mean particle size to the optimum, the stronger the pigment will be [2, 3, 8].

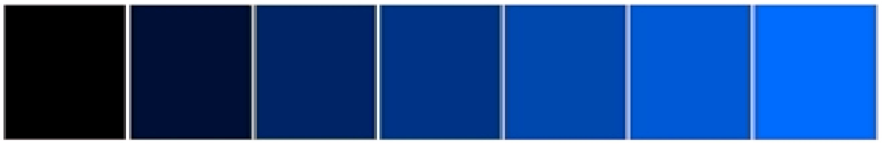


Tint [8]

Figure 2.4.5

Shade:

Shade is the opposite of tint. A shade is created by the introduction of black to a pure hue. The addition of black decreases the object's lightness [8].

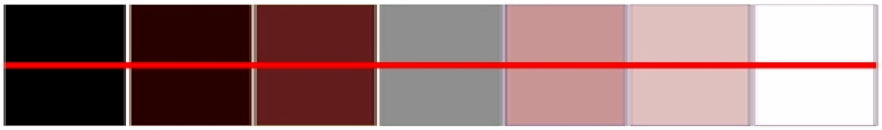


Shade [8]

Figure 2.4.6

Tone:

Tone results from the addition of black and white to a pure color, so tone in reality is just hue plus gray [8]



Tone [8]

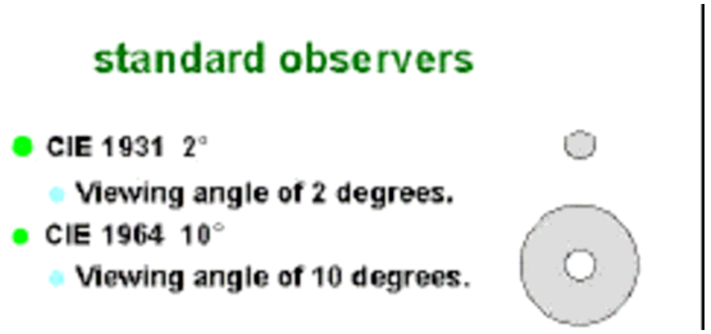
Figure 2.4.7

## 2.6 STANDARD OBSERVER AND CIE SYSTEM:

Human eye, without any hesitation, is the most important color observer. This is also true in any industry that relies on a product which is colored. However, it is also true that the color of a product ascertained by the production supervisor's eye may not be the same as viewed by the manager. There are many factors such as surrounding color, difference in different parts of our eyes, viewing area and angle and brain's interpretation mechanism that cause differences in color perception between human observers.

To overcome this problem, in 1931, the CIE (*Commission Internationale de l'Eclairage*) developed standard observers from experiments in which people matched a spectral color with mixtures of red; green and blue lights also known as three primary colors. This experiment was based on the fact that all colors can be produced by shining combination of red, green and blue on the cones which are light detectors situated in the retina of the eye and responsible for color vision [9]. Therefore, according to CIE, a standard observer can be characterized by matching the entire wavelength of the visible spectrum [7]

The experimental observations, CIE performed on 2 degrees viewing condition, which means subjects viewed a circular field that covered 2 degrees of the visual field. The results of this experiment for a number of individuals were averaged to create the first CIE standard observer. In practice, such observer is commonly called the CIE $2^{o}$ standard observer. For larger-field visual color judgments, the 2 degrees observer is not appropriate because this is a much narrower field of view than normally used for critical color appraisal and further, the distribution coefficients being too low at short wavelengths. So, in 1964, CIE performed experiments using a visual field 10 degrees- commonly called the CIE 10 degree standard observer. Most colorimetric calculations are made using the 10 degree standard observer because it is most closely approximates industrial color matching and quality control viewing conditions [2,3,7,9].



CIE Standard viewing degree [9]

Figure 2.6

To simplify color calculations, the vision scientist working in CIE created a special set of mathematical lights $X$ , $Y$ and $Z$ to replace actual red, green and blue lights. All real colors can be matched using positive proportion of three imaginary primaries situated at $X$ , $Y$ and $Z$ respectively. The values of $X$ , $Y$ and $Z$ are known as CIE 1931 tristimuls values which specify the color stimulus. The CIE tristmuls values for a reflecting or transmitting sample are calculated by adding the product of the spectral power distribution of the illuminant, the reflectance or transmittance factor of the sample and the color matching functions of the observer at each wave length of the visible spectrum [3,7]

Mathematically, we use following equations (2.6.1 to 2.6.4) to calculate the tristimulas values of a sample after measuring its reflectance.

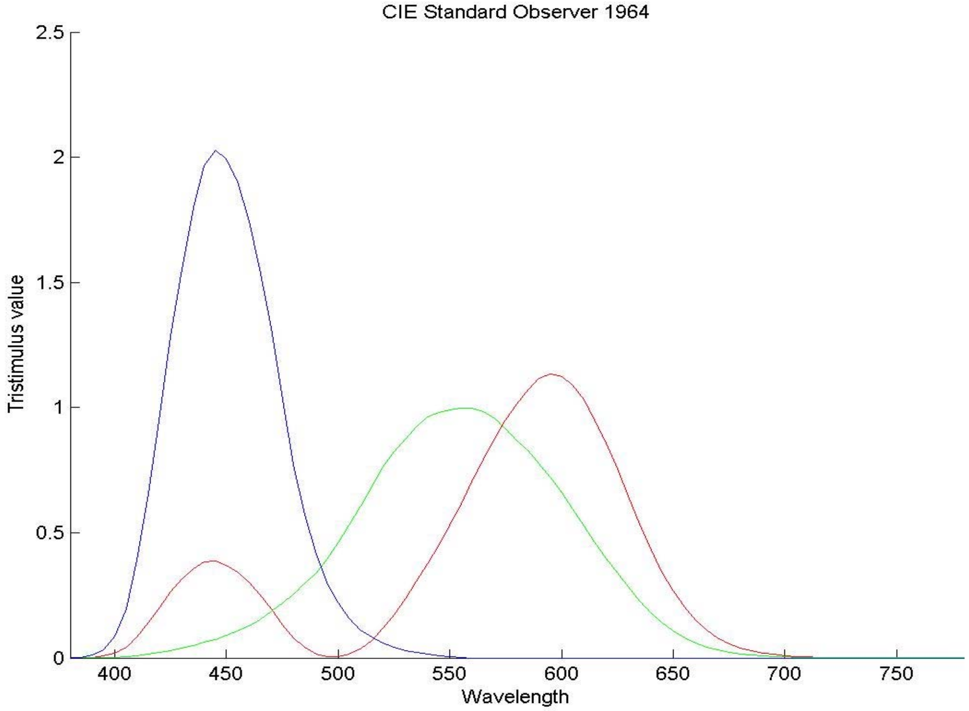
$$X = k\sum P(\lambda)\overline{x}(\lambda)R(\lambda) \tag{2.6.1}$$

$$Y = k\sum P(\lambda)\overline{y}(\lambda)R(\lambda) \tag{2.6.2}$$

$$Z = k\sum P(\lambda)\overline{z}(\lambda)R(\lambda) \tag{2.6.3}$$

$$k = \frac{100}{\sum P(\lambda)\overline{y}(\lambda)} \tag{2.6.4}$$

where, $P(\lambda)$ is the value of the spectral power distribution of the illuminant at wave length $\lambda$, $R(\lambda)$ is the reflectance factor of the sample at the wavelength $\lambda$, and $\overline{x}(\lambda), \overline{y}(\lambda), \overline{z}(\lambda)$ are the CIE color matching functions for the standard observer at the wave length $\lambda$. The factor $k$ normalizes the tristimulus values so that $Y$ will have a value of 100 for the perfect white diffuser- a theoretical material that reflects or transmits 100 percent of the incident light[1,7,9]



CIE standard observer 1964

Figure 2.6.2

In summary, in CIE system, we have a standard observer, standard illuminants standard illuminating and viewing geometries and a mathematical set of primaries $X$ , $Y$ and $Z$ . In practice, $X$ , $Y$ and $Z$ for colored material are calculated from measured reflectance values together with $\overline{x}(\lambda), \overline{y}(\lambda), \overline{z}(\lambda)$ and $P(\lambda)$ for standard illuminants and observers.

# CHAPTER THREE

## 3. OPTICAL THEORIES FOR PRODUCING COLOR:

The optical theories here point out the Kubelka-Munk theory and its various forms. It links the optical properties of the components or colorants to the bulk properties of the material. In this chapter, detail explanation of Kubelka-Munk theory and its various forms as well as practical methods are explained starting from the historical background.

### 3.1 HISTORICAL BACKGROUND OF KUBELKA MUNK THEORY:

An important part of color physics is the prediction of the amount of light that a surface will reflect or transmit at each wave length. In 1905, Arthur Schuster, an astrophysicist studied first, the passage of light through scattering and absorbing layers. In 1931, on the basis of Schuster's theory, Kubelka and Munk presented a theory which describes simultaneous absorption and scattering of light from the colorant in the layer. Kubelka-Munk made a simplifying assumption that the light travels up or down perpendicular to the plane of the sample none preferentially. Finally, they derived an equation which predicts internal reflectance.

Although the Kubelka-Munk theory and CIE color specification were available by the mid 1930s, the practical application for colorant formulation took many years from theoretical model. In 1955, commercial application of colorant formulation technique became a realistic proposition when Atherton and Cowgill showed how colorant formulation could be done very fast by use of digital computer. Since that time, computer colorant formulation by theoretical model has become popular in textile and paint industries.

The nature of computing has changed very rapidly due to the sky-scraping progress in computer and information technology. To cope with emerging computing technique, many authors such as Judd(1975), Allen(1980), Park(1994), Völz(1995), McDonald(1997) and Nobbs (1997) has been elaborating Kubelka-Munk theory for the development of color technology[2, 3,15, 25].

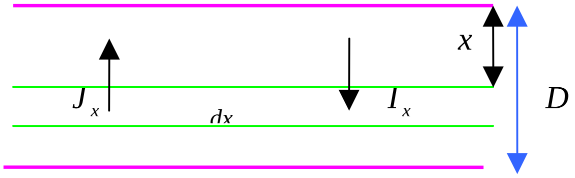
### 3.2 THE KUBELKA-MUNK THEORY OF REFLECTANCE:

The Kubelka-Munk theory models the reflected and transmitted spectrum of a colored layer based on a material dependent scattering and absorption function [14].The assumptions of this theoretical model are:

- A translucent colorant layer on the top of an opaque background
- Within the colorant layer both absorption and scattering occur
- Light within the colorant layer is completely diffuse
- Geometry should be diffuse illumination and diffuse collection

The basic Kubelka-Munk theory is a two flux model which explains light propagation in parallel colorant layers [18]. If we consider the situation within a horizontal colorant layer, then any light that is traveling to the parallel to the boundaries of the layer need not be considered except at near an edge of the layer. Therefore, a flux of light traveling in any direction can be divided into its vertical and horizontal component and since the horizontal components can be ignored [1], our consideration is only for vertical components. To explain the theory, we consider the following figure where a thin section of thickness $dx$ at a distance x from illuminated surface of the layer. The total thickness of the layer is denoted by $D$.In the figure; we consider two intensities of light $I_x$ and $J_x$ after scattering and absorption.

They travel upwards and downwards through the thickness $dx$.



Light traveling in colorant layer

Figure 3.1

Now, we define $K$ and $S$ as follows:

$K$ is the Absorption coefficient which equals the limiting fraction of absorption of light energy per unit thickness, as thickness becomes very small.

$S$ is the Scattering coefficient which equals the limiting fraction of light energy scattered backwards per unit thickness tends to zero. [17]

Again, the effects on light intensities when they travel upwards and downwards through the thin layer are as follows:

The downward flux intensity is decreased by $J_x\,(S+K)dx$ (absorption and scattering) and increased by $I_x\,Sdx$.

At the same time, the upward flux is decreased by $I_x\,(S+K)dx$ and increased by $J_x\,Sdx$

The net change in each flux is obtained by adding the energy lost and gained as the flux passes through the thin section $dx$ can be expressed by following equations:

$$dI_x = -(S+K)I_x dx + J_x S dx \tag{3.1}$$

$$-dJ_x = -(S+K)J_x dx + I_x S dx \tag{3.2}$$

The negative sign for the change in the $J_x$ flux arises because the direction of $J_x$ is opposite to that of $x$. We will get two differential equation when we divide equation (3.1) and (3.2) by $dx$.

$$\frac{dI_x}{dx} = -(S+K)I_x + J_x S \tag{3.3}$$

$$\frac{dJ_x}{dx} = -SI_x + (S+K)J_x \tag{3.4}$$ [3]

The ratio of the upward to the downward fluxes at a point $x$ from the top of the surface layer is called the reflectance ratio $r_x$

$$r_x = \frac{j_x}{I_x} \tag{3.5}$$

The way in which $r_x$ changes with position in the layer is found by differentiating the equation number (3.5) with respect to $x$

$$\frac{dr_x}{dx} = \frac{(I_x(\frac{dJ_x}{dx}) - J_x(\frac{dI_x}{dx}))}{I_x^{\,2}} \tag{3.6}$$

Now, putting the values of $\frac{dJ_x}{dx}$ and $\frac{dI_x}{dx}$ from equation (3) and (4) into equation number (6), we get

$$\frac{dr_x}{dx} = -Sr_x{}^2 + 2(K+S)r_x - S \qquad (3.7)$$

if we now consider that the layer is so thick that further increases in thickness however great, do not significantly change its reflectance , then the reflectance ratio $r_x$ will not change with x, so that:

$$\frac{dr_x}{dx} = 0 = -Sr_x{}^2 + 2(K+S)r_x - S \qquad (3.8)$$

The value of $r_x$ in this situation is denoted by $R_\infty$ and hence

$$0 = -SR_\infty{}^2 + 2(K+S)R_\infty - S \qquad (3.9)$$

This is a quadratic equation which can be solved to give:

$$R_\infty = 1 + \frac{K}{S} - \left[(1+\frac{K}{S})^2 - 1\right]^{\frac{1}{2}} \qquad (3.10)$$

Finally, from equation number (10), we can deduce

$$\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \qquad (3.11)$$

This is known as the Kubelka-Munk function. It shows that the reflectance of an opaque layer depends only on the ratio of $K$ to $S$ and not on their individual values [1], Equation (3.11) also implies that $R_\infty$ can only be < 1 if $K$ is non zero. This is reasonable too in physical realization, because if there is no absorption, all light must be scattered until it reappears from the top surface.

## 3.3 KUBELKA-MUNK COLORANT MIXING LAWS:

One important feature of Kubelka-Munk theory is that the absorption and scattering coefficients of a colored material (mixture) can be built up from the individual absorption and scattering coefficients of the individual pigments [3].In other words, the theory assumed that the additives are valid for the absorption and scattering coefficients. It means that the absorption coefficient of a colored material is the summation of the weighted absorption coefficients of individual pigments included in the material. This phenomenon also applies in the same way for scattering coefficients. Mathematically, we can express the additive laws as given in following equations [3,16].

$$K = c_1 k_1 + c_2 k_2 + \ldots\ldots + c_s k_s \qquad (3.12)$$

$$S = c_1 s_1 + c_2 s_2 + \ldots\ldots + c_s s_s \qquad (3.13)$$

Where, $K$ and $S$ are the absorption and scattering coefficients of the mixtures.

$c_1 c_2$ are the concentrations of individual pigments

$c_s$ is the concentration of base or substrate material.

$k_1 k_2$ are the unit absorption coefficients of individual pigments

$s_1 s_2$ are the unit scattering coefficients of individual pigments

the subscript s indicates substrate.

### 3.3.1 SINGLE AND DOUBLE CONSTANT KUBELKA-MUNK THEORY:

The $\frac{K}{S}$ ratio of a mixture is the additive combination of each pigment's unit absorptivity $k_i$ and unit scattering $s_i$ scaled by effective concentration $c_i$ plus the absorption and scattering of substrate.

Dividing equation (12) by equation (13), we obtain,

$$\frac{K}{S} = \frac{c_1 k_1 + c_2 k_2 + \ldots\ldots + k_s}{c_1 s_1 + c_2 s_2 + \ldots\ldots + s_s} \qquad (3.14)$$

Where $c_i$ is the concentration of pigments and expressed in percentage.

$K$ is the absorption coefficient

$S$ is the scattering coefficient

Subscript s identifies the substrate

Equation (14) is called two constant Kubelka-Munk theory. Calculating $\frac{K}{S}$ of a mixture by using this equation is known two constant method or classical approach.

In two constant method, it is assumed that the colorants or pigments have both absorbing and scattering power. However in some cases, when pigments are mixed, they loose their own scattering power and only the substrate is responsible for scattering of light. In such cases, in the denominator of equation (14), we set $s_1$, $s_2$ to zero which reduces this equation in the following form.

$$\frac{K}{S} = c_1(\frac{k_1}{s_1}) + c_2(\frac{k_2}{s_1}) + ............. + \frac{k_s}{s_s} \tag{3.15}$$

Equation (15) is known as single constant Kubelka-Munk theory.
For a given wave length the equation (15) can be written as follows:

$$(\frac{K}{S})_\lambda = c_1(\frac{k_1}{s_1})_\lambda + c_2(\frac{k_2}{s_1})_\lambda + ............. + (\frac{k_s}{s_s})_\lambda$$

If we set $(\frac{K}{S})_\lambda = f(R)_\lambda$, $(\frac{k_s}{s_s})_\lambda = f(R_s)_\lambda$, $c_1(\frac{k_1}{s_1})_\lambda = a_{1,\lambda}c_1$ and $c_2(\frac{k_2}{s_1})_\lambda = a_{2,\lambda}c_2$ in equation (14) we have,

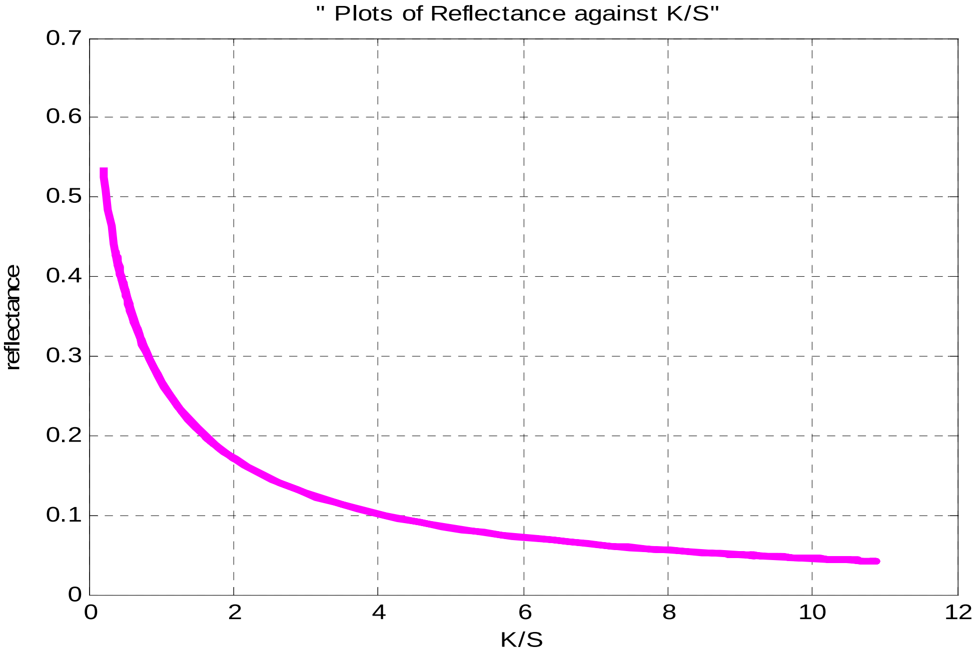
$$f(R)_\lambda = c_1 a_{1,\lambda} + c_2 a_{2,\lambda} + ............. + f(R_s)_\lambda \tag{3.16}$$

Equation (16) gives relationship between $f(R)_\lambda$ and pigments concentration at wavelength $\lambda$. It means that we are able to calculate $f(R)_\lambda$ values of a colored material if we know the concentration of pigments and ultimately by using equation (10) the reflectance of material at any wavelength. Similarly, if we know the reflectance value, $f(R)_\lambda$ can be easily calculated by using equation (11). The individual concentration is obtained from the inverse of equation (16). For example, if we consider one pigment, equation (16) is reduced as follows:

$$f(R)_\lambda = c_1 a_{1,\lambda} + f(R_s)_\lambda \tag{3.17}$$

$$c_1 = \frac{f(R_\lambda) - f(R_s)_\lambda}{a_{1,\lambda}} \tag{3.18}$$

Equation (18) tells us the linear relationship between concentration and $(\frac{k_1}{s_1})_\lambda$ or $a_{1,\lambda}$ and this is also the assumption of Kubelka-Munk theory. But in practice, we generally found the deviation in the above relationship. This means that linearity does not hold between concentrations and $(\frac{k_1}{s_1})_\lambda$ or $a_{1,\lambda}$ especially at high concentration which gives low reflectance value. Therefore, accuracy of Kubelka-Munk theory depends upon level of concentration and correction is necessary to apply the theory over wide range of concentration. The figure below shows the nonlinear relationship. We can see that reflectance decreases exponentially as the concentration increases and approaches to the limiting value [3,15,16].



Relation of reflectance with ratio of optical coefficients

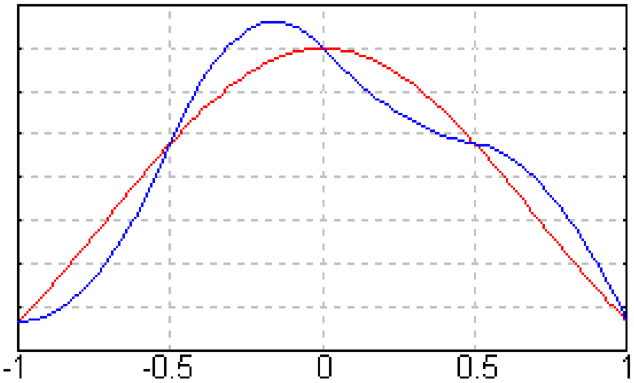
Figure 3.2

## 3.3.2 INTERPOLATION FOR NONLINEARITY CORRECTION:

Interpolation is one of the simple approaches to obtain new data points from a discrete set of known data points. In color science, interpolation is a specific case of curve fitting in which the function must go exactly through the data points. As it is discussed in sub-section 3.3.1 that concentration is nonlinear with respect to reflectance and to obtain new concentration becomes complex from the given concentration of mixture. To solve this complexity, we pick a few known data points i.e. a range of known concentrations and calculate new data points i.e. a set of new concentrations by interpolation. Although, the interpolated data is not exactly same as the original one, but the aim is to solve complex function by the simple way with minimum error. Among the varieties of interpolation techniques, spline interpolation is preferred in the above case due to its inherent characteristics of giving minimum interpolation error even when using low degree of polynomials.

For a data set $\{x_i\}$of $n+1$ points we can construct a cubic spline with $n$ piece wise cubic polynomials between the data points. Solving system of equations, one can find the coefficients which are the new data points and in our case new values of concentration.

The graph below is the example of spline interpolation where red line is approximated new line (values) from the blue line. [13,19].



Spline interpolation.

Figure

## 3.4 KUBELKA-MUNK THEORY FOR SEMITRANSPARENT LAYER:

Determination of optical properties in semi-transparent layer is more complex than in opaque layer as described in section 3.1. The reason arises from the fact that in such layer light scattering as well as transmission is took place. And, from equation 3.11, it is evident that the reflectance is a function of $\frac{K}{S}$ which implies, reflection measurement alone can not give true value of either $K$ or $S$. However, the Kubelka-Munk theory provides solution for the semi-transparent layer and it can be developed by first establishing the optical properties of the layer in isolation and then determining the effect when a substrate is placed beneath the layer.

If we consider an isolated semi-transparent layer as described by the figure 3.4, the reflectance $R_o$, Transmittance $T$ and absorbance $A$ due to the interaction of light energy can be described by equations 3.4.1, 3.4.2 and 3.4.3

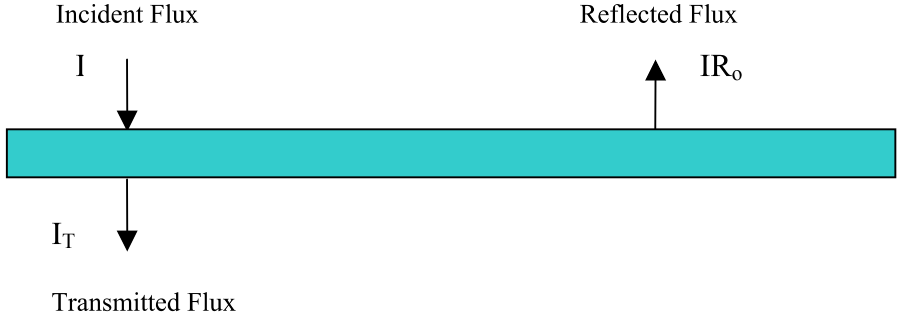


Figure 3.4

$$R_o = \frac{IR_o}{I} \quad (3.19)$$

$$T = \frac{I_T}{I} \quad (3.20)$$

$$A = 1 - R_o - T \quad (3.21)$$

Again, if we consider the effects on light intensities when they travel upwards and downwards through the thin layer as described in section 3.1 and assumptions of the Kubelka-Munk theory are satisfied, Reflectance $R_o$, Transmittance $T$ can be represented in terms of the Kubelka-Munk absorption and scattering coefficients $K$ and $S$ and the reflectance of opaque layer via the general solution of the theory.

Therefore, mathematically, we express these quantities as follows:

$$R_o = R_\infty \left[ \frac{1 - \exp(-2z)}{1 - R_\infty^2 \exp(-2z)} \right] \tag{3.22}$$

$$T = (1 - R_\infty^2) \left[ \frac{\exp(-z)}{1 - R_\infty^2 \exp(-2z)} \right] \tag{3.23}$$

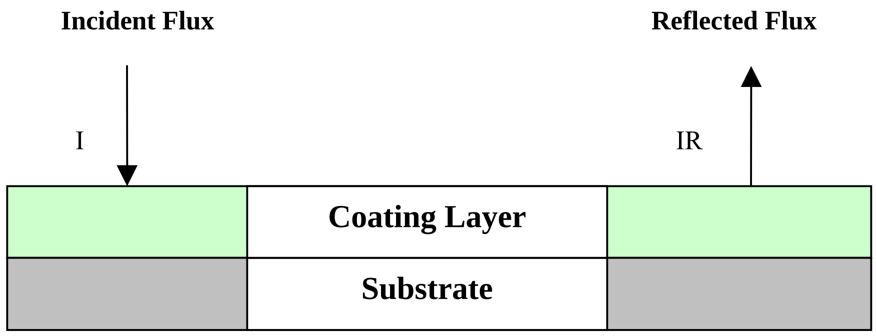
In the above expression, $z$ represents the optical thickness of the layer and can be defined by the equation (3.24) given below:

$$z = D[K(K + 2S)]^{\frac{1}{2}} \tag{3.24}$$

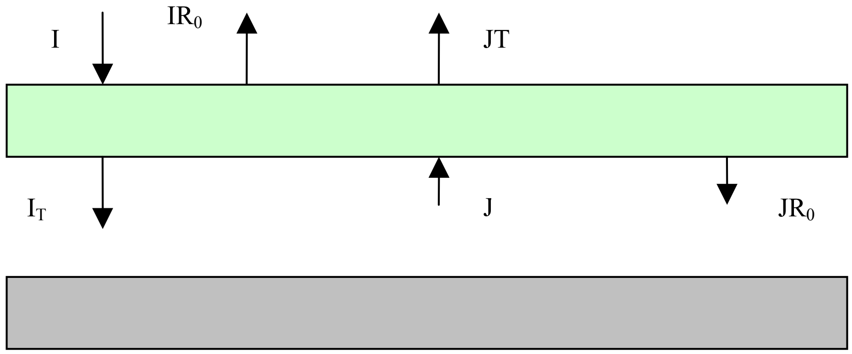
Where $D$ is the physical thickness of the layer.

Now, in the second part, it is needed to determine optical properties of the coating on a substrate. We begin the process by the assumption that the reflectance of composite system is obtained by imagining the coating layer split from the substrate as shown in figure 3.5.According to the separate system, two reflectance expressions are needed to define.

$$\begin{aligned} R_g &= \frac{\text{Energy Flux Reflected by Substrate}}{\text{Energy Flux Incident on Substrate}} \\ R &= \frac{\text{Energy Flux Reflected by System}}{\text{Energy Flux Incident on System}} \end{aligned} \tag{3.25}$$



Composite System



Splitting the coating from the substrate

Figure 3.5

In the figure 3.5, a light flux I is incident on the top layer. Part of this light transmitted through the layer is $I_T$ and the amount $IR_0$ is reflected by the layer. Similarly, a second flux J is assumed reflected back from the substrate and is incident on the bottom surface of the layer. The amount $JR_0$ and JT transmitted through the layer.

From the definition of R as given in equation (3.25), we can develop the following relation in equation 3.26

$$R = \frac{IR_0 + JT}{I} \tag{3.26}$$

Again, the flux J can be related to I from the definition of $R_g$ as given in equation (3.25)

$$J = R_g (IT + JR_0) \tag{3.27}$$

From equation (3.26) and (3.27) the following equation (3.28) can be deduced after some algebraic manipulation.

$$J = \frac{ITR_g}{1 - R_g R_0} \quad (3.28)$$

Substituting the value of J in equation (3.26), we get

$$R = R_0 + \frac{T^2 R_g}{1 - R_g R_0} \tag{3.29}$$

Equation (3.29) gives the relationship between, $R_0$ , $T$ and reflectance of the substrate $R_g$ and ultimately with $K$ and $S$ via equations (3.22), (3.23) and (3.24). This means, theoretically optical properties of semitransparent layer can be determined. To apply practically, it is necessary to simplify equation (3.29) further by defining two terms $\alpha$ and $\beta$ as follows:

$$\alpha = \frac{1 - R_\infty^2}{1 - R_g R_\infty} \tag{3.30}$$

where $\alpha$ is the function of opaque reflectance $R_\infty$ and the reflectance of the substrate $R_g$

$$\beta = \exp(2z) - 1 \tag{3.31}$$

In terms of $z$ equation 3.31 comes as

$$z = \frac{1}{2}\ln(\beta + 1) \tag{3.32}$$

We already know from equation (3.24) that $z$ is function of $K$ and $S$ , so $\beta$ when expressed in terms of $z$ also becomes the function of optical coefficients along with thickness D.

Finally, the equation (3.29) is reduced to the expression containing $R_g$ , $R_\infty$ $\alpha$ and $\beta$ as given by equation (3.32)

$$R = \frac{\alpha R_g + \beta R_\infty}{\alpha + \beta} \tag{3.33}$$

Further, if we put the value of $\alpha$ in equation 3.33, and doing algebraic arrangements, new expression of $\beta$ containing $R_g$ $R_\infty$ and R is obtained as follows:

$$\beta = \left(\frac{R_g - R}{R - R_\infty}\right)\left(\frac{1 - R_\infty^2}{1 - R_g R_\infty}\right) \tag{3.34}$$

Again, from equation (3.24), (3.32) and (3.34), the values of $K$ and $S$ are determined.

$$K = \frac{z}{D}\left(\frac{1-R_\infty}{1+R_\infty}\right)$$

(3.35)

$$S = \frac{z}{D}\left(\frac{2R_\infty}{1-R_\infty^2}\right)$$

We often say equation (3.35) reflectance method to determine $K$ and $S$ for semitransparent layer. The values $K$ and $S$ obtained by the above equations are referred to effective values [3,16,26]

### 3.4.1 DETERMINATION OF $R_\infty$ FOR A SEMITRANSPARENT LAYER:

The value of $R_\infty$ for opaque system is easily obtained from the measurement of reflectance. But, for the semitransparent system, it is not appropriate to use $R_\infty$ measured from opaque layer because of the complex scattering properties offered by such system and the limitation of theory itself[3].The usual practice to determine a value of $R_\infty$ is from the reflectance of sample measured over a white and over a black substrate for the same thickness. To describe, the process more systematically, let us consider $R_w$ and $R_{g,w}$ , the reflectance of a sample over white and of the white substrate respectively and $R_b$, $R_{g,b}$ correspond the reflectance over black and the black substrate.

Now, if we go back to equations (3.30) and (3.32), one can easily relate the function $\beta$ via opaque reflectance $R_\infty$ and the reflectance of the substrate $R_g$ by substituting the value of $\alpha$ in equation (3.32) as given in equation (3.34). Therefore, the value of $\beta$ in terms of over the black and white substrates is given as follows [3].:

$$\beta = \left(\frac{R_{g,b}-R_b}{R_b-R_\infty}\right)\left(\frac{1-R_\infty^2}{1-R_{g,b}R_\infty}\right) \tag{3.36}$$

$$\beta = \left( \frac{R_{g,w} - R_w}{R_w - R_\infty} \right) \left( \frac{1 - R_\infty^2}{1 - R_{g,w} R_\infty} \right) \tag{3.37}$$

Solving equation 3.33 and 3.34 for $R_\infty$, we get a quadratic equation:

$$R_\infty = A - \left(A^2 - 1\right)^{\frac{1}{2}} \tag{3.38}$$

where $A = \dfrac{(1 + R_b R_w)(R_{g,w} - R_{g,b}) - (1 + R_{g,b} R_{g,w})(R_w - R_b)}{2\left(R_b R_{g,w} - R_{g,b} R_w\right)}$

## 3.5 INVERSION TECHNIQUES FROM KUBELKA-MUNK FOR SEMITRANSPARENT LAYER:

The differential equations given by equation 3.3 and 3.4 for the forward and the backward diffuse radiation intensities, according to Kubelka-Munk can be solved by varieties of way. One can obtain the explicit expression on solving the differential equations as given in equation (3.39)

$$R = \frac{1 - R_g \left[a - b \coth(bsh)\right]}{a + b \coth(bsh) - R_g} \tag{3.39}$$

where $R_g$ is the reflectance of substrate

$h$ is the thickness of coating

$a = \dfrac{(S + K)}{S}$

$b = \left(a^2 - 1\right)^{\frac{1}{2}}$

When we measure reflectance of coating layer or sample over black and white, $R_g$ becomes zero and one for black and white substrate respectively. Under these conditions, from equation (3.39) two expressions of reflectance, one for over white ($R_w$) and other for over black ($R_b$) are obtained.

$$R_w = \frac{1 - a + y}{a + y - 1} \tag{3.40}$$

$$R_b = \frac{1}{a+y} \tag{3.41}$$

Where, $y = b\coth(bSh)$

From equations (3.40) and (3.41) $\frac{K}{S}$ is easily calculated as expressed by equation (3.42)

$$\frac{K}{S} = \frac{(1-R_b)(1-R_w)}{2R_b} \tag{3.42}$$

Once the ratio $\frac{K}{S}$ is evaluated, and consequently the values of a and b, an explicit expression for the effective scattering coefficient is obtained:

$$S = \frac{1}{bh}\coth^{-1}\left(\frac{1-aR_b}{bR_b}\right) \tag{3.43}$$

$$K = \left(\frac{K}{S}\right)S \tag{3.45}$$

Finally, the inversion technique is finished by the application of equation (3.43) and (3.45) to obtain the effective scattering and absorption coefficient. [3,16,20]

## 3.6 REFLECTANCE-TRANSMITTANCE TECHNIQUES FROM KUBELKA-MUNK FOR SEMIT-RANSPARENT LAYER :

In many literatures, it is described that reflectance measurement alone can not give true value of either scattering or absorption coefficient [2,26]. This fact come from the relationship between the reflectance and the ratio of optical coefficients as described in equation (3.11). Although, the reflectance model is very satisfactory for the treatment of semitransparent samples in many cases, the situation is poorer when semitransparent layer becomes more transparent [26].An excellent experimental method has been described by Van Gemert *et al.* for determining the absorption and scattering coefficients on the basis of simple analytical expressions proposed by Kottler. According to Kottler, the Kubelka–Munk coefficients $K$ and $S$ can be expressed in terms of diffuse reflectance $R_d$, diffuse transmittance $T_d$ and thickness $t$ of the sample as follows [22].

$$S = \frac{1}{bt}\ln\left(\frac{1 - R_d(a-b)}{T_d}\right) \tag{3.46}$$

$$K = S(a-1) \tag{3.47}$$

where

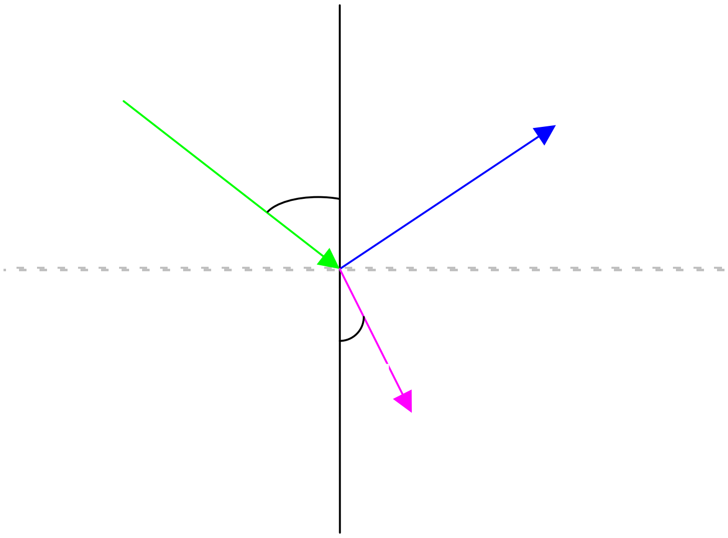
$$a = \frac{\left(1 + R_d^2 - T_d^2\right)}{2R_d} \tag{3.48}$$

$$b = \left(a^2 - 1\right)^{\frac{1}{2}} \tag{3.49}$$

Combining the above equations, we can determine $K$ and $S$ values for any given colorant layer experimentally using spectral measurements from layers of known thickness.

### 3.7 SAUNDERSON'S CORRECTION EQUATION FOR PARTIAL REFLECTION:

On plain surfaces like plastic or glass, when a beam of light strikes the surface, part of the light is reflected from the surface and the remainder is transmitted and scattered [influence of pigment].In colored plastic material, the reflection arises from the difference in the refractive index of air to that of the coating material [3].The reflection and refraction that can occur are illustrated in figure 3.7.



Reflection and transmission of light beam at air/ coating interface

Figure 3.7

The amount of light reflected from the surface can be fixed by Fresnel's law.

$$r_p = \frac{I_{rf}}{I} = \frac{1}{2}\left[\frac{Sin^2(i-r)}{Sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)}\right] \tag{3.50}$$

where $r_p$ is the partial reflection, $I_{rf}$ is the intensity of reflected beam and $I$ is the intensity of the incident beam.

For normal incidence, the equation may be written in the form:

$$r_p = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \tag{3.51}$$

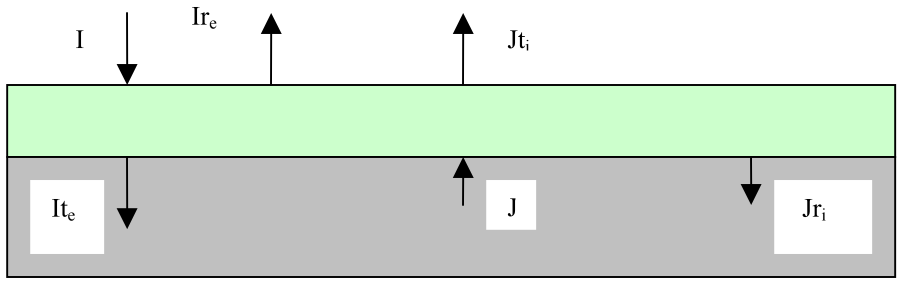
where $n_2$ and $n_1$ are the refractive index of surface coating material and air respectively. If the refractive index of the material is about 1.5, about 4 % of the incident light is reflected and if the refractive index of the material is 2.5, about 18 % of the incident light is reflected [6] which can be calculated easily by the equation (3.51).

The above discussion tells us that if the light loss is significant, considerable error may occur while determining the scattering coefficient as the reflected light has had no opportunity to interact with the colorants present in the coating layer [3].If we recall the assumption made by Kubelka-Munk, it is found that they did not take account for the partial reflection of light at the boundary between air and coating layer while postulating their theory. Thus, to avoid error, the effect of the boundary has to be included in the calculation of the measured reflectance of the material irrespective of whether the coating layer is opaque or semitransparent.

J.L. Saunderson[1] derived a correction equation by considering the interaction of two light fluxes with the boundary as shown in the figure.

---

[1] J.L. Saunderson, Spectroscopy Laboratory, The Dow Chemical Company, Midland, Michigan, USA.



Partial reflection of the fluxes I and J at boundary

Figure 3.8

In the above figure, a light flux I is considered traveling towards the boundary from the air and flux J traveling towards the boundary from within the boundary. The fractions of incident light flux I that are reflected and transmitted by the interface are $r_e$ and $t_e$ respectively. The fractions of the incident flux J that are transmitted by the boundary are $r_i$ and $t_i$ respectively.

The measured reflectance $R_M$ of the layer is given by the following relation:

$$R_M = \frac{\text{Total Reflected light flux}}{\text{Total Incident light flux}} \tag{3.52}$$

Equation (3.52) can be written further as follows:

$$R_M = \frac{r_e I + t_i J}{I} \tag{3.53}$$

The flux J can be linked to flux I via reflectance modeled by the Kubelka-Munk theory. Such reflectance $R_{KM}$ is also called the true or body reflectance of the layer and expressed by the following equation.

$$R_{KM} = \frac{J}{t_e I + r_i J} \tag{3.54}$$

The relation between $R_M$ and $R_{KM}$ is found from equation (3.53) and (3.54) by algebraic manipulation.

$$R_M = r_e + \frac{t_e t_i R_{KM}}{1 - r_i R_{KM}} \quad (3.56)$$

Equation (3.56) is popularly known as Saunderson’s correction equation.

Again, from figure, $t_e$ equals 1- $r_e$ and $t_i$ equals 1- $r_i$, equation (3.56) can be rewritten as follows:

$$R_M = r_e + \frac{(1 - r_e)(1 - r_i) R_{KM}}{1 - r_i R_{KM}} \quad (3.57)$$

The term $r_e$ and $r_i$ are known as the Fresnel reflection coefficient for collimated light and the Fresnel reflection coefficient for diffuse light striking the surface from the inside.

The value of re is around 0.04 and $r_i$ is from 0.4 to 0.6. For the reflectance measured by using bidirectional geometries and specular excluded mode of the integrating sphere spectrometer, the term re is removed.

Equation (3.57) can be rearranged to allow the calculation of the true or body reflectance from the measured value.

$$R_{KM} = \frac{R_M - r_e}{1 - r_e - r_i + r_i R_M} \quad (3.58)$$

It is therefore necessary to convert measured reflectance to body reflectance in all calculations involving the Kubelka-Munk theory. [2,3,26].

### 3.8 DETERMINATION OF RELATIVE SCATTERING AND ABSORPTION COEFFICIENTS:

The practical interest on Kubelka-Munk theory is to determine $K$ and $S$ values of pigments. After making calculations and building a catalog of pigments, it is possible to calculate the mixture required to achieve a desired color. Therefore, in order to predict the color of a mixture of pigments $K$ and $S$ values are determined relative to those of some standard material. It is normal practice to take the scattering power of a standard white paint with consistent properties [26].

The process can be described systematically by considering a sample panel of a paint containing a volume concentrations $C_a$ of pigment $P_a$ and $C_w$ of the standard white. By using integrating sphere spectrometer or other suitable spectrophotometer the reflectance spectrum of the sample can be measured and values of the reflectance at desired wavelength are thus obtained.

As described in section 3.3, the mixture ratio of $K$ and $S$ can be expressed in terms of individual components by following equation:

$$\frac{K_M}{S_M}=\frac{K_a+K_W}{S_a+S_W} \tag{3.59}$$

The optical coefficients are made relative to the scattering power of white by dividing the numerator and denominator terms by $S_W$.

$$\frac{K_M}{S_M}=\frac{\frac{K_a}{S_W}+\frac{K_W}{S_W}}{\frac{S_a}{S_W}+1} \tag{3.60}$$

To simplify the equation (3.60), it is necessary to define some terms to represent the ratio of $K$ to $S$.

$$\omega_M=\frac{K_M}{S_M} \tag{3.61}$$

$$\omega_a=\frac{K_a}{S_a} \tag{3.62}$$

$$K_a=S_a\omega_a \tag{3.63}$$

$$\omega_W=\frac{K_W}{S_W} \tag{3.64}$$

Equation (3.609 can be rewritten using the relations expressed in equations (3.61), (3.62),(3.63) and (3.64)

$$\omega_M=\frac{\omega_a\left(\frac{S_a}{S_W}\right)+\omega_W}{\frac{S_a}{S_W}+1} \tag{3.65}$$

After rearranging the equation (3.65), we are able to express the scattering coefficient of the colored pigment relative to the scattering power of the white as follows:

$$\frac{S_a}{S_W} = \frac{\omega_M - \omega_W}{\omega_a - \omega_M} \tag{3.66}$$

Similarly, the absorption coefficient can be expressed in the same way

$$\frac{K_a}{S_W} = (\omega_a)\frac{\omega_M - \omega_W}{\omega_a - \omega_M} \tag{3.67}$$

In equations (3.66) and (3.67) the known parameter is $\omega_M$ which can be obtained from the measurement of the mixture panel. The unknown terms $\omega_a$ and $\omega_W$ represent the ratio of $K$ and $S$ for a colorant component 'a' and the white standard respectively. If it is assumed that the value of $\frac{K}{S}$ of a colorant is constant, the ratio has the same value irrespective of weather the colorant is a component in a mixture or is present in a formulation on its own. Therefore, the value of $\omega_a$ can be determined from the reflectance of an opaque panel with only component 'a' in the formulation and that of $\omega_W$ from the reflectance of an opaque panel with only the white standard in the formulation[cpi] .

Again, equations (3.66) and (3.67) can be expressed further with fixed value of white reference by assuming that scattering properties of white holds linearity with concentration in the test sample. So, equation (3.66) now becomes:

$$\frac{K_a}{C_W s_W} = (\omega_a)\frac{\omega_M - \omega_W}{\omega_a - \omega_M} \tag{3.68}$$

where $C_W$ is the concentration of reference white in the mixture and $s_W$ is the scattering coefficient of unit concentration of white per unit layer thickness.

The absorption and scattering coefficients with reference to the unit scattering coefficient of white can be defined as follows:

$$K_{aW} = \frac{K_a}{s_W} \qquad\qquad S_{aW} = \frac{S_a}{s_W} \tag{3.69}$$

By linearity property, we can express equation (3.69) in terms of unit absorption coefficient.

$$k_{aW} = \frac{k_a}{s_W} \tag{3.70}$$

where, $k_{aW}$ is the unit absorption coefficient with reference to the unit scattering coefficient of white and $k_a$ is the absorption coefficient of unit concentration of colorant 'a' per unit layer thickness.

From equations (3.66), (3.68), (3.69) and (3.70) the following expressions can be obtained after algebraic rearrangement:

$$K_{aW} = C_W(\omega_a)\frac{\omega_M - \omega_W}{\omega_a - \omega_M} \tag{3.71}$$

$$S_{aW} = \frac{K_{aW}}{\omega_a} \tag{3.72}$$

Finally, the values of $K_{aW}$ and $S_{aW}$ can be easily calculated using equations (3.71) and (3.72) after the measurements of reflectance of colorant only, reference white only and mixture samples [2, 3, 20,26].

The accuracy of the calculated values of $K_{aW}$ and $S_{aW}$ depend on the accuracy of reflectance measurements as well as the precision of the instrument itself.

## 3.9 DETERMINATION OF ABSORPTION AND SCATTERING COEFFICIENTS BY LEAST-SQUARES:

Determination of absorption and scattering coefficients based on the theory of least-squares is often found useful to solve practical difficulties. Generally, producing opaque sample at full range of visible spectrum is a challenging job and if the test sample contains very bright colors such as yellow, orange and red having low scattering power then even thick sample will be transparent in long wavelength. Finding $K$ and $S$ in such case by the conventional method is not appropriate because of occurring high errors in the values of $K$ and $S$ .For bright colors, it also necessary to produce a test sample with the mixture of standard black colorant because the reflectance of bright colorants approach close to or even greater than that reference white at longer wavelength. Thus, to overcome from all these above discussed difficulties, as described by Walowit et al. the least- squares method is an alternative way to do analysis $K$ and $S$ .

Least-square method deals $K_a$ and $S_a$ of colorant only panel as independent quantities and the values are adjusted automatically until the sum of squares is as small as possible. In the fitting process, it takes information from a set of colorant panels mixed with both the standard white and the standard black. To elaborate the process more systematically, we consider a set of sample panels containing colorant only, white only, black only, white and black, colorant and white and colorant and black. The absorption and scattering ratio of mixture panel can be expressed according to additive laws as follows:

$$\frac{K_M}{S_M} = \frac{K_a + K_b + K_W}{S_a + S_b + S_W} \tag{3.73}$$

Where, $\frac{K_M}{S_M}$ is the ratio of coefficients of mixture, $\frac{K_a}{S_a}$ is the ratio of coefficients of colorant only, $\frac{K_b}{S_b}$ is the ratio of coefficients of black only and $\frac{K_W}{S_W}$ is the ratio of white only.

Equation (3.73) can also be written in terms of relative to white and black standard reference.

$$\frac{K_M}{S_M} = \frac{K_{aW} + K_{bW} + K_{WW}}{S_{aW} + S_{bW} + S_{WW}} \tag{3.74}$$

Equation (3.74) should be converted to linear form for the fitting process and it can be done by defining the relative reference coefficients by their concentration multiplied with per unit relative coefficients. Therefore, in equation form the individual terms of equation (3.74) can be written as follows:

$$K_{aW} = C_a k_{aW} \tag{3.75}$$

$$K_{bW} = C_b k_{bW} \tag{3.76}$$

$$K_{WW} = C_W k_{WW} = C_W \omega_W \tag{3.77}$$

where, $K_{aW}$ is the relative absorption coefficient of colorant with standard white.

$K_{bW}$ is the relative absorption coefficient of black with standard white.

$K_{WW}$ is the relative absorption coefficient of white with white.

$C_a$ $C_b$ and $C_W$ are the concentrations of colorant, black and white in the mixture.

Similarly, relative scattering coefficients can be expressed in the same fashion.

$$S_{aW} = C_a s_{aW} \tag{3.78}$$

$$S_{bW} = C_a s_{bW} \tag{3.79}$$

$$S_{WW} = C_W s_{WW} = C_W \tag{3.80}$$

where, $S_{aW}$ is the relative Scattering coefficient of colorant with standard white.

$S_{bW}$ is the relative Scattering coefficient of black with standard white.

$S_{WW}$ is the relative Scattering coefficient of white with white.

$C_a$ $C_b$ and $C_W$ are the concentrations of colorant, black and white in the mixture.

Now, the equation (3.74) can be re-expressed putting the expression of individual terms defined in equations starting from (3.75) to (3.80) as follows:

$$\omega_M = \frac{K_M}{S_M} = \frac{C_a k_{aW} + C_b k_{bW} + C_W \omega_W}{C_a s_{aW} + C_b s_{bW} + C_W} \tag{3.81}$$

Now, in linear form, equation (3.81) is written as

$$C_W(\omega_M - \omega_W) = C_a k_{aW} - C_a s_{aW} \omega_M + C_b k_{bW} - C_b s_{bW} \omega_M \tag{3.82}$$

The object of the fitting process is to obtain values for the optical coefficients $k_{aW}$ , $s_{aW}$ , $k_{bW}$ and $s_{bW}$ such that when the concentrations in a calibration mixture are used in equation (3.81) the value of $\omega_M$ matches the measured value of $\omega$ for that mixture. The ratio $\omega$ is obtained by the reflectance R of the calibration panel using equation (3.11).

Therefore, to fit the equation (3.82) , it is necessary to replace $\omega_M$ by $\omega$. The new fitting equation becomes

$$C_W(\omega - \omega_W) = C_a k_{aW} - C_a s_{aW}\omega + C_b k_{bW} - C_b s_{bW}\omega \tag{3.83}$$

In the equation (3.83) the known quantities are $C_W, C_a, C_b\ \omega, and \omega_W$. The unknown quantities are $k_{aW}$ , $s_{aW}$ , $k_{bW}$ and $s_{bW}$ .

To apply the least squares technique, it is necessary to formulate a general equation which can be compared with equation (3.83).Let us consider two variables V and F for n data set. The variable V consist values of dependent variables and the variable F consists independent variables. V is related with independent variables via F. Mathematically, it can be expressed as follows:

$$F = a_1 f_1 + a_2 f_2 + a_3 f_3 + a_4 f_4 \tag{3.84}$$

where $a_1, a_2, a_3, and, a_4$ are constant coefficients.

The value of the expression for the i set of data can be written as

$$F_i = a_1 f_{1,i} + a_2 f_{2,i} + a_3 f_{3,i} + a_4 f_{4,i} \tag{3.85}$$

The deviation of i^th^ value of F from the value of V is

$$\varepsilon_i = V_i - F_i \tag{3.86}$$

The least square method calculates the constants $a_1, a_2, a_3, and, a_4$ that produce minimum deviation $\varepsilon_i$.

The sum of the squares of the deviation E over the n data set is

$$E = \sum_{i=1}^{n} \varepsilon_i \tag{3.87}$$

In general, each deviation is equally weighted in the fitting process. But in the above equation, the least square of the deviation $\varepsilon_i$ does not necessarily represent the best fit. Therefore, the deviations can be weighted so that minimum in the sum of squares of the weighted deviations coincides with the best fit. In such case, equation (3.86) should be multiplied by weight factor $W_i$

$$W_i \varepsilon_i = W_i (V_i - F_i) \tag{3.88}$$

In this analysis, the overall aim is to obtain the optical coefficients that would best fit the reflectance values of the sample panels. Therefore, the appropriate weight factor would be equivalent to reflectance R.

Again, weighted version of equation (3.85) for a particular wavelength can be expressed as follows:

$$WV_i = Wa_1 f_{1,i} + Wa_2 f_{2,i} + Wa_3 f_{3,i} + Wa_4 f_{4,i} \tag{3.89}$$

Now, comparing equation (3.82) with (3.89) , we get following relationships

$$WV_i = C_W (\omega - \omega_M) W \tag{3.90}$$

$$f_{1,i} = C_a W \quad f_{2,i} = -C_a \omega(W) \quad f_{3,i} = C_b W \quad f_{4,i} = -C_b \omega(W) \tag{3.91}$$

The optical coefficients are given by following relationships

$$k_{aW} = a_1 \quad s_{aW} = a_2 \quad k_{bW} = a_3 \quad s_{bW} = a_4 \tag{3.92}$$

The set of n weighted equations can be represented in matrix notations

$$[WV] = [Wf][a] \tag{3.93}$$

where $[a]$ and $[WV]$ are (4×1) and (n×1) matrices and $[Wf]$ is an (n×4) matrix.
similarly,

$$[a] = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \qquad [WV] = \begin{bmatrix} W_1 V_1 \\ W_2 V_2 \\ \cdots\cdots \\ W_n V_n \end{bmatrix} \qquad [Wf] = \begin{bmatrix} W_1 f_{1,1} & W_2 f_{2,1} & \cdots\cdots & W_1 f_{4,1} \\ W_2 f_{1,2} & W_2 f_{2,2} & \cdots\cdots & W_2 f_{4,2} \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ W_n f_{1,n} & W_n f_{2,n} & \cdots\cdots & W_n f_{4,n} \end{bmatrix} \tag{3.94}$$

The matrix form of least squares solution is given by

$$[a] = \left\{ [Wf]^T [Wf] \right\}^{-1} [Wf]^T [WV] \tag{3.95}$$

where the subscript T and -1 denote taking the transpose and inverse of the matrix[3,16].

## 3.10 LIMITATIONS OF KUBELKA-MUNK THEORY:

The Kubelka-Munk theory can be considered as an approximation theory because of the restrictions and assumption imposed during its derivation. It is therefore necessary to satisfy certain conditions for the theory to be an acceptable approximation to the measured value. Categorically these conditions are explained as below:

Diffuse illumination:
The Kubelka-Munk coefficients K and S describe optical properties of the material under diffuse light conditions. Thus, the sample should be illuminated with diffuse light which means the light incident on the surface should be of the same intensity from all directions [15]. Practically, this condition can be satisfied by measuring the sample using spectrophotometer which provides integrating sphere [2, 3, 6].

Diffuse reflection: Kubelka-Munk model assumes that light is isotropically scattered and under this condition one half of the total scattered light will be directed upward and contribute to the reflectance[15]. Therefore, the sample should meet with the property of Lambertian reflector.

Layer composition: Kubelka-Munk theory assumes that the angular light distribution is the same for upward and downward light flux which means the coefficients K and S are dependent linearly and directly on the physical properties of the material. So, to apply this model, it requires that the sample's surface should be smooth, have a large illuminated area compared to its thickness and be homogenous in composition. [3, 15, 18].

Ignorance of light medium: The Kubelka-Munk theory assumes uniform light traveling media. In this aspect, it is clear that it does not take account of any change of refractive index when light travels from air to the surface of the sample. A separate model is required to deal with partial reflection and refraction that arises from change in refractive index in air-to-layer and vice versa. Similarly, it also ignores the effect of polarization.

### 3.11 COLOR PERCEPTION BY THE DICHROMATIC REFLECTION MODEL:

For general color analysis, an important color property is color invariance. The color appearance of an object is influenced by the spectral power distribution of the light source and the surface spectral reflectance of that object. Therefore, one important role that the surface – spectral reflectance plays is to supply the physical basis for the perception of an object's color. The human perceptual ability known as color constancy means that surface reflectance is greater than that of the spectral composition of the light reflected from the object [27, 28, 30].

In computational vision, this fact has motivated the construction of algorithm for stable object color perception under variable conditions of illumination. Another important aspect of surface-spectral reflectance is the property that the spectral reflectance curve is based on the material composition of the object surface. Two different objects, even if they appear to be identical color, will reveal distinguishable reflectance curves if their surfaces are composed of different coloring materials. Thus, knowing the surface – spectral reflectance of an object is important and perhaps crucial to predicting color appearance, realizing color constancy and recognizing objects in a scene [30].

The reflectance is divided into two parts: interface (specular or regular) reflectance and body (diffuse) reflectance [33].The interface reflectance characterizes light reflection at the interface between the object's surface and the air. Reflection from homogenous materials like metals and crystals is based on this interface reflection. For inhomogeneous materials like plastics and paints, the body reflectance components are meaningful [32].That is why theories like Kubelka-Munk, which determines the objects optical properties, are widely applicable in such materials. However, in some extent the surface spectral reflectance varies with the illumination geometries of an object. Shafer has proposed the dichromatic reflection model for inhomogeneous materials [28, 32].

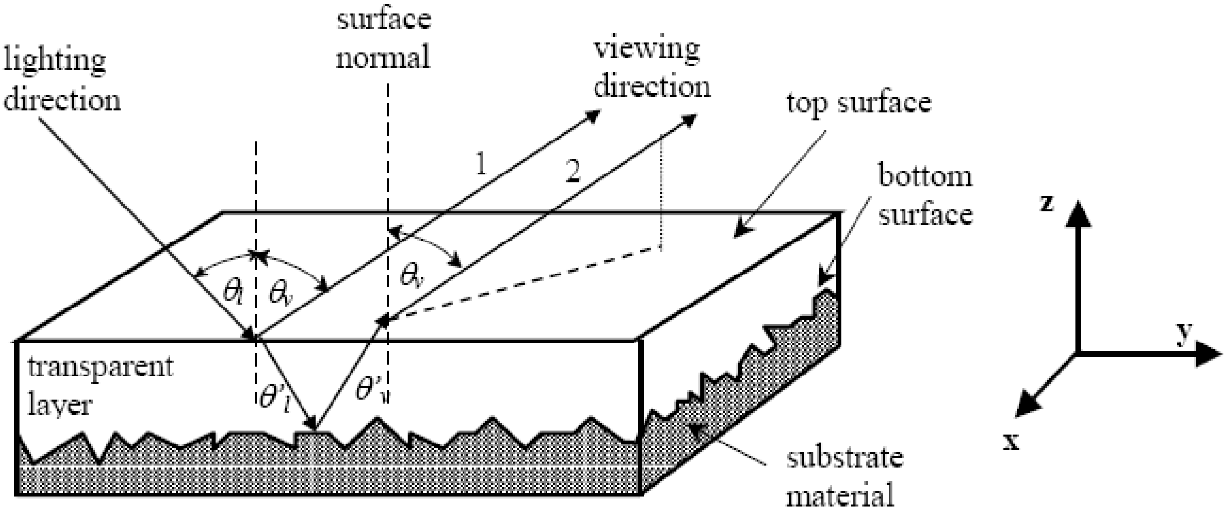


Figure 3.9

Physical structure and geometry notation for interface reflection [30].

### 3.11.1 DICHROMATIC MODEL:

The dichromatic reflection model for inhomogeneous dielectric objects states that the color signal is composed of two additive components, one being associated with the interface reflectance and the other describing the body (or matte) reflectance part. The dichromatic model is physics based model for color analysis [27, 28, 29].

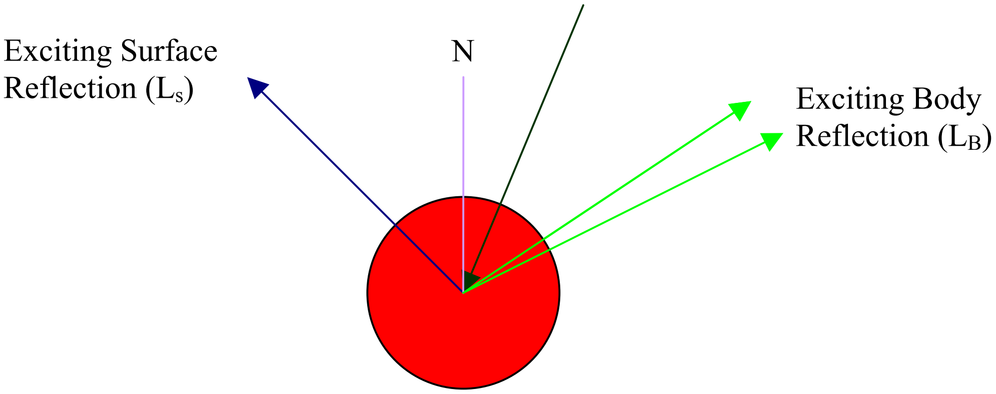


Figure 3.10

Dichromatic Reflection model

The dichromatic reflection model describes the reflected radiance or light L as an additive mixture of the light $L_s$ reflected at the materials surface and the light $L_b$ reflected from the body

$$L\left(i,e,g,\lambda\right)=L_s\left(i,e,g,\lambda\right)+L_b\left(i,e,g,\lambda\right) \tag{3.96}$$

where e is the viewing angle, g is the phase angle, i is the illumination direction angle and $\lambda$ is the wave length.[4]. These angles are called photometric angles and calculated from the angles $\left(\theta_l,\phi_l,\theta_v,\phi_v\right)$ as shown in the figure. These angles are described by bi-directional reflectance distribution function (BRDF). This function depends on the incident direction $\left(\theta_l,\phi_l\right)$ and the outgoing direction $\left(\theta_v,\phi_v\right)$, as well as light wavelength $\lambda$ (Figure 2). Thus, we express the overall BRDF for glossy reflection as [30]

$$\rho\left(\theta_l,\phi_l,\theta_v,\phi_v\right)=\rho_1\left(\theta_l,\phi_l,\theta_v,\phi_v\right)+\rho_2\left(\theta_l,\phi_l,\theta_v,\phi_v\right) \tag{3.97}$$

where the two terms account for the contributions from ray types 1 and 2 in Figure 1, respectively. For the first term, according to the microfacet theory [35], one-bounce reflection can be expressed as a product of the Fresnel coefficient, a self-shadowing factor, and a statistical distribution function that is related to the surface orientation [33]. The figure below describes the bi-directional geometry.

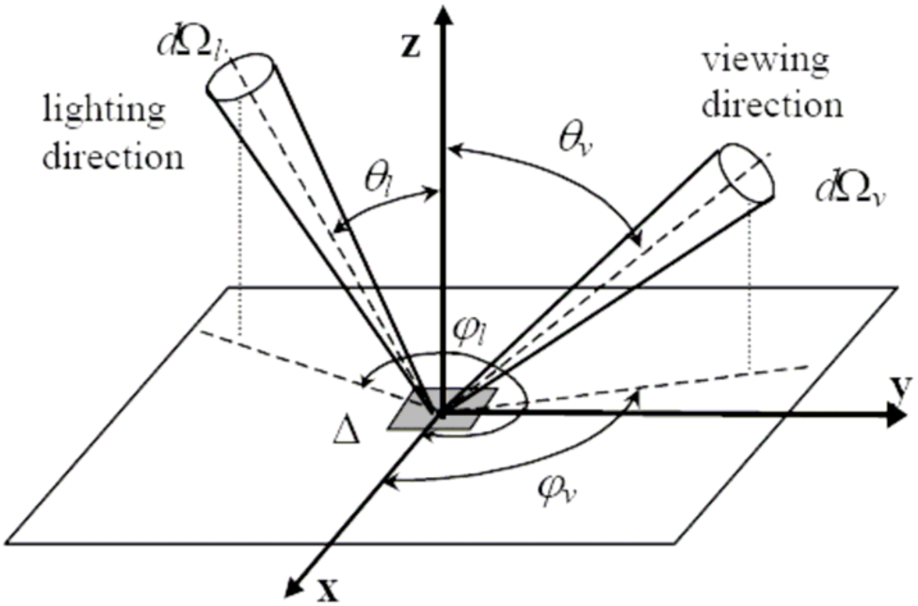


Figure 3.11

Bi-directional geometry and ray notation [30 ]

Since self shadowing factor is neglected from the top surface, the first term of equation (3.97) becomes as:

$$\rho_1(\theta_l,\phi_l,\theta_v,\phi_v)=\frac{\overline{R}\left(\frac{\delta}{2},\lambda\right)}{16\pi\left(\cos^3\theta\right)\left(\cos\left(\frac{\delta}{2}\right)\right)}s^2\exp\left(-s^2\left(\tan^2\left(\frac{\theta}{4}\right)\right)\right) \tag{3.98}$$

Where $\overline{R}\left(\frac{\delta}{2},\lambda\right)$ is Fersenal coefficient averaged over all polarizations for incident angle $\frac{\delta}{2}$ and the rest corresponds to the probability distribution for the top surface for slope tanɵ. In equation (3.98), parameter‘s’ describes surface smoothness and defined as:

$$s=\frac{\tau}{\sigma} \qquad (3.98(1))$$

where $\sigma$ and $\tau$ are the height deviation and correlation length of the top surface. In other words, larger s implies a smoother surface. According to Microfacet theory, the scattering geometry looks as shown in the figure below:

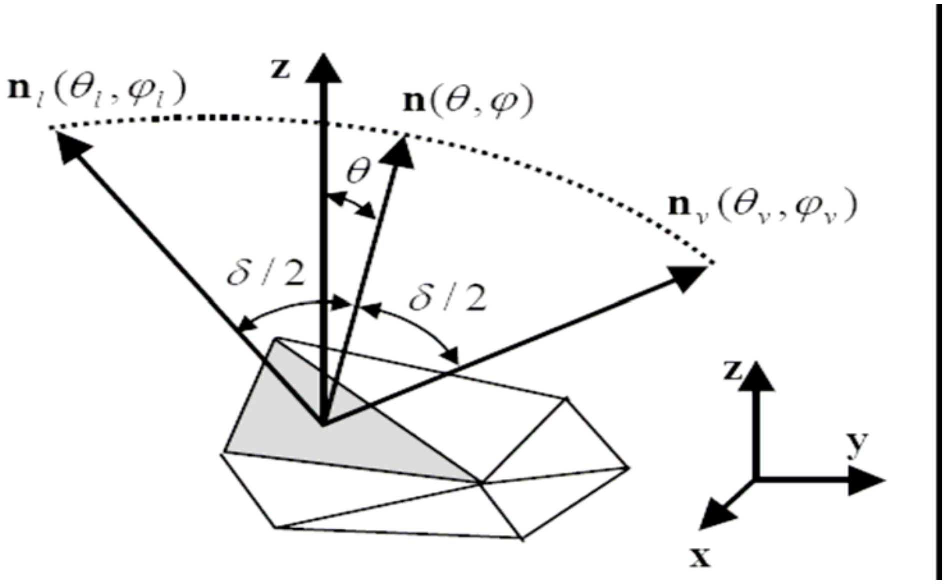


Figure 3.12

Scattering and viewing direction geometry [30]

As shown in figure, $\delta$ is the angle between the lighting and viewing directions and $\theta$ is the polar angle of the half vector that equally divides the lighting and viewing directions. From the figure, one can easily determine the following relations [30]:

$$\cos\delta = \sin\theta_1 \sin\theta_v \cos(\phi_l - \phi_v) + \cos\theta_l \cos\theta_v \tag{3.99}$$

$$\cos\theta = \frac{\cos\theta_l + \cos\theta_v}{2\cos\left(\frac{\delta}{2}\right)} = \frac{\cos\theta_l + \cos\theta_v}{\sqrt{2 + 2\cos\delta}} \tag{3.100}$$

Now, Shafer [33] showed that the spectra of surface and body reflection of dielectric materials are invariant to the illumination geometry and thus the surface and body reflection may be split into a geometrical scaling factor and a spectrum respectively.

$$L(\theta,\lambda) = m_s(\theta)c_s(\lambda) + m_B(\theta)c_B(\lambda) \tag{3.101}$$

where, $m_s(\theta)$ and $m_B(\theta)$are geometrical scaling factors, $c_s(\lambda)$ and $c_B(\lambda)$ are the light spectra for the surface and body reflection respectively. Again, these light spectra can be expressed as:

$$c_s(\lambda) = E(\lambda)R_s(\lambda) \tag{3.102}$$

$$c_B(\lambda) = E(\lambda)R_B(\lambda) \tag{3.103}$$

where, $E(\lambda)$ is the incident light spectrum and $R_s(\lambda)$ and $R_B(\lambda)$ are surface and body reflectance respectively.

Now, equation (3.49) can be written as:

$$L(\theta,\lambda) = m_s(\theta)E(\lambda)R_s(\lambda) + m_B(\theta)E(\lambda)R_B(\lambda) \tag{3.104}$$

The equation (3.104) fully describes the total reflection. The geometrical factor of specular reflection is determined by equation (3.98) and the body reflection by Lambert's cosine law as given below in equation (3.105)

$$m_B(i) = IA\cos(i) \tag{3.105}$$

where I is the incident light, A is the scaling constant and i is the angle between normal and incident light. This law states that body reflection is independent from viewing directions, so color appearance does not change with respect to viewing direction [31].

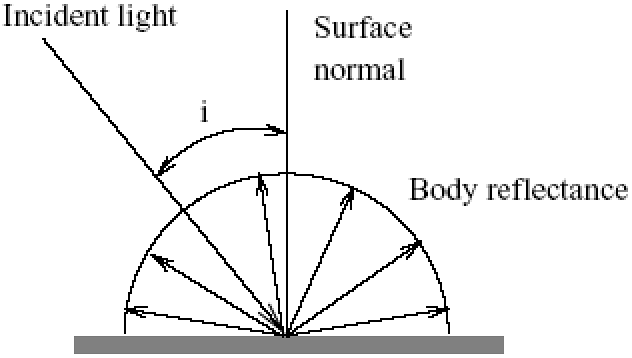


Figure 3.13

Body reflectance [31]

### 3.11.2 RGB COLOR SPACE FOR DICHROMATIC MODEL:

Generally, a color space maps qualities of color in three coordinate axis.[]. There are varieties color spaces such as RGB, HSI family, Lab and LUV. However, the camera output response falls on RGB model. The linear relationship between reflected light and body color and surface color can be obtained by spectral integration. Thus, the dichromatic reflection model in three-dimensional RGB color space can be expressed as follows:

$$C_{RGB} = m_s(\theta)c_{surface} + m_B(\theta)c_{Body} \tag{3.106}$$

$C_{RGB}$ is a linear combination of surface vectors $c_{surface}$ and $c_{Body}$. These two vectors span a plane in RGB space called the dichromatic plane and all color falls on this plane. This is illustrated in the figure below

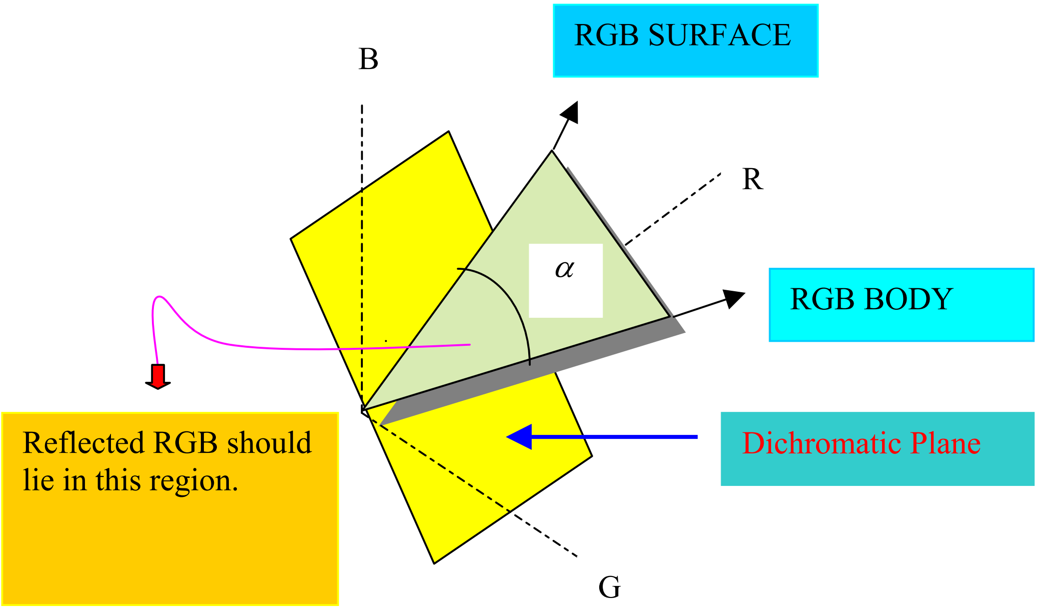


Figure 3.14

Dichromatic Plane

For small $\alpha$ RGB will be in the body direction and as $\alpha$ becomes large, it goes to surface direction [29,31,36].

# CHAPTER FOUR

## 4. INDUSTRIAL SAMPLES AND COLOR MEASUREMENT:

In industry, color measurement is concerned with the color of a product or component and basically points toward the measurement of spectral characteristics (Reflectance and Transmittance).Perhaps, the greatest industrial use of color measurement is in calculating approximately the color of a product batch to the color standard for that color[7]. Therefore, standard sample and color measurement are very sensitive in industrial coloring process as well as maintaining data base of standard samples or calibration panels. In colorant measurement, we seek information about sample's coloration. This information can be used variety of ways [2]. For example, measurement data serves as the input to many theoretical models for the analysis of color.

The above discussions tell that it is necessary to follow general guidelines for preparing standard samples. Similarly, for measurement part, it is not simply a matter of pointing an instrument (generally spectrometer) and taking a reading [4]. We should deal color measurement like as a system. It involves set of procedure, analysis and finally the result. The detail information must have to be provided with regard to the type of sample (colored object) and its configuration, the type of instrument used, measurement parameters including averaging, deviation and curve fitting for error calculation with tolerance details. With a good computer program, we can measure color much more accurately than even a trained human eye [9]. We will discuss more in the following sub sections of this chapter.

### 4.1 SAMPLE PREPARATION:

Sample preparation and presentation to the instrument is very important for measurement of spectral characteristics (Reflectance and Transmittance).In general, a sample is the representation of the larger population. Hence, color of a sample means color of whole population [2]. Therefore, samples should always be prepared in ways that will make them easy to reproduce. In the case of colorants such as dyes or pigments, dry powders do not give any judgment about color and it is usual practice to prepare samples containing mixtures of pre-dispersed colorants (Sandosperse) in a heat-set resin(Synthese)[ [2,3,7].

Before starting measurement, it is also necessary to identify perfect sample as well as to know its types and material properties. In color measurement, perfect sample indicates uniformity. If dirt, bubbles and variations in flatness are present in samples, we get very misleading result. To avoid such uncharacteristic samples, our first task is to do visual inspection. It is a very sensitive method of detecting the presence of such defects [4].For example, a paint panel is being looked at and compared to a standard, a trained observer can notice whether or not the sample and the standard are in good condition, or whether the coating has been applied correctly[2].

Another factor, to know about the sample is its type. To apply appropriate measurement technique, it is essential to know what type of sample we have. For example, if the sample is translucent then its appearance and the results of measurement made upon it, will be very dependent on the nature of material behind them [1]. In such type of sample, measurements are carried out with both white and black backings (backgrounds) and detailed the number of thickness used. If the readings of two backgrounds are different, it indicates the presence of translucency and its extent. While, in the case of opaque sample, only one type of background is used. Similarly, configuration of sample's surface must be taken in account because light that reflects off of a materials surface leads to seculars, gloss and texture, luster and so on.

The last important factor to know about the sample is its material properties. For example, some pigments used in plastics are thermo chromic and change color with temperature. Before measuring thermo chromic materials, it should be confirmed that they are at the proper temperature. Heat given off by the light source of some instruments will affect thermo chromic samples, and it is necessary to wait for a specified period of time. Similarly, fluorescent materials absorb light and then re-emit it with a change of wave length and at each wave length; the total light re-emitted consists of sum of that caused by reflection and that caused by fluorescence [1]. It is commonly found that measured value of the reflectance of fluorescent materials using a conventional spectrophotometer or radiometer appears greater than 100 % at some wavelengths. Thus, special procedure is necessary to measure fluorescent materials.

Some industrial test samples the author has measured are shown in figures below:

Pigment testing samples
Figure 4.1

### 4.2 SETTING WORKING PLACE ENVIRONMENT:

Color Laboratory is the workplace for the conduct of research on color. This implies that setting of working place is very important before conducting color measurement or any research [8]. Theoretically, it seems unimportant for modern laboratory, but in practice, it is necessary to manage working place properly. Otherwise, if physical disturbance occurs either in instrument or sample while doing color measurement or research, we may get serious error. The basic guiding principles to manage workplace for color measurement are as follows:

Flexibility: Flexibility in working place means sufficient space for the movement and instruments should be arranged to meet this goal. It gives us security to avoid collision with instruments as well as easy access to read what is going on within instruments.
Collection of tools and accessories: It is required to determine and collect tools and accessories which we may need during measurement process. For example, screw driver, wrench, measuring scale and tape are necessary tools and accessories and they should be available on our working table at handy position.

Monitor adjustment:  In most instrumental color measurement, color is visualized in the computer monitor. To visualize good quality of color, proper calibration of the monitor is essential. And, calibration is the process of setting our monitor, to known color conditions. For example, we have to make sure that our CRT monitor has been turned on for at least a half hour. This gives it sufficient time to warm up for a more accurate color reading. Similarly, we have to remove colorful background patterns on our monitor desktop. Because busy or bright patterns surrounding a document interfere with accurate color perception. We again have to set our desktop to display neutral grays only, using RGB values of 128.

Room lights should be set to the level to maintain consistently.

### 4.3 INSTRUMENTAL COLOR MEASUREMENT:

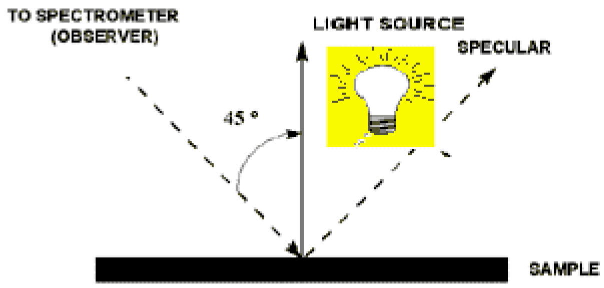
In coloring industries, the particular interest is the measurement of the spectral characteristics (reflectance or transmittance) of materials such as dyes and pigments suspended in an appropriate substrate. These spectral characteristics are used for colorant formulation through the existing theories. Varieties of instruments are in existence to measure the spectral characteristics of materials. Spectrophotometer and spectroradiometer are most commonly used instruments to achieve the above discussed goal. These instruments made for measuring reflectance or transmittance consists of an illuminator, a sample holder and a receiver. The illuminator contains standard light source with associated optics, and electronics. The receiver contains components needed to gather and analyze the light reflected from the sample being measured. There are number of ways these components can be arranged and in colorimetry, it is known as measurement geometries or instrument geometries. For all types of instruments, instrument geometries come up to a critical factor to be taken into account [1, 2, 6,,7].

### 4.3.1 INSTRUMENT GEOMETRIES:

In measurement of color by using instruments, the angles and method by which we illuminate and view a sample affect the observed color dramatically [7]. Hence the instrument geometries are an important factor for accurate color measurement. For example, the glossy surfaces look more saturated in directional view than in diffuse illumination because the specular reflections add white light to the color of the surface [4]. And, we say this effect de-saturation of the color. In the case of completely matt surface, it is no matter what the incidence angle of light on the surface, because matt surface do not appear as saturated as glossy surface [2].

Instrument geometries generally give reference the illumination and detection angle (angle of view) in their name. The CIE has recommended four different instrument geometries for the purpose of color measurement.

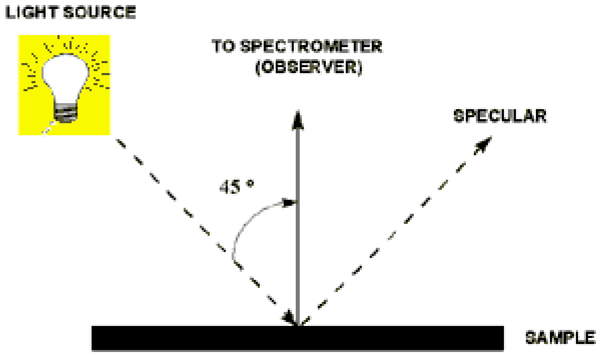
0/45 geometry: A 0/45 geometry describes illumination at 0 degree, perpendicular to the sample plane and the instrument is at 45 degree. The angle between the axis and any ray of the illuminating beam should not exceed 5 degree. Figure 4.3 below illustrates this geometry.



0/45 Bidirectional Geometry

Figure 4.2

45/0 geometry: A 45/0 geometry describes illumination at 45 degree, and the instrument is at perpendicular to the sample plane. The angle between the direction of viewing and normal to the sample should not exceed 10 degree. Figure 4.4 below illustrates this geometry.



45/0 Bidirectional Geometry

Figure 4.3

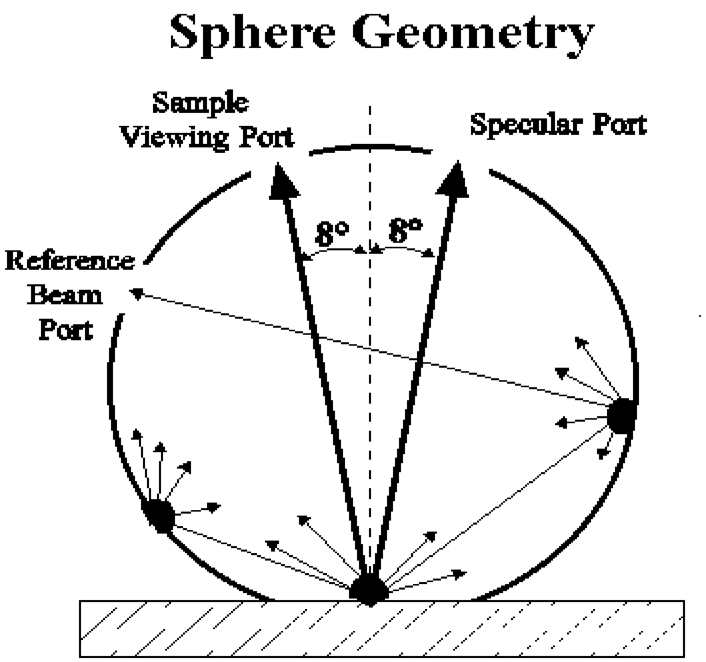
The above two geometries, 0/45 and 45/0 are commonly known as bi-directional geometries. In practice, these geometries are used to measure glossy samples [4]. To measure reflectance by using these bi-directional geometries, we need to illuminate the sample by a single collimated beam of light. Insufficient light power is the main demerit often found in bidirectional geometries while doing measurement.

Diffuse/normal (D/0): This geometry refers to the use of integrating spheres and the angle between the normal to the sample and the axis of beam should not exceed 10 degree as per CIE standard. The integrating sphere may be of any diameter provided the total area of ports does not exceed 10 % of the internal reflecting sphere area.

Normal/Diffuse (0/D): This geometry also refer to the use integrating sphere and in this configuration, the sample is illuminated by a beam whose axis is at an angle not exceeding 10 degree from the normal to the sample as per CIE standard[3].

In industries, sphere geometries are generally used for a general purpose color measurement. In spectrophotometers, we can find a gloss port at an angle 8 degree from the normal to measure the specular (gloss) component of reflection. This port gives the choice to measure reflectance in two different modes: the specular excluded and specular included. In excluded mode, we are able to detect gloss or texture difference of two samples of identical pigmentation. This situation occurs especially, in painted plastic materials [8]. This is a very useful facility, particularly in quality control, when we have to compare two samples of identical pigmentation but having different surface characteristics [2].

In practice, we use gloss trap for the excluded mode measurement and if we do not have to take care about specular component, we use include mode. The figure below shows the general configuration of sphere geometry. In the figure, specular port is seen at 8 degree which is less that CIE, standard of 10 degree. Most sphere spectrometers have this angle of viewing and detecting.



Integrating Sphere Geometry

Figure 4.4

### 4.3.2 SPECTROPHOTOMETER:

A spectrophotometer is an apparatus designed to measure the spectral transmittance and spectral reflectance factors of objects [6]. The main components of all spectrophotometers are a source of optical radiation, an optical system for defining the geometric conditions of measurement , some means of dispersing light with a detector and signal processing system that converts light into signals suitable for analysis[2].

Most spectrophotometer measures reflectance factor rather than reflectance. The range of wavelengths illuminating the sample is described by the instruments spectral bandwidth or band pass. Spectrophotometers are available commercially having bandwidths from 20 nm to bandwidth as low as 1 nm. Before making reflectance factor measurement, the instruments must be calibrated, i.e. the zero point and high end of the photometric scale are determined at each wavelength. The zero point of the photometric scale is usually set by measuring the reflectance factor of a light trap or a black calibration standard. The high end of scale is set by measuring the reflectance factor of a white calibration standard. A number of materials have been used as the white calibration standard including optical grade barium sulfate ($BaSO_4$), opal glasses and ceramic plaques. [2, 6]. Generally, instrument manufactures supply white calibration standards having known reflectance factors. When a single beam instrument uses an integrating sphere, a correction for the reduction of sphere efficiency caused by the sample absorption is necessary according to The CIE 1986a. In practice, such correction is done automatically by the computer software supplied with the instrument. The author has used Konica Minolta spectrophotometer as shown in the figure 4.5 below to measure samples.

Spectrophotometer

Figure 4.5

### 4.3.3 SPECTRORADIOMETER:

Instruments designed to measure the spectral properties of the light sources are known as spectroradiometer [2]. With the obvious exception of a light source, they have the same principle components as spectrophotometers. In practice, the measurement of a spectral radiometric quantity involves the comparison of the test source with a suitable reference source of known spectral power distribution. Spectroradiometers sample the spectrum with narrow wavelength increment and bandwidth [2,6]. In most cases, spectral data are taken at 2 nm intervals. The author also used PR705 spectroradiometer as shown in figure 4.6 to measure reflectance of samples.

Spectroradiometer

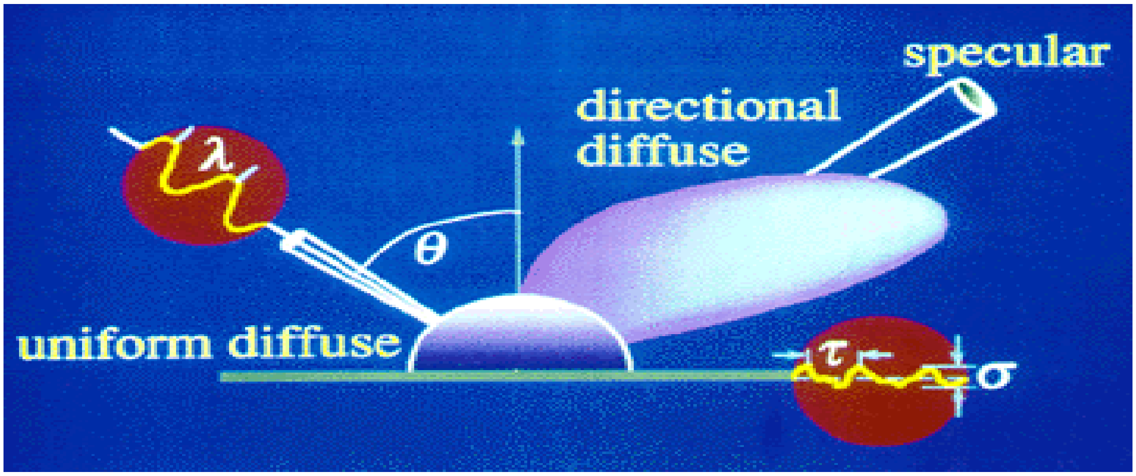
Figure 4.6

### 4.4 MEASURING REFLECTANCE:

The term reflection refers to the process of radiation being returned by a medium or passed on through a medium respectively. In particular, it is the quantity required for quantitatively analyzing directional effects. The surface leaving radiance is assumed to be dependent on the incident radiation onto the surface, thus the reflectance is defined as the ratio of reflected to incident flux. Mathematically, we write: $R_x = \frac{J_x}{I_x}$ where $J_x$ is reflected flux and $I_x$ is incident flux.

The amount of radiation reflected by the perfect diffuser is expressed by means of different terms according to the geometrical arrangement for collecting the radiation. Reflectance factor and transmittance factor are used when the radiations reflected or transmitted by the sample and by the perfect diffuser lie within a defined cone. If the cone is hemisphere, the term reflectance is used. If the cone is very small, the term radiance factor is used [1].

In practice, it is necessary to take account of how light interacts with the object. If a beam of light shines on a mirror at 45 degree to its normal, it will entirely reflected in the opposite direction at the same angle giving specular reflection. If the light leaving the object will exit at many angles from the normal, this is called diffuse reflection. A high gloss material such as a white paint gives both specular and diffuse reflection. The figure 4.7 illustrates various light reflection patterns.



Light reflection patterns

Source:http://www.graphics.cornell.edu/research/globillum/reflmodel.html

Figure 4.7

Reflectance measurements of opaque samples are performed relative to the perfect reflecting diffuser. A perfect diffuser has capability to reflect radiation equally and strongly in directions. It is considered that the perfect reflecting diffuser is completely matt and free from any gloss [2]. Similarly, the reflectance is equal to unity at all wave length, so that the diffusion is independent of wavelength. It is also known as Lambertian reflector. In most of cases, the material used as a perfect reflecting diffuser is an integral part of a particular instrument and used in it as a working standard and its spectral reflectance is considered valid only in conjunction with the particular instrument and its peculiar geometries [6].

Reflectance measurement of semitransparent samples such as plastic and paper depends upon their level of translucency. In such materials, reflectance measurements are common on the nearly opaque samples whereas transmittance measurements are common on the more transparent samples. When a semitransparent material or sample is measured, the area viewed by the instrument is limited to the size of the sample port. Some of the light reaching the sample will be lost by the sideways scattering and not detected. The light that passes through the sample will be lost if the sample is kept on black backing, or it will be reflected back through the sample if the sample is kept on white backing. The difference between two such readings is a rough measure of the translucency. [1,2,7].

Best agreement with visual evaluations will happen if the area illuminated by the instrument is very much larger than the area viewed. This is equivalent to illuminating a small area and viewing an area very much larger. Spectrophotometers typically come equipped with a range of aperture sizes to allow measurement of both small and large samples [2]. We always have to prefer to use the largest aperture size to minimize the influence of uninformed level dyeing as well as surface [9]. But we can use smaller aperture size for measuring the smallest of samples. For efficient reflectance measurement, industries should also prepare samples with the intention of using the largest area view available on the spectrophotometer. Samples measured with small apertures will require additional reads to insure minimal measurement error.

### 4.4.1 REFLECTANCE DATA:

By reflectance data, we mean the measured numerical value of reflectance at different wave length. We express such value as percentage with the perfect reflecting diffuser having a reflectance of 100%.

For research purpose, it is common practice to measure the reflectance at 2nm intervals from 380 to 780 nm which is also the CIE recommended bandwidth to measure the reflectance. However, in industries, it is not necessary to measure 2nm bandwidth because our eyes are not sensitive at either end of the spectrum. Hence, from commercial point of view, reflectance values are measured from 400 to 700 nm at 20 nm intervals. When we visualize reflectance data in the computer by using suitable software, they follow a smooth curve with few hills and valleys which depend upon the color properties of samples or objects. The author has used mat lab for the visualization and analysis of reflectance data.

Reflectance data varies from point to point if the sample has spherical or cylindrical configuration and long in length. This is due to various reasons such as uninformed distribution of pigments, loss of light from the surface curvature and variation in the surface texture. This situation generally occurs while measuring reflectance in bi-directional geometry and it is necessary to do analysis on reflectance data. In such case, it is useful to measure reflectance at least five different points. After doing average of different reflectance values, again, it is necessary to identify that how much actual measured reflectance data differ from the average value. For this purpose, the author has used least square curve fitting technique and the analysis is given in subsection 4.5 below for sample number 6. . This technique also calculates residual values which give the difference value between measured data and the average data. By residual values, one can easily determine that whether the average reflectance values are acceptable or not. [1,4,9].

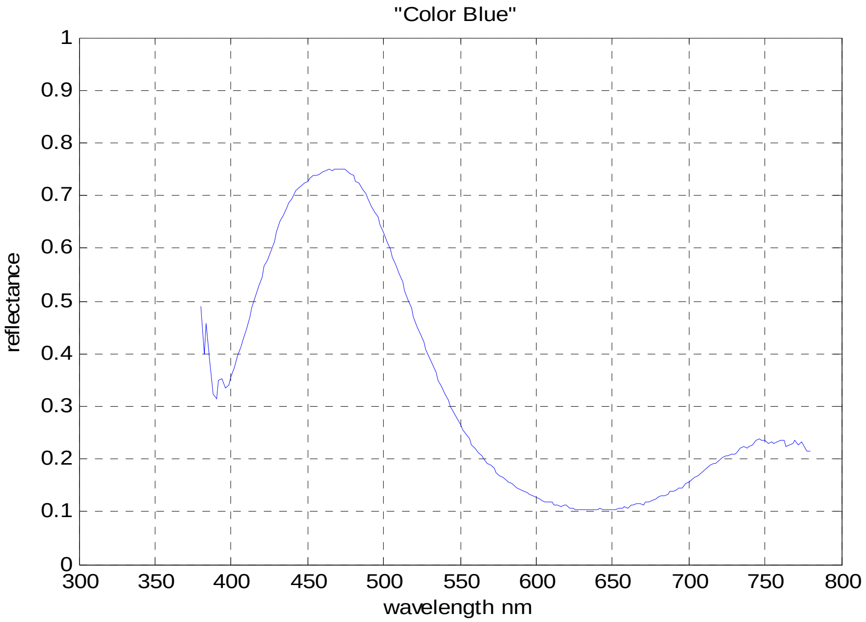
### 4.4.2 MEASURED REFLECTANCE OF SOME SAMPLES:

Sample 1.

TECHNICAL DATA:

| | |
|---|---|
| SAMPLE TYPE | STANDARD PAINT SAMPLE |
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | METAL |
| SURFACE TYPE | GLOSSY |
| PAINT MATERIAL PROPERTIES | NORMAL |

| | |
|---|---|
| SAMPLE THICKNESS | LESS THAN .2 mm(Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | PR 705 Radiometer |
| GEOMETRY | BI-DIRECTONAL |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | D65 |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 2 nm |
| MEASUREMENT RANGE | 380 to 780 nm |
| MAXIMUM REFLECTANCE VALUE | 0.7514 at 464 nm |
| MINIMUM REFLECTANCE VALUE | 0.1024 at 636 nm |



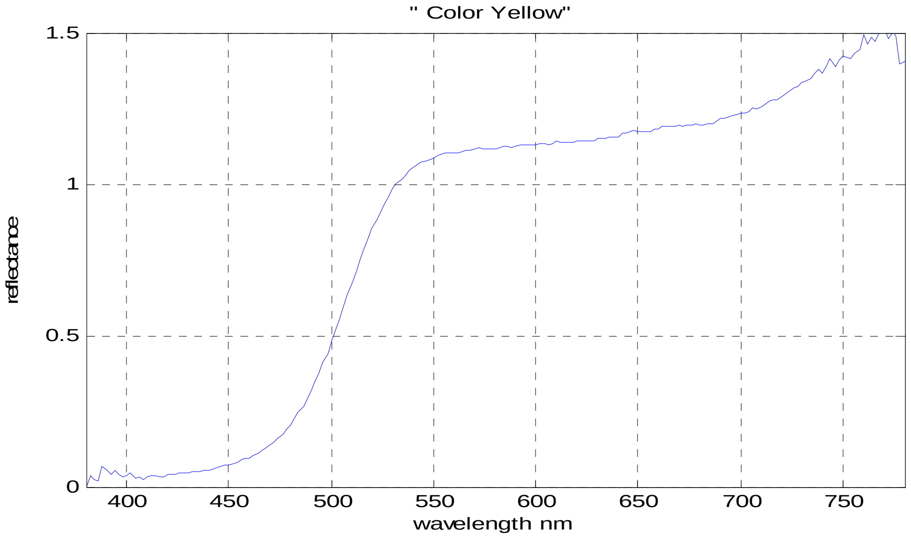
Reflectance of opaque paint sample

Figure 4.8

## Sample 2:

<u>TECHNICAL DATA</u>:

| | |
|---|---|
| SAMPLE TYPE | INDUSTRIAL PAINT SAMPLE |
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | METAL |
| SURFACE TYPE | GLOSSY |
| PAINT MATERIAL PROPERTIES | NORMAL + FLUORESCENT |
| SAMPLE THICKNESS | LESS THAN .2 mm(Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | PR 705 Radiometer |
| GEOMETRY | BI-DIRECTONAL |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | D65 |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 2 nm |
| MEASUREMENT RANGE | 380 to 780 nm |
| MAXIMUM REFLECTANCE VALUE | 1.5297at 770 nm |
| MINIMUM REFLECTANCE VALUE | 0 at 380 nm |



Reflectance of Fluorescent sample

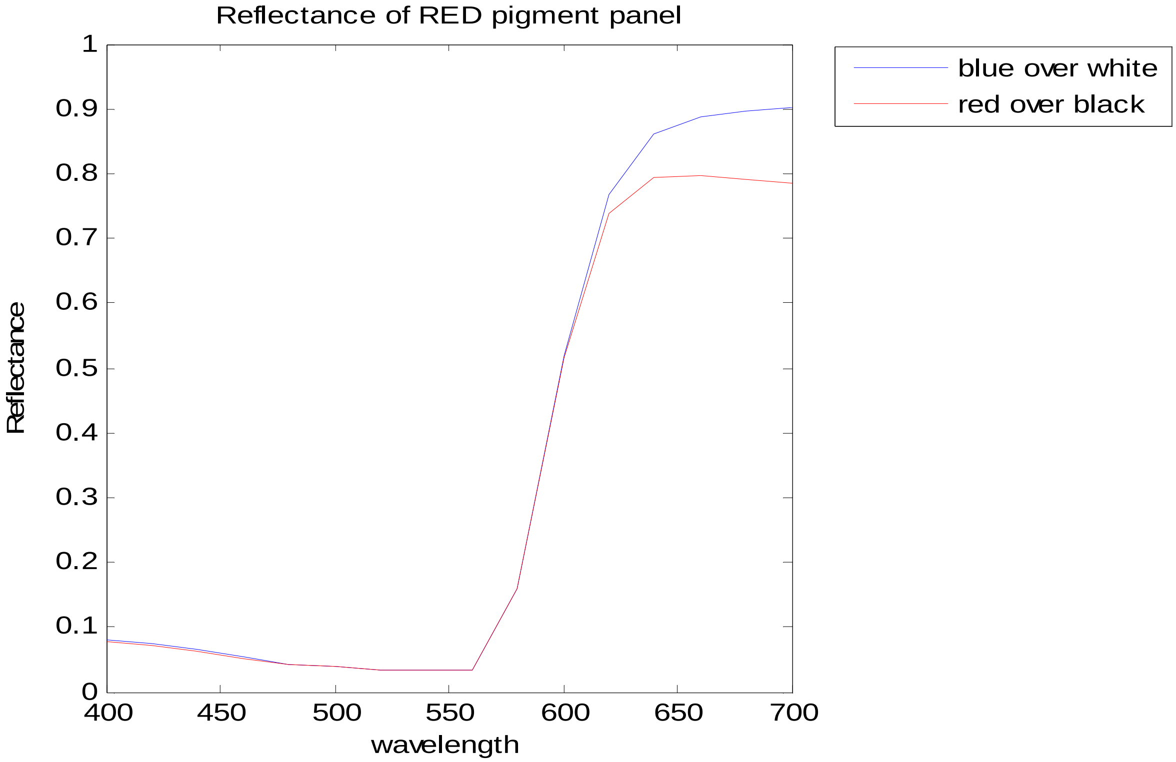
Figure 4.9

.

## Sample 3:

TECHNICAL DATA:

| | |
|---|---|
| SAMPLE TYPE | INDUSTRIAL PIGMENT PANEL (RED) |
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | PLASTIC |
| SURFACE TYPE | GLOSSY |
| MATERIAL PROPERTIES | TRANSLUCENT |
| SAMPLE THICKNESS | 1 mm (Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | SPECTROPHOTOMETER CM-3600D |
| GEOMETRY | INTEGRATING SPHERE |
| APERATUR SIZE | 10 degree |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 20 nm |
| MEASUREMENT RANGE | 400 to 700 nm |



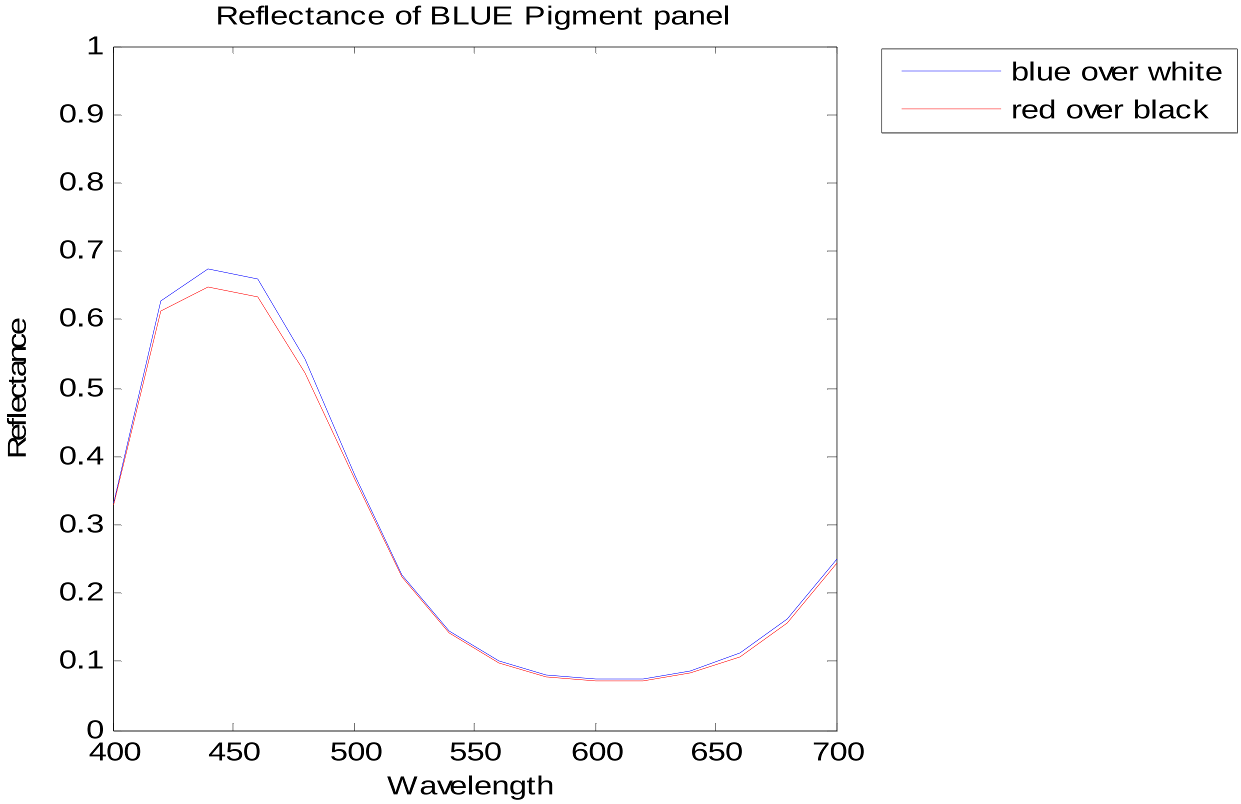
Reflectance of translucent sample

Figure 4.10

Sample 4:

TECHNICAL DATA:

| | |
|---|---|
| SAMPLE TYPE | INDUSTRIAL PIGMENT PANEL (BLUE) |
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | PLASTIC |
| SURFACE TYPE | GLOSSY |
| MATERIAL PROPERTIES | TRANSLUCENT |
| SAMPLE THICKNESS | 1 mm (Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | SPECTROPHOTOMETER CM-3600D |
| GEOMETRY | INTEGRATING SPHERE |
| APERATUR SIZE | 10 degree |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 20 nm |
| MEASUREMENT RANGE | 400 to 700 nm |


Reflectance of BLUE Pigment panel
Reflectance
Wavelength
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
400
450
500
550
600
650
700
blue over white
red over black

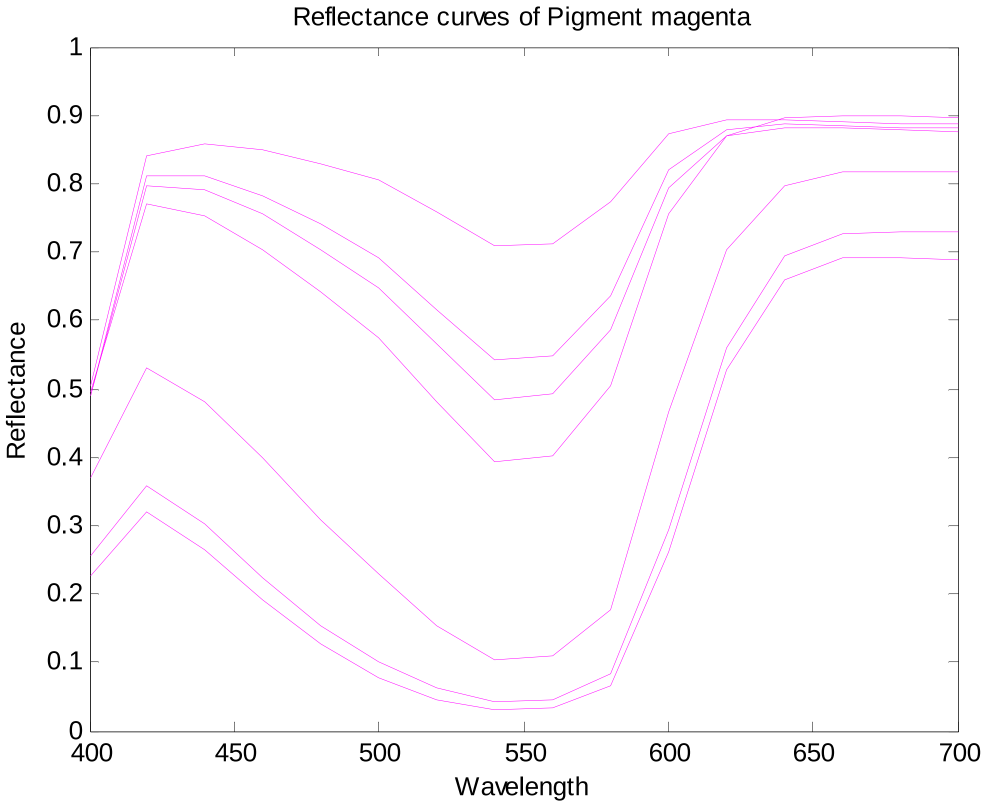
Reflectance of translucent sample

Figure 4.11

Sample 5:

TECHNICAL DATA:

| | |
|---|---|
| SAMPLE TYPE | INDUSTRIAL PIGMENT PANELS (MAGENTA) |
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | PLASTIC |
| SURFACE TYPE | GLOSSY |
| MATERIAL PROPERTIES | TRANSLUCENT |
| SAMPLE THICKNESS | 1 mm (Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | SPECTROPHOTOMETER CM-3600D |
| GEOMETRY | INTEGRATING SPHERE |
| APERATUR SIZE | 10 degree |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 20 nm |
| MEASUREMENT RANGE | 400 to 700 nm |



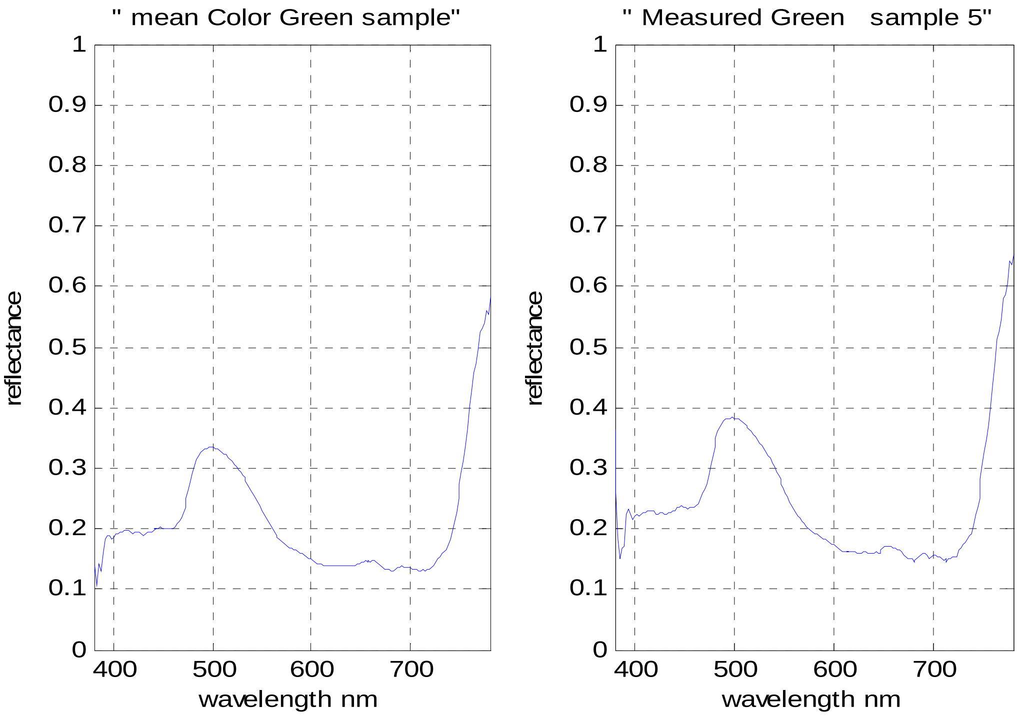
Reflectance of pigment panels of color Magenta with varying concentrations

Figure 4.12

## Sample 6:

TECHNICAL DATA:

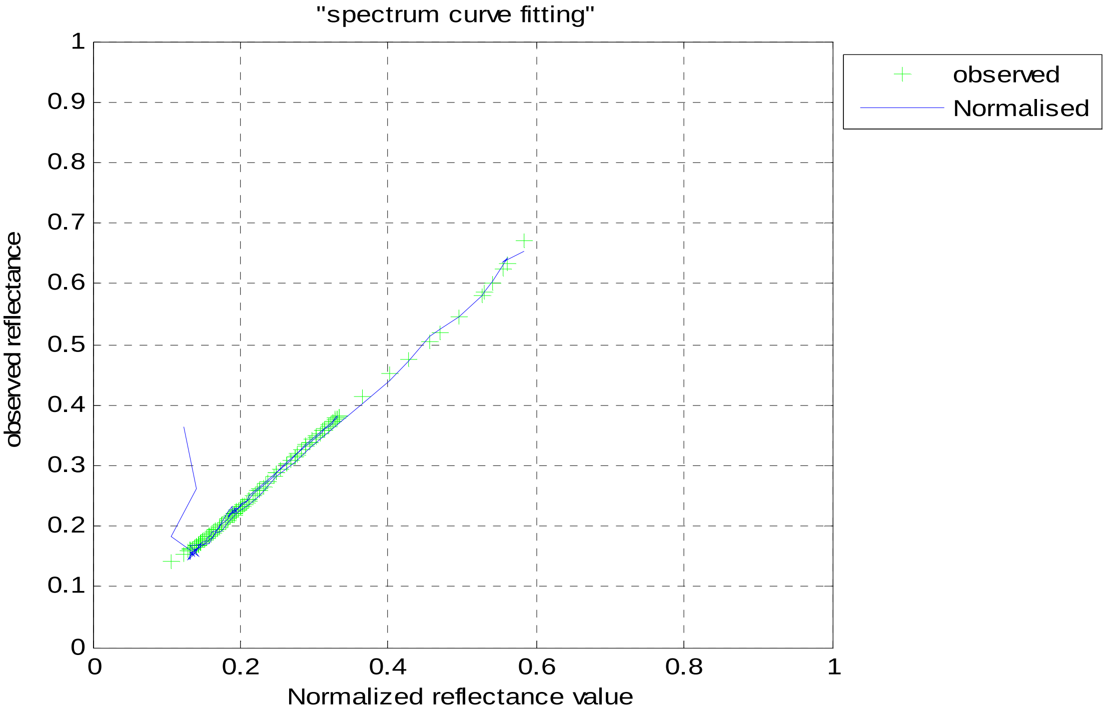
| | |
|---|---|
| SAMPLE TYPE | INDUSTRIAL SAMPLE |
| SAMPLE CONSTRUCTION | CYLINDERICAL |
| MATERIAL OF SAMPLE | PLASTIC |
| SURFACE TYPE | GLOSSY |
| PAINT MATERIAL PROPERTIES | NORMAL |
| SAMPLE THICKNESS | 1 mm(Approximately) |
| SAMPLE DIMENSION | 1 meter in length(approximately) |
| INSTRUMENT | PR 705 Radiometer |
| GEOMETRY | BI-DIRECTONAL |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | D65 |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 2 nm |
| MEASUREMENT RANGE | 380 to 780 nm |
| NUMBER OF SAMPLE POINTS MEASURED | 5 |
| MAXIMUM REFLECTANCE VALUE | 0.5830at 780 nm (average value) |
| MINIMUM REFLECTANCE VALUE | 0.1069 at 384 nm (average value) |
| STANDARD DEVIATION | 0.095346 |
| MAXIMUM ERROR VALUE (Difference Value between measured and average or residual) | 0.2115 at transition point |



Measured and average Reflectance curve of opaque paint sample

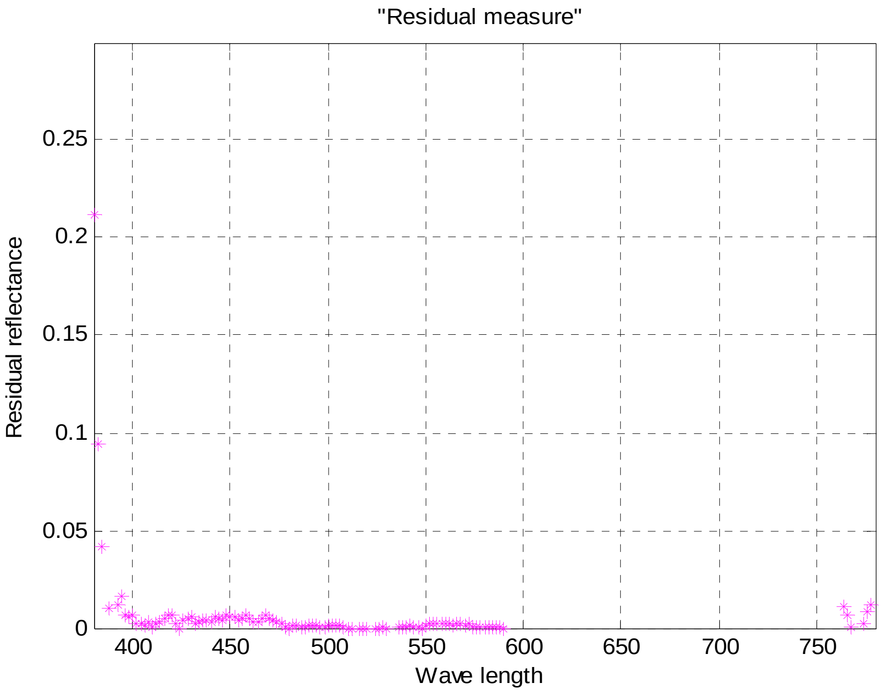
Figure 4.13

In the above curve, we have seen the difference between the measured value and average value. In such case, we have to do analysis that how much they differ. For this purpose, as mentioned above the author has applied Curve fitting technique .By this technique, one can find a curve which matches a series of data points and possibly other constraints. Least square is one method to fit curve method. It is a mathematical optimization technique that attempts to find a "best fit" to a set of data by attempting to minimize the sum of the squares of the ordinate differences (called *residuals*) between the fitted function and the data. [10]. The curve fitting can be visualized in figure 4.4. In this figure, it can be seen clearly the observed reflectance points (mean reflectance values) are fitted with the curve of normalised measured reflectance values. Again, some errors are traced in transition points.To find out the differnce in values between the calculated and measured reflectance, the author has calculated residual and plotted it with repect to wavelength which we can see in figure 4.5. The figure shows very nominal difference in calculated and measured reflectance values except in transition region.



Curve fitting of measured and average reflectance

Figure 4.14



Error measurement between measured and average reflectance value

Figure 4.15

### 4.5 MEASURING TRANSMITTANCE:

The principle of Physics for transmittance is same as the reflectance. So, transmittance is defined as the ratio of the transmitted light to incident light under specified geometric condition [2]. In equation form, $T = \frac{I_T}{I_o}$ where $I_o$ is the intensity of incident light and $I_T$ is the intensity of transmitted light.

Measurement of transmittance is vital to identify color of transparent material. It gives straight forward result by the fact that the color of a transparent material depends on what region of spectrum it is transparent in and what other color it absorbs. For example, blue transparent material is very transparent in the blue region of the spectrum but absorbent in the yellow-orange red region. So, while measuring transmittance, we also have to take account of another factor known as absorbance.

Two famous laws, known as Beer and Lambert laws describes us in a well manner about the transmission and absorption of light of a transparent material. Beer's law states that the absorption of light is proportional to the number of absorbing particles (molecules) in its path[3]. This means for a given path length, the amount of light transmitted decreases with the concentration of light absorbing particles. Lambert's law states that the layers of equal thickness of the same substance transmit the same fraction of the incident monochromatic radiation, what ever its intensity. This implies that transmittance of light varies exponentially as it passes through an absorbing medium [3].

Mathematically, we can express Beer-Lambert law in logarithmic form

$$\log\frac{I_o}{I_T} = \log\frac{1}{T} = abc = A$$

Where, $I_o$ = Incident light intensity

$I_T$ = Light intensity transmitted

$T$ = Transmittance

$a$ = absorption coefficient

$b$ = light path length

c= concentration of light absorbing particles, $A$ = absorbance

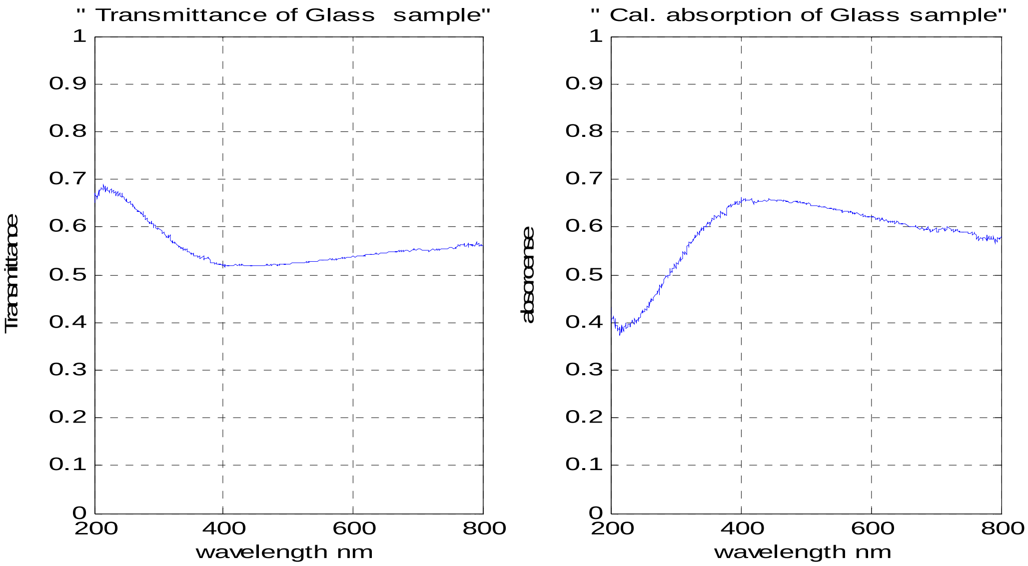
### 4.5.1 MEASUREMENT OF TRANSMITTANCE OF SOME SAMPLES:

Sample 1:

<u>TECHNICAL DATA</u>:

| | |
|---|---|
| SAMPLE TYPE | HOUSE HOPLD SAMPLE |
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | GLASS |
| SURFACE TYPE | GLOSSY |
| PAINT MATERIAL PROPERTIES | NORMAL |
| SAMPLE THICKNESS | LESS THAN 1 mm(Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | PERKIN-ELMER LAMBDA UV |
| GEOMETRY | SPHERE |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | DEUTERIUM LAMP (ULTRA-VIOLET REGION),<br>TUNGSTEN LAMP (VISIBLE REGION), |

| | |
|---|---|
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 2 nm |
| MEASUREMENT RANGE | 200 to 800 nm |



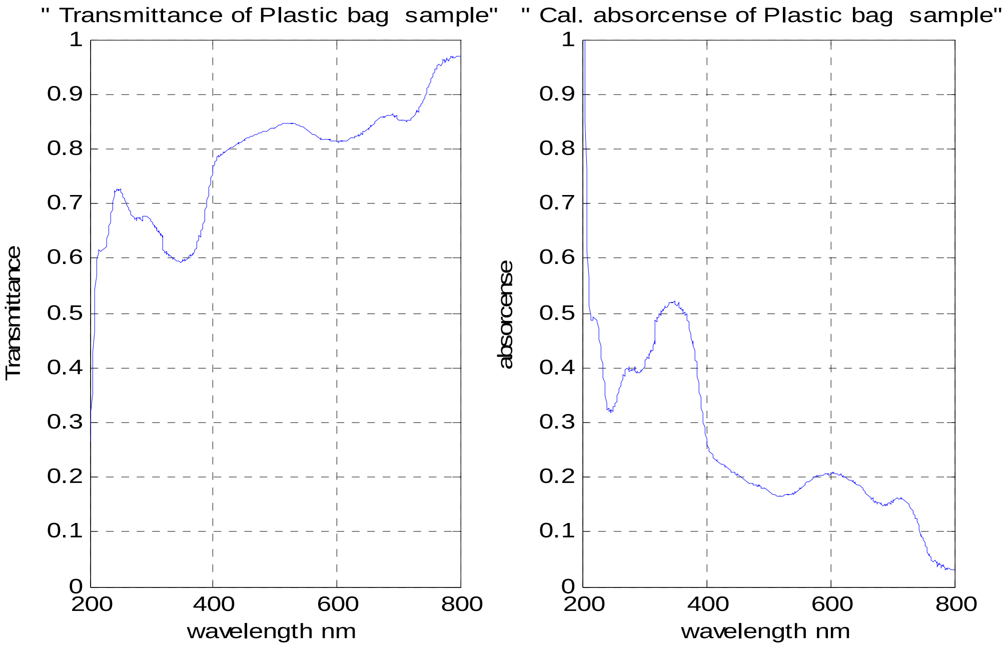
Transmittance and calculated Absorption of glass

Figure: 4.16

## Sample 2

TECHNICAL DATA

| | |
|---|---|
| SAMPLE TYPE | HOUSE HOPLD SAMPLE |
| SAMPLECONSTRUCTION | ARBITARY |
| SAMPLE MATERIAL | PLASTIC |
| SURFACE TYPE | GLOSSY |
| MATERIAL PROPERTIES | NORMAL |
| SAMPLE THICKNESS | 1 micron (Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | PERKIN-ELMER LAMBDA UV |
| GEOMETRY | SPHERE |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | DEUTERIUMLAMP (ULTRAVIOLETREGION), TUNGSTEN LAMP (VISIBLE REGION), |
| STRAY LIGHT | NEGLIGIBLE |
| BANDWIDTH | 2 nm |
| MEASUREMENT RANGE | 200 to 800 nm |



Transmittance and calculated Absorption of plastic bag

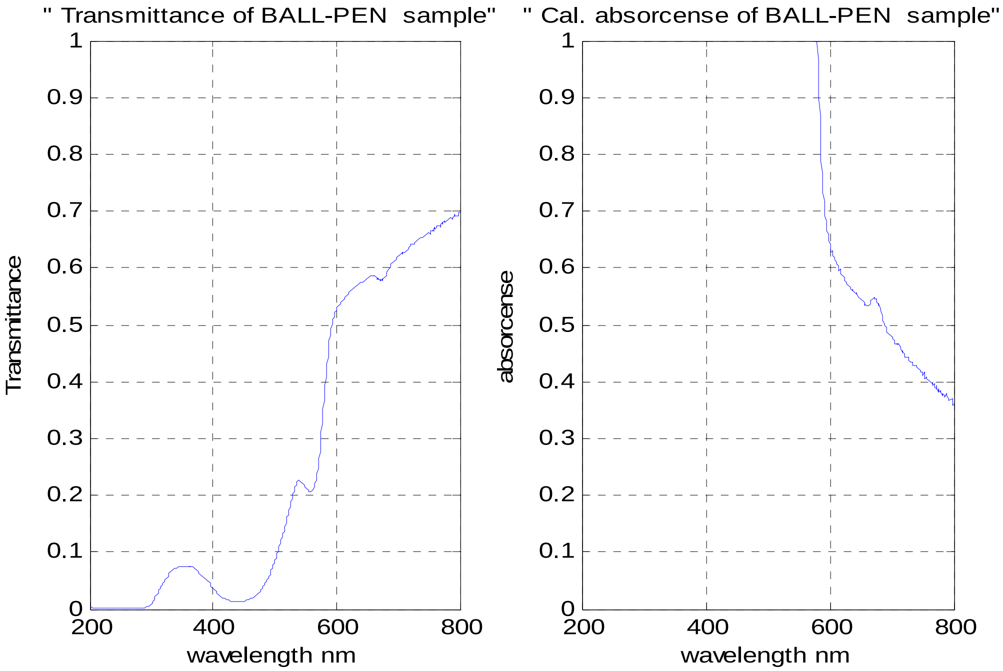
Figure 4.17

Sample 3

TECHNICAL DATA

| | |
|---|---|
| SAMPLE TYPE | HOUSE HOPLD SAMPLE (BALL PEN COVER) |
| SAMPLECONSTRUCTION | CYLINDERICAL |

| | |
|---|---|
| SAMPLE MATERIAL | PLASTIC |
| SURFACE TYPE | GLOSSY |
| PAINT MATERIAL PROPERTIES | NORMAL |
| SAMPLE THICKNESS | 1 micron (Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | PERKIN-ELMER LAMBDA UV |
| GEOMETRY | SPHERE |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | DEUTERIUMLAMP (ULTRAVIOLETREGION), TUNGSTEN LAMP (VISIBLE REGION), |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 2 nm |
| MEASUREMENT RANGE | 200 to 800 nm |



Transmittance and calculated Absorption of pen holder

Figure 4.18

Sample 4

<u>TECHNICAL DATA</u>:

SAMPLE TYPE PIGMENT PANEL (BLUE)

| | |
|---|---|
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | (PLASTIC) |
| SURFACE TYPE | GLOSSY |
| MATERIAL PROPERTIES | TRANSLUCENT |
| SAMPLE THICKNESS | 1 mm(Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | SPECTROPHOTOMETER CM-3600D |
| GEOMETRY | INTEGRATING SPHERE |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | TUNGSTEN LAMP (VISIBLE REGION), |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 20 nm |
| MEASUREMENT RANGE | 400 to 700 nm |

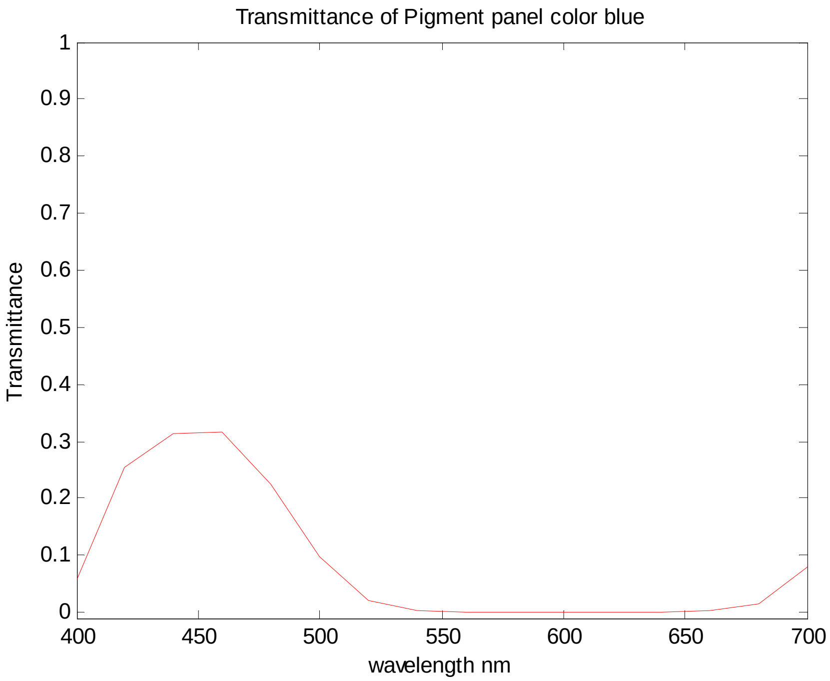


Figure 4.19

Transmittance of semi-transparent material (blue pigment)

Sample 5

TECHNICAL DATA:

| | |
|---|---|
| SAMPLE TYPE | PIGMENT PANEL (BLUE) |
| SAMPLE CONSTRUCTION | RECTUANGULAR |
| MATERIAL OF SAMPLE | (PLASTIC) |
| SURFACE TYPE | GLOSSY |
| MATERIAL PROPERTIES | TRANSLUCENT |
| SAMPLE THICKNESS | 1 mm(Approximately) |
| SAMPLE DIMENSION | |
| INSTRUMENT | SPECTROPHOTOMETER CM-3600D |
| GEOMETRY | INTEGRATING SPHERE |
| APERATUR SIZE | 10 degree |
| ILLUMINANT | TUNGSTEN LAMP (VISIBLE REGION), |
| STRAY LIGHT | NEGLIGIBLE |
| MEASUREMENT BANDWIDTH | 20 nm |
| MEASUREMENT RANGE | 400 to 700 nm |

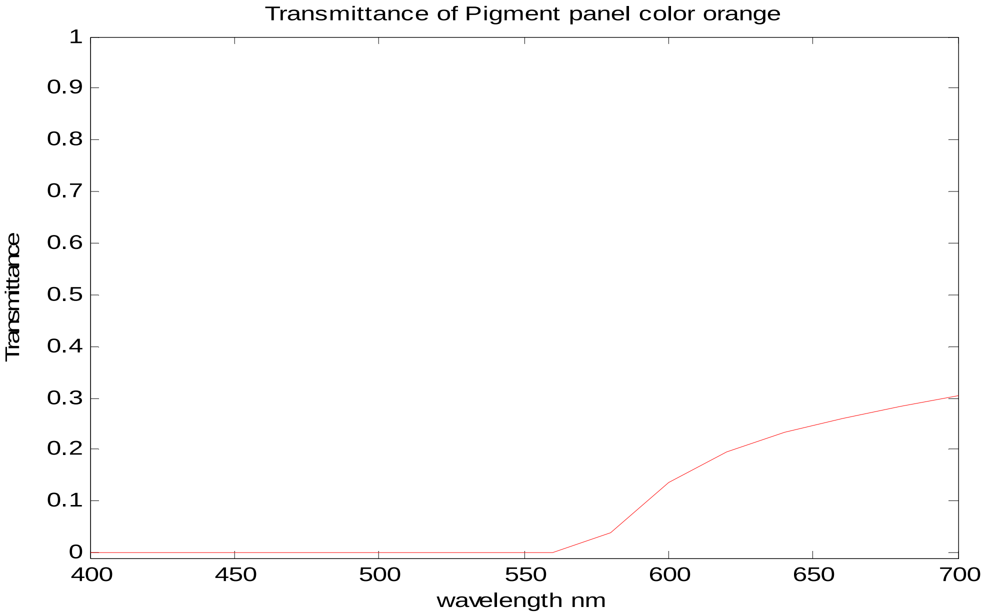


Figure 4.20

Transmittance of semi-transparent material (orange pigment)

## 4.6 MEASURMENT ACCURACY:

In general sense, accuracy of measurement is generally determined by comparing the instrumental values to a known standard. Unfortunately, in color measurement, no such standard exists. However, some techniques are used to evaluate accuracy of instrumental measurement for color measurement of materials or samples. These are as follows:

Calibration: Calibration is the process of adjusting an instrument such that its readings reproduce a national or international scale. Using reflectance factor is a good example; if an instrument reports a value of 100 % the sample has reflectance equal to that of the perfect reflecting diffuser. Two transfer standards are used to calibrate the photometric scale, a white and a black. The first is used to transfer the scale at close to 100 % reflectance factor and the last is used to transfer the scale at 0 % reflectance factor.

Repeatability: The repeatability of an instrument is how close the same operator, using the same measurement procedure, can duplicate the measurement of a test sample on the same instrument over a short period of time. This provides a good measure of the instrument's short term stability. Everyone who uses color measuring instruments should monitor their instruments short term repeatability.

Reproducibility: The reproducibility of an instrument is how close the measurements of a single test sample are when the same measurement procedures are used but when the operator, the instrument and the laboratory are changed. it provides a measure of a single instruments long term stability.

By considering above factors one can measure accurately color of a sample. But, comparing measurement results of similar instruments from different instruments is difficult because two different manufacturers may use two different sets of weighting factors to calculate tristimulus values which will appear as differences in accuracy. To check such problem, it is necessary to calculate standard deviation of the reflectance values of the test sample. The large standard deviation in the reflectance value derives partly from the varying bandwidths of the different instruments. [1,2,7].

# CHAPTER FIVE

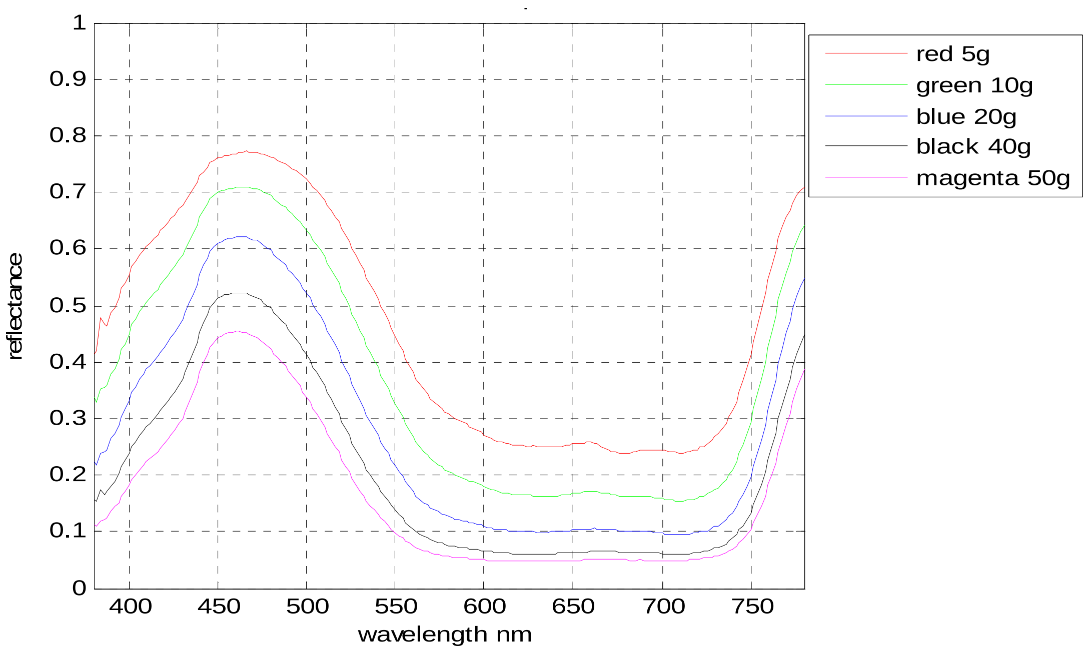
# 5. EXPERIMENTAL ANALYSIS OF COLOR BY KUBELKA MUNK MODEL:

This chapter is mainly concerned with the author's work on the application of Kubelka-Munk theory. The results are shown in graphical forms.

## 5.1 OPAQUE MATERIAL:

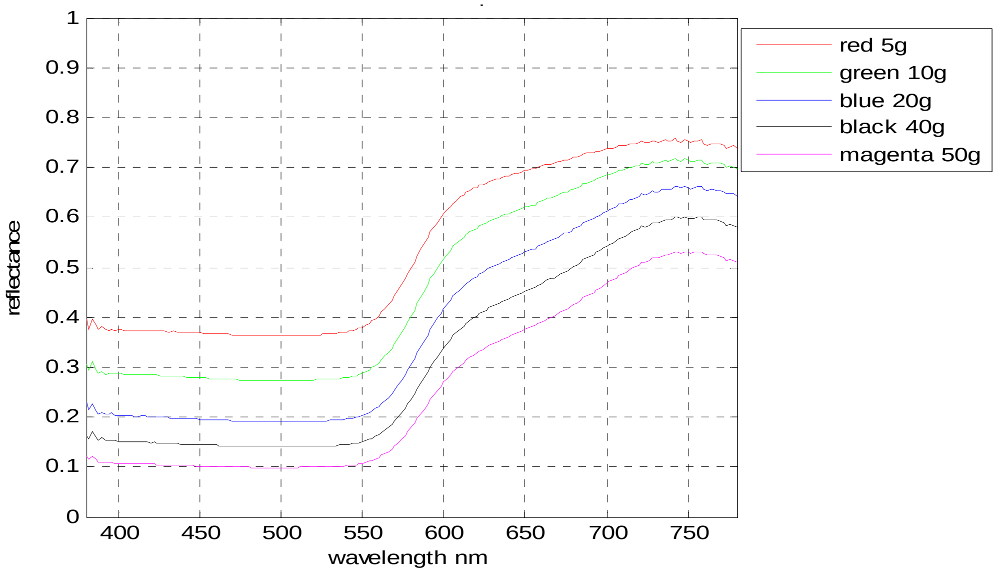
The author has applied Kubelka-Munk model as mentioned in chapter 3 to some industrial opaque paint samples to reproduce reflectance curves by mixing different concentration. The different concentration values of pigments are calculated theoretically by spline interpolation. Again, the author calculated mean and standard deviation of theoretical mixture reflectance curves and compared them to actual measured mixture reflectance curves.

The reflectance of curves of different pigments measured from Bi-directional geometry looks as follows:



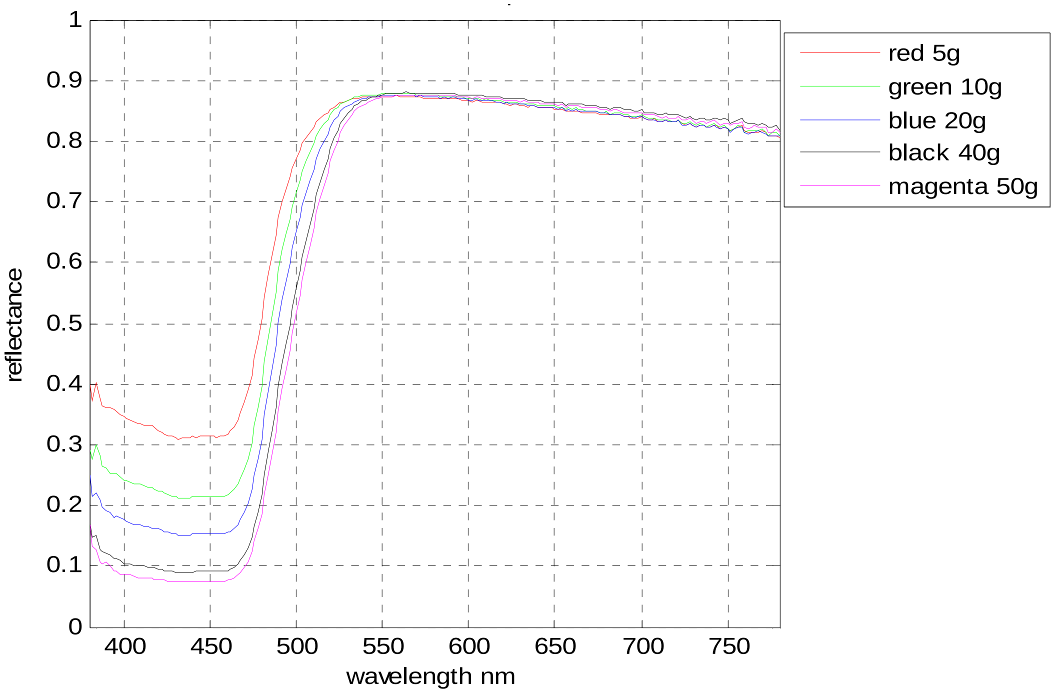
Reflectance of pigment A

Figure 5.1



Reflectance of pigment B

Figure 5.2

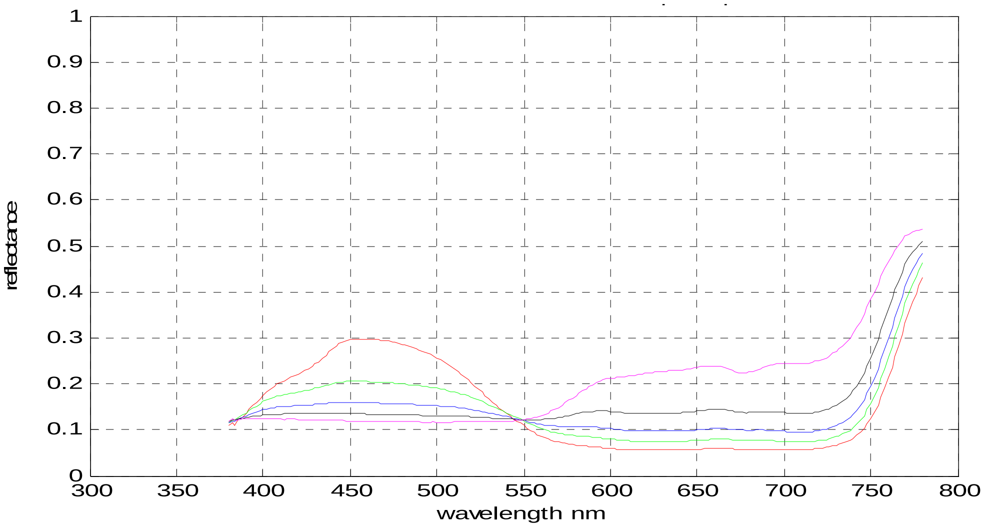


Reflectance of pigment C

Figure 5.3

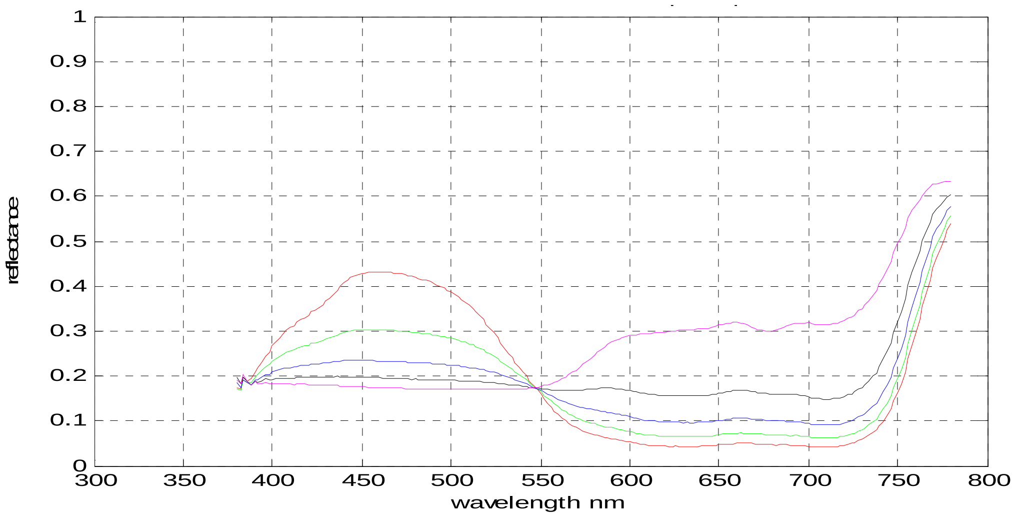
In all mixture types explained above have concentrations different than measured pigments concentrations. The first step is to calculate new concentrations for the pigments. As mentioned above, the author has applied interpolation technique to obtain new concentrations of pigments. The calculated reflectance curves by using Kubelka-Munk and Measured reflectance curves of three types of mixtures mentioned above are shown in figures below:

<u>Type1:</u>



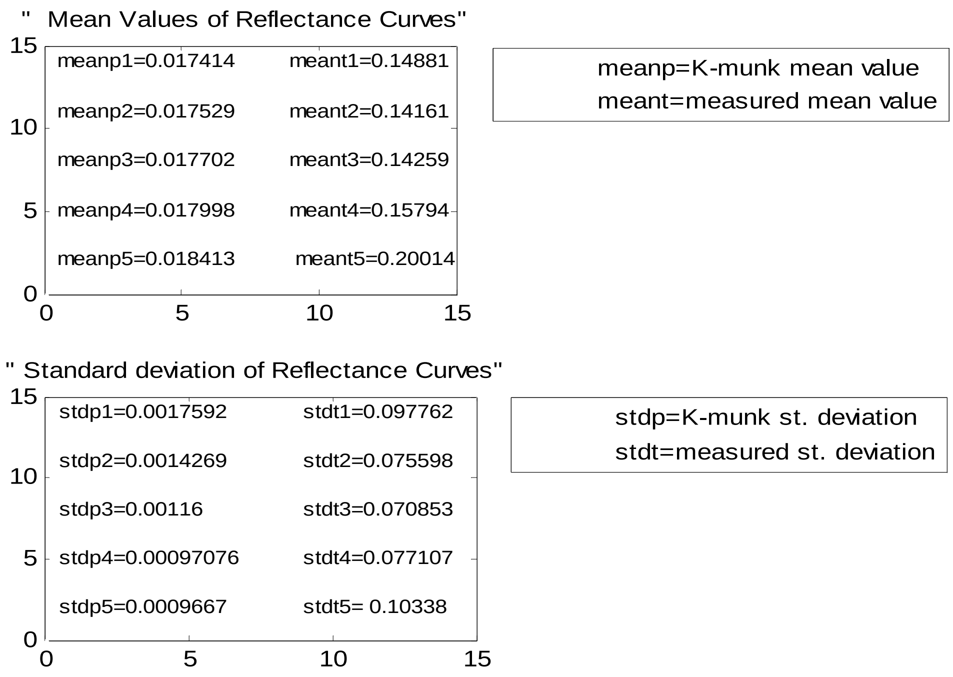
Measured Reflectance curves of different mixtures of colorants A and B

Figure 5.4



Kubelka-Munk (calculated) Reflectance curves of different mixtures of colorants A and B

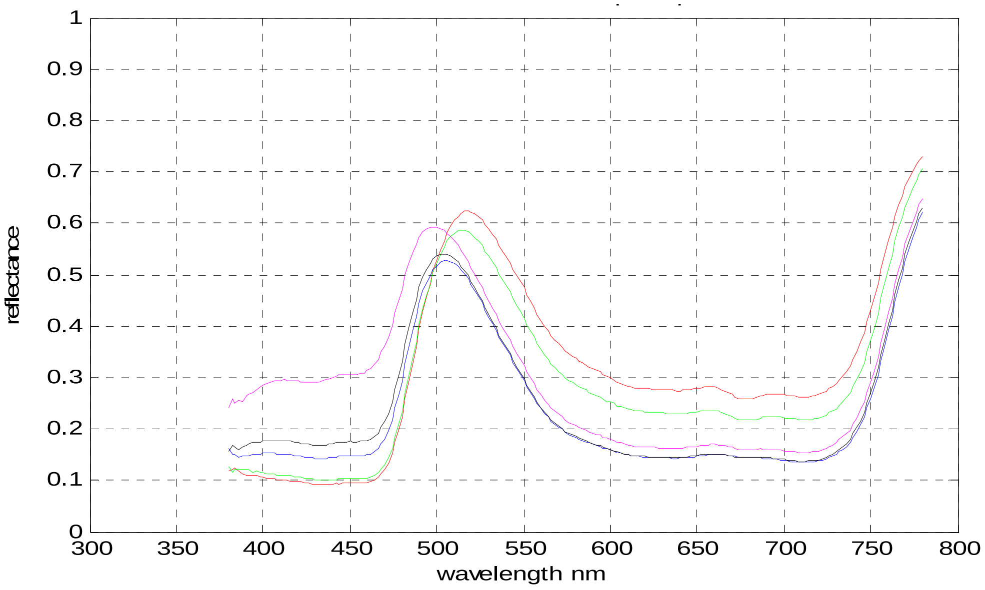
Figure 5.5



Mean and standard deviation values of Kubelka-Munk model reflectance and measured reflectance curves of colorants Ip33Ip38.

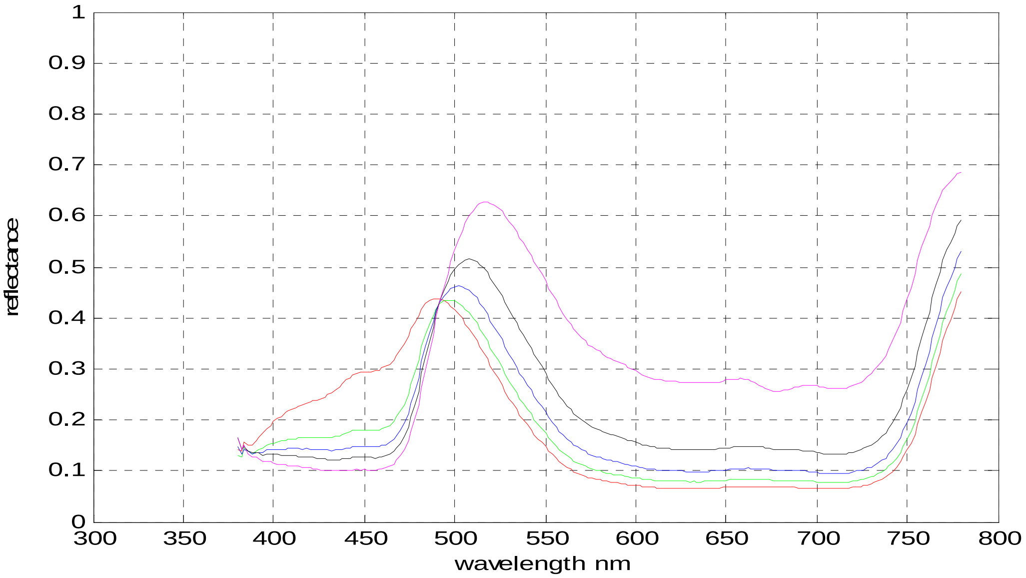
Figure 5.6

## Type 2:



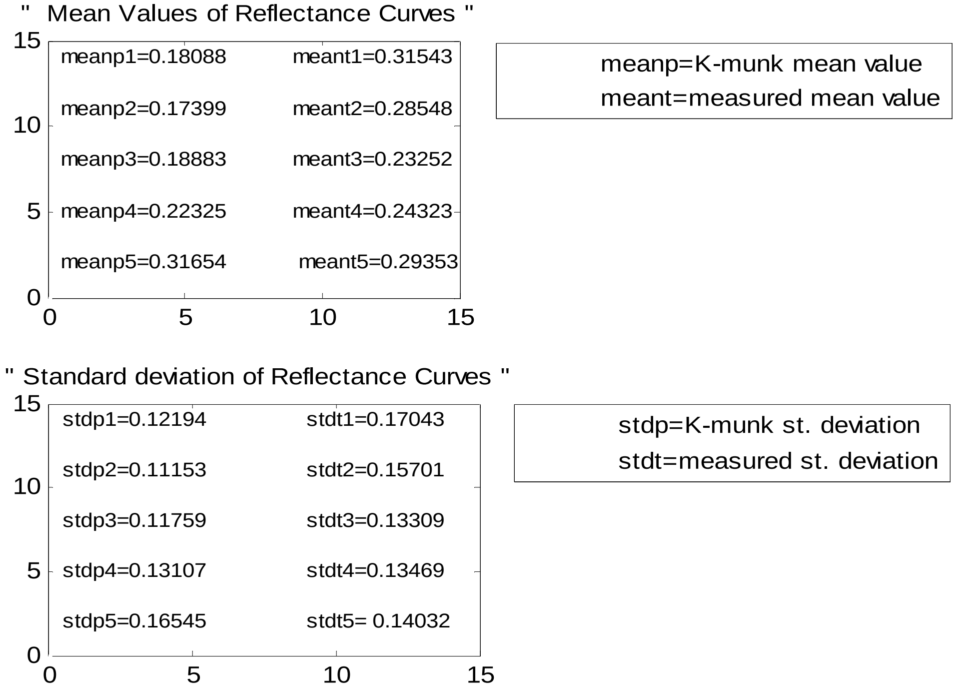
Measured Reflectance curves of different mixtures of colorants A and C

Figure 5.7



Kubelka-Munk (calculated) Reflectance curves of different mixtures of colorants A and C

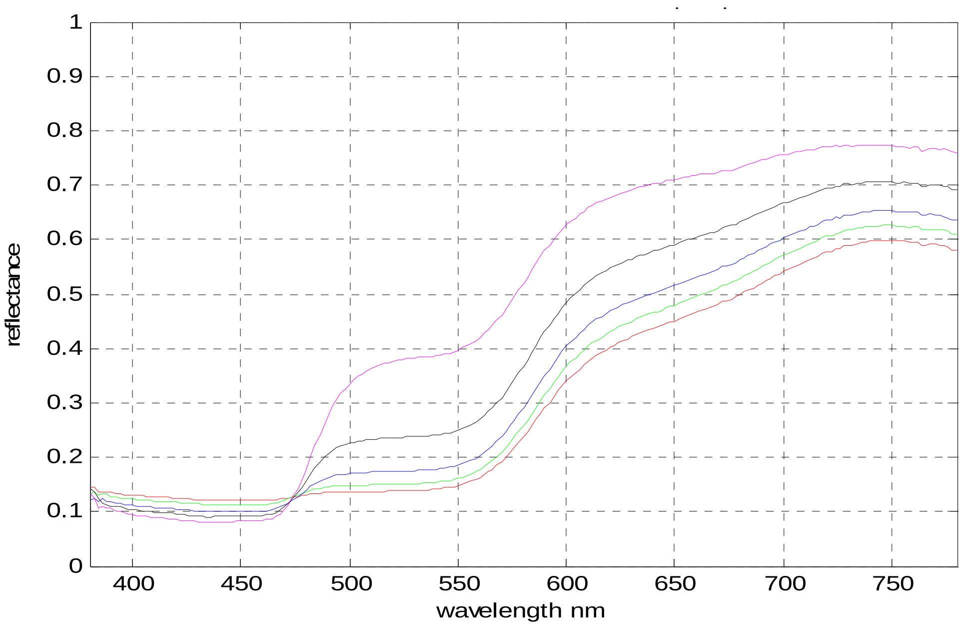
Figure 5.8



Mean and standard deviation values of Kubelka-Munk model reflectance and measured reflectance curves of colorants A and C.

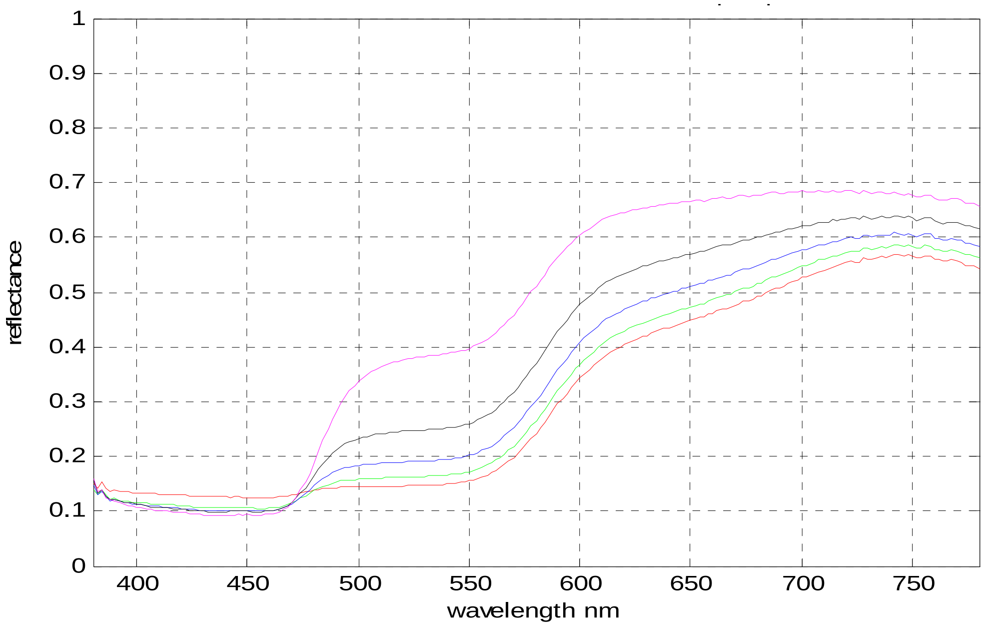
Figure 5.9

<u>Type 3</u>



Measured Reflectance curves of different mixtures of colorants B and C

Figure 5.10



Kubelka-Munk (calculated) Reflectance curves of different mixtures of colorants B and C

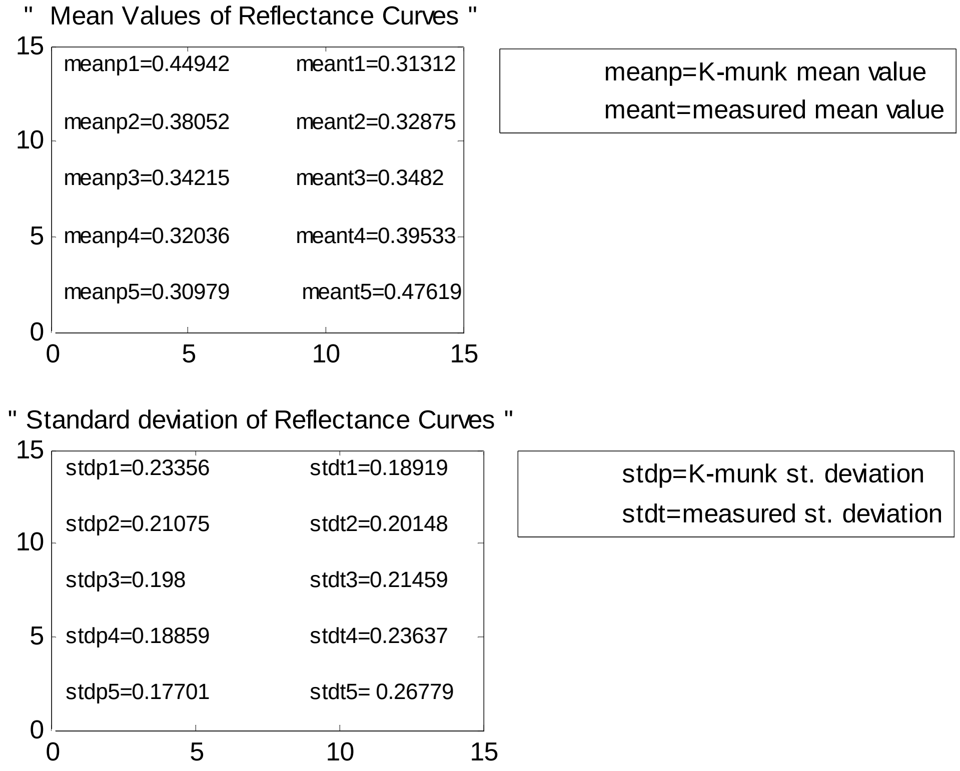

" Mean Values of Reflectance Curves "
meanp1=0.44942
meant1=0.31312
meanp2=0.38052
meant2=0.32875
meanp3=0.34215
meant3=0.3482
meanp4=0.32036
meant4=0.39533
meanp5=0.30979
meant5=0.47619
meanp=K-munk mean value
meant=measured mean value
0
5
10
15
0
5
10
15
" Standard deviation of Reflectance Curves "
stdp1=0.23356
stdt1=0.18919
stdp2=0.21075
stdt2=0.20148
stdp3=0.198
stdt3=0.21459
stdp4=0.18859
stdt4=0.23637
stdp5=0.17701
stdt5= 0.26779
stdp=K-munk st. deviation
stdt=measured st. deviation
0
5
10
15
0
5
10
15

Figure 5.11

Mean and standard deviation values of Kubelka-Munk model reflectance and measured reflectance curves of colorants B and C.

Figure 5.12

## 5.2 SEMI-TRANSPARENT MATERIAL:

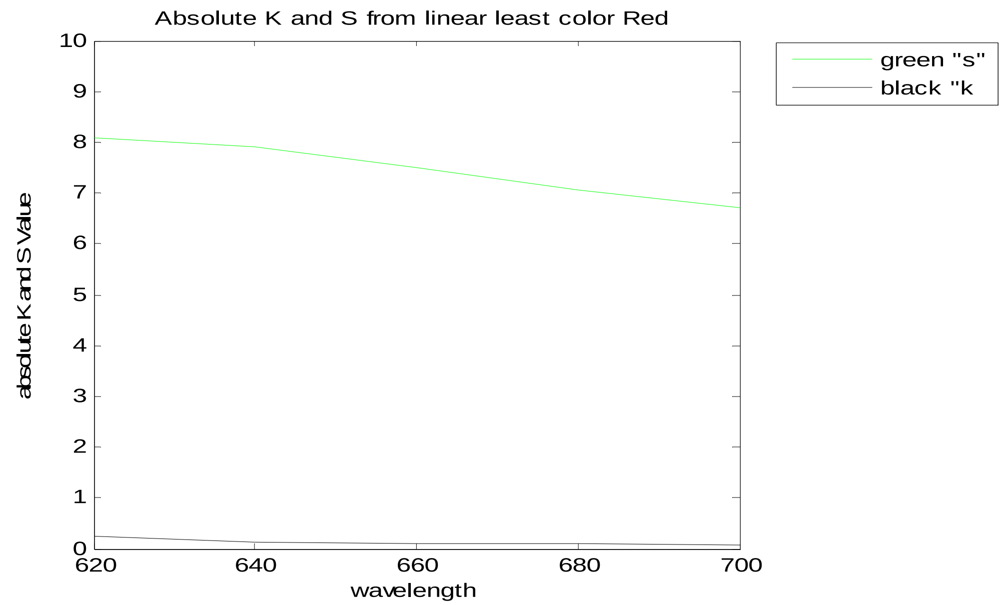
The author has applied Kubelka-Munk model described in the chapter 3 sub-sections 3.4 for translucent or semitransparent samples to calculate effective K and S values and described it as Reflectance technique. Similarly, Reflectance-Transmittance technique as described in chapter 3 subsection 3.6 has also applied to calculate effective K and S values. Absolute values of K and S are calculated from effective K and S values using Kubelka-Munk mixing laws as described in subsection 3.3. To approximate, different absolute K and S values of the same colorant of different concentrations samples linear least square technique is applied. The reflectance curves are calculated by using double constant Kubelka-Munk theory. Comparison between calculated reflectance and measured reflectance curves are done plotting on the same graph as well as reproducing RGB images of calculated and measured reflectance.

Absolute K and S values are also calculated using the method least square for opaque samples for reference study. Similarly, K and S values with relative to white are also calculated to study linearity of optical coefficients.

The figures below describes absolute K and S values, and calculated reflectance curves comparing with measured reflectance curves for some industrial semitransparent samples.

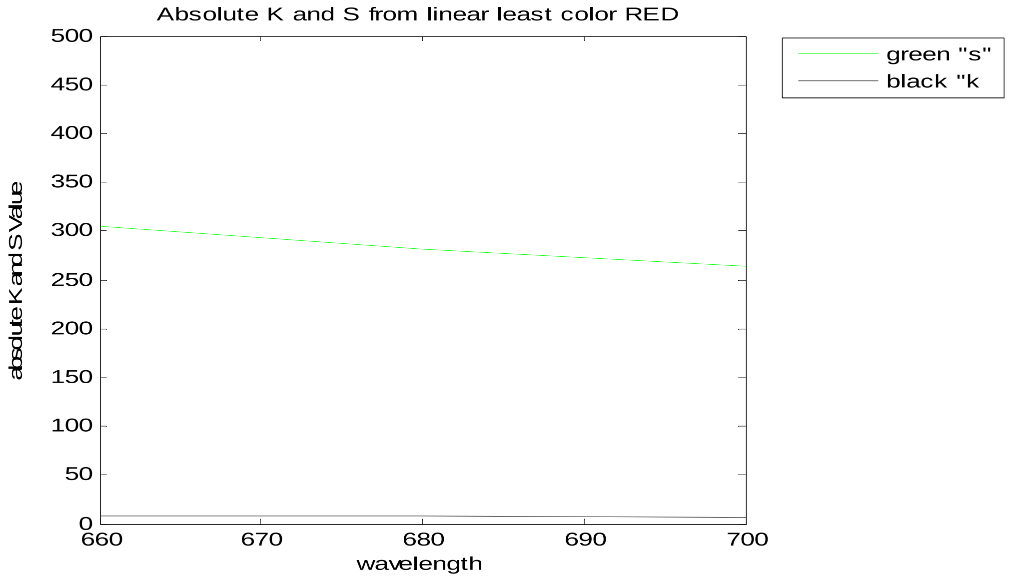
Type 1 : Red Colorant Sample

1. Figures of absolute K and S values from different methods:



Approximated Absolute K and S values from reflectance method for different concentrations of colorant red samples.

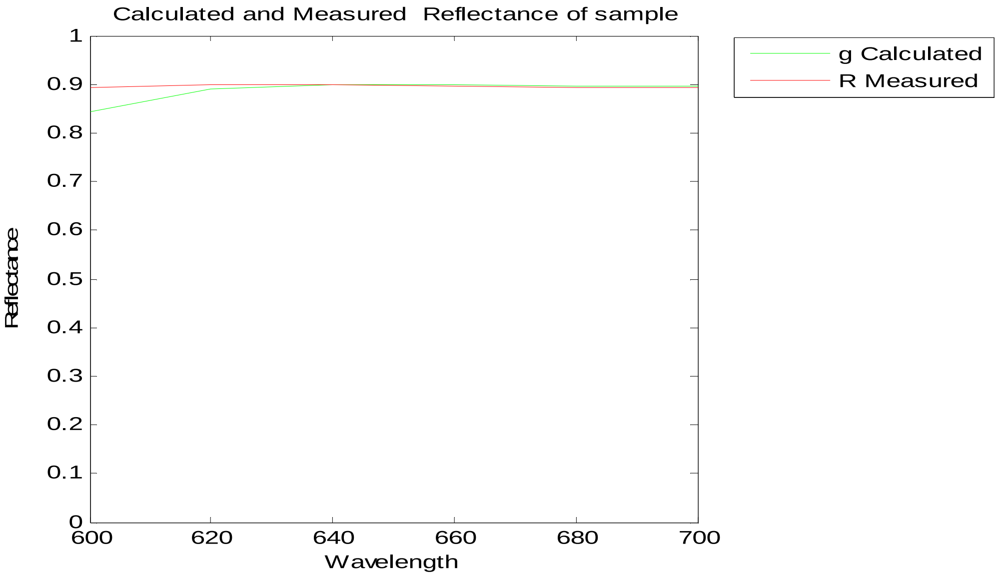
Figure 5.13



Approximated Absolute K and S values from reflectance-transmittance method for different concentrations of colorant red samples.

Figure 5.14

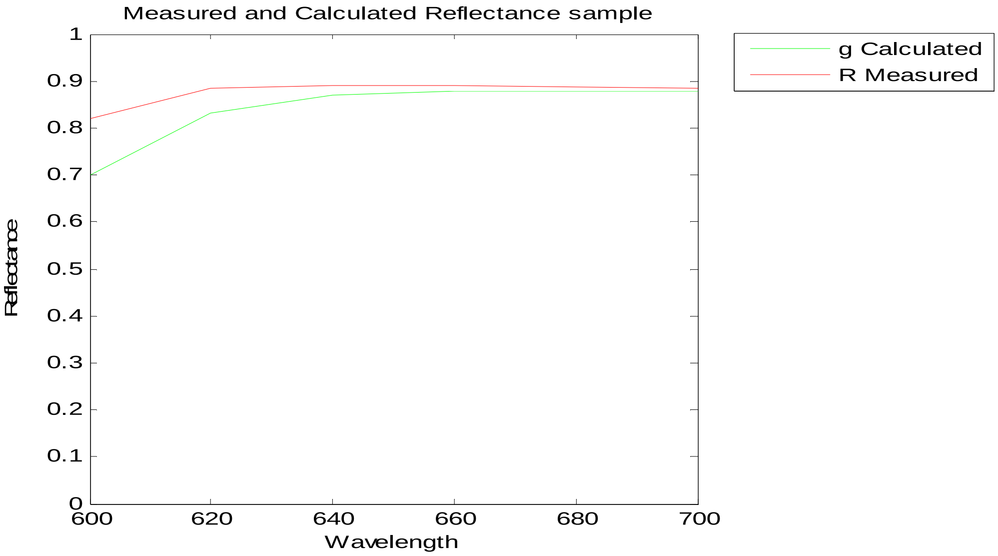
2. Figures of reproduced or calculated reflectance curves and measured or original reflectance curves



Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 2%)

(Using Absolute K and S values from reflectance method)

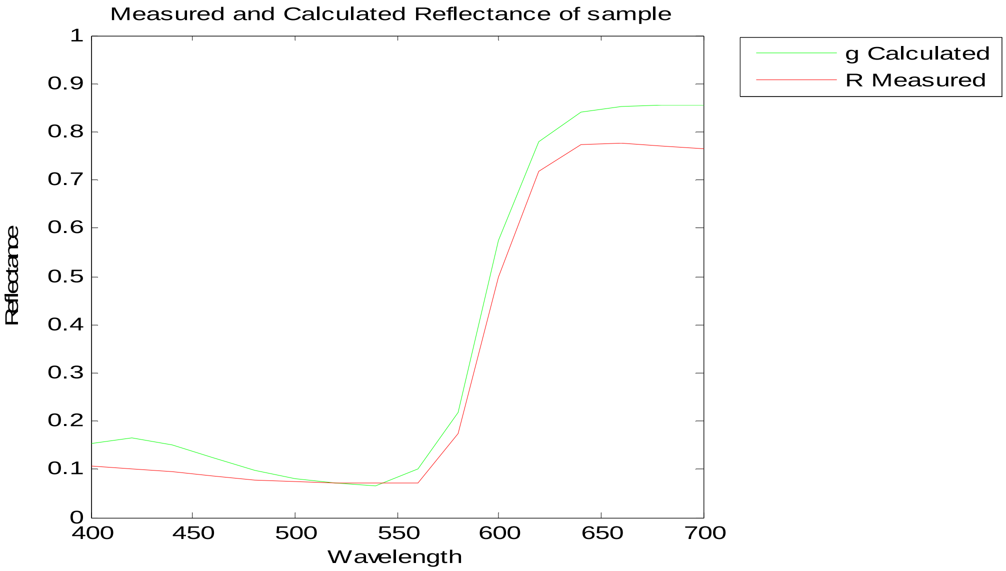
Figure 5.15



Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 15%)

(Using Absolute K and S values from reflectance method)

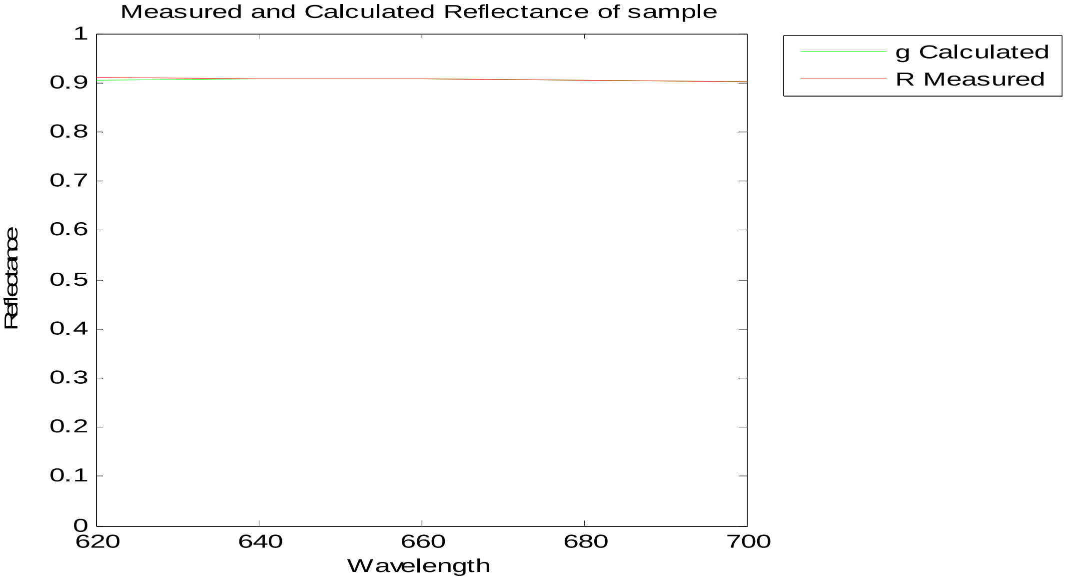
Figure 5.16



Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 85%)

(Using Absolute K and S values from reflectance method)

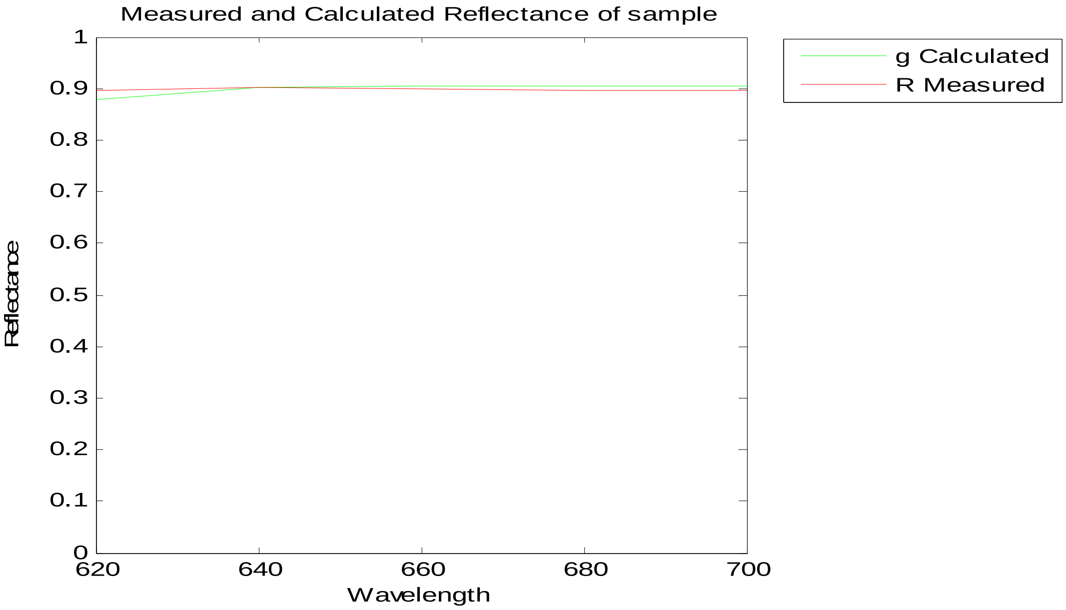
Figure 5.17



Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 2%)

(Using Absolute K and S values from reflectance-transmittance method)

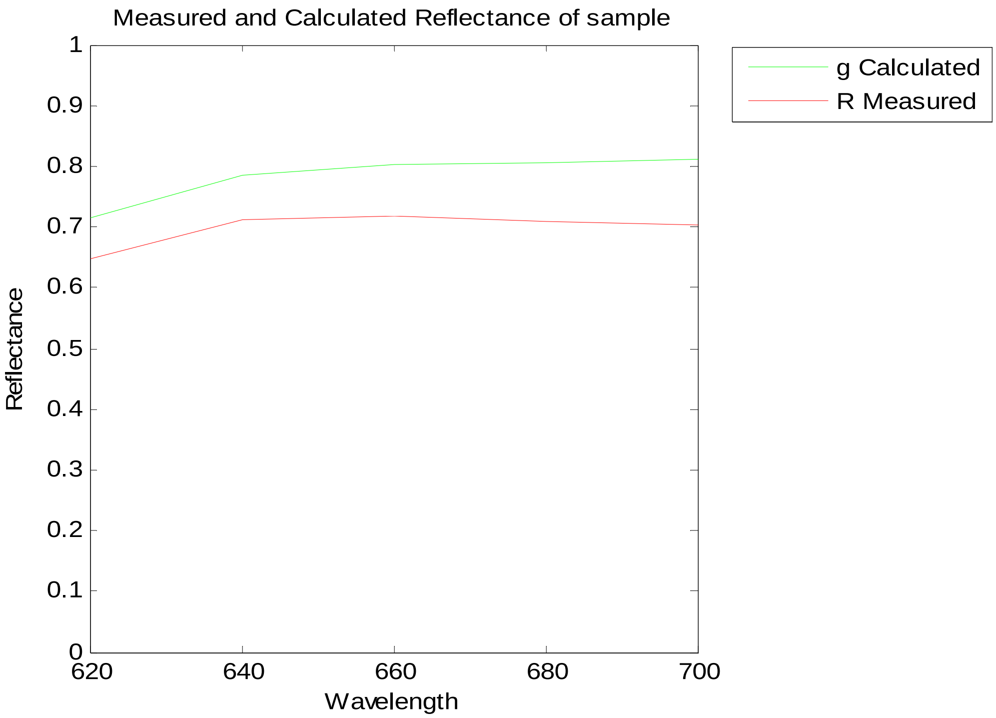
Figure 5.18



Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 15%)

(Using Absolute K and S values from reflectance-transmittance method)

Figure 5.19

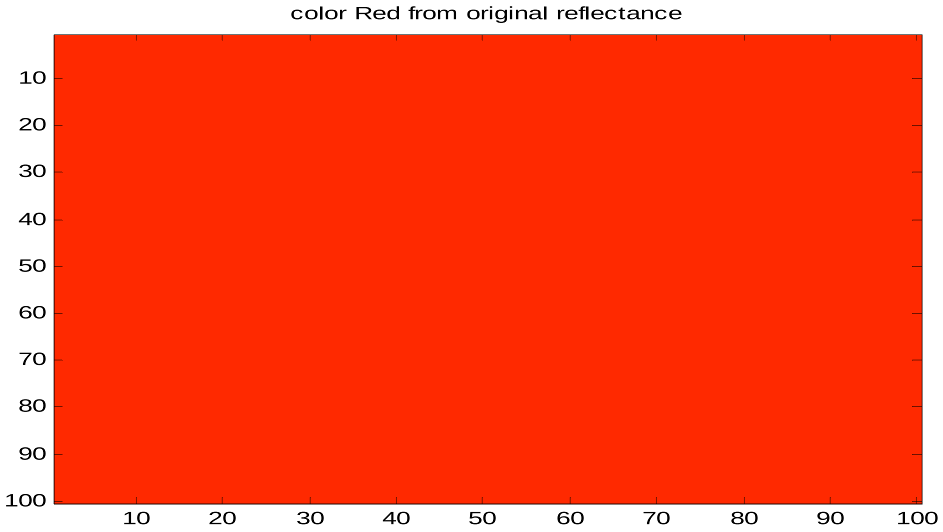


Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 85%)

(Using Absolute K and S values from reflectance-transmittance method)

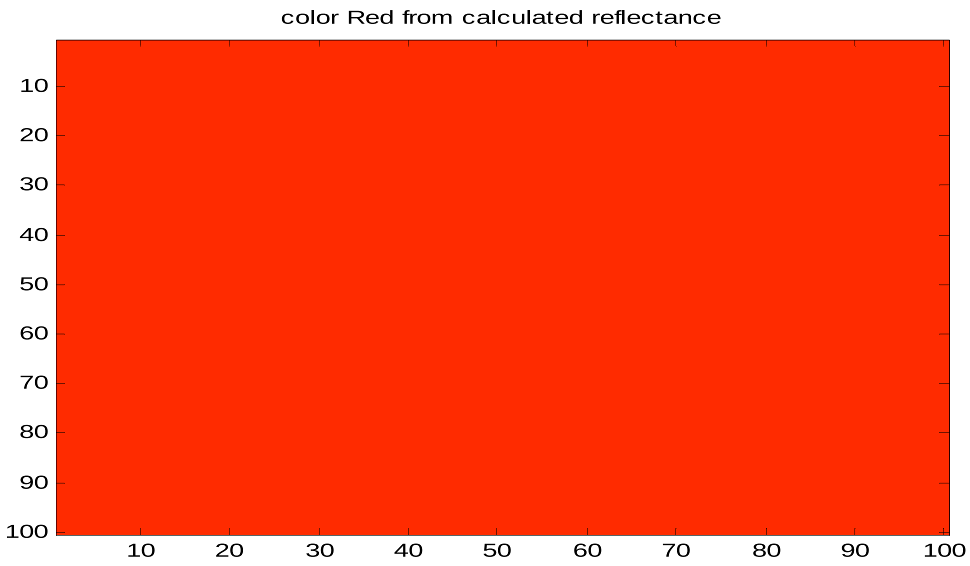
Figure 5.20

## 3. Figures of reproduced RGB image from reflectance



Original RGB image of colorant sample

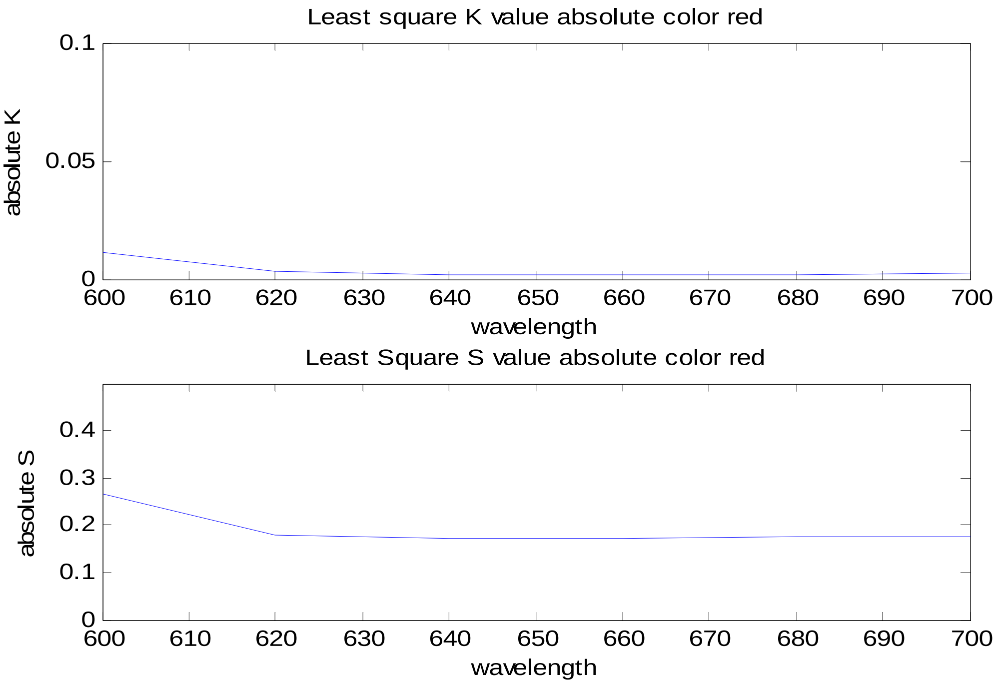
Figure 5.21



Reproduced or calculated RGB image of colorant sample

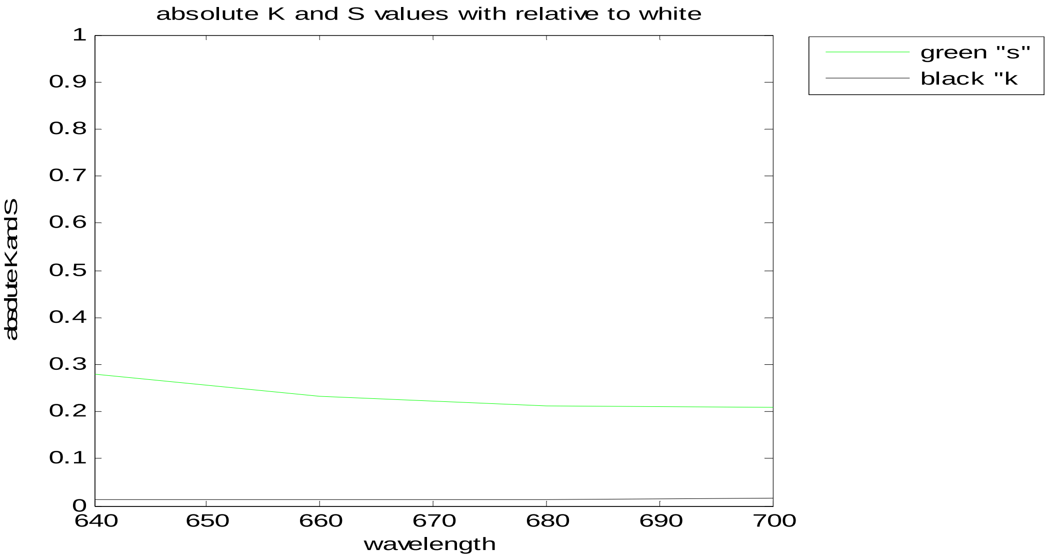
Figure 5.22

4. Figures of K and S values from method least square for opaque panels and with relative to white



Absolute K and S values from method least square for opaque panels

Figure 5.23

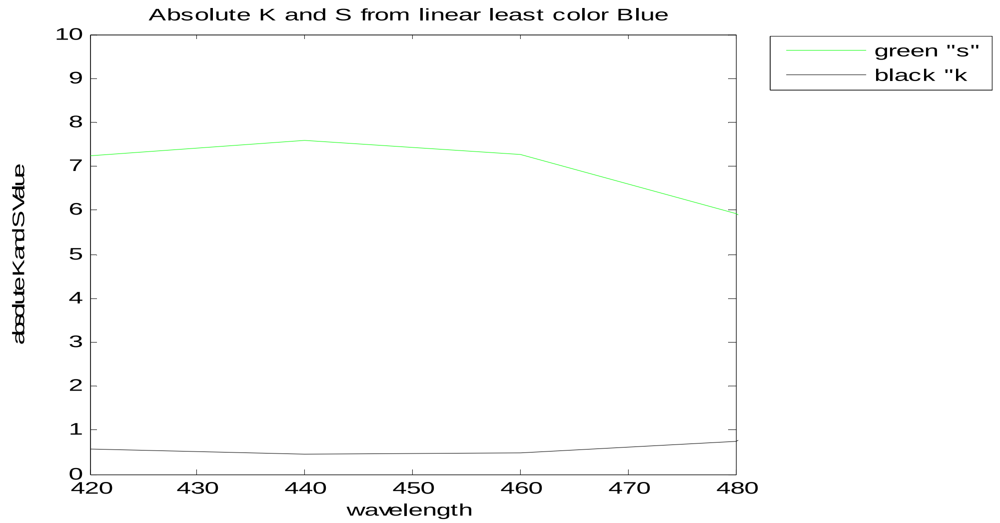


Absolute K and S values with relative to white colorant for opaque panels

Figure 5.24

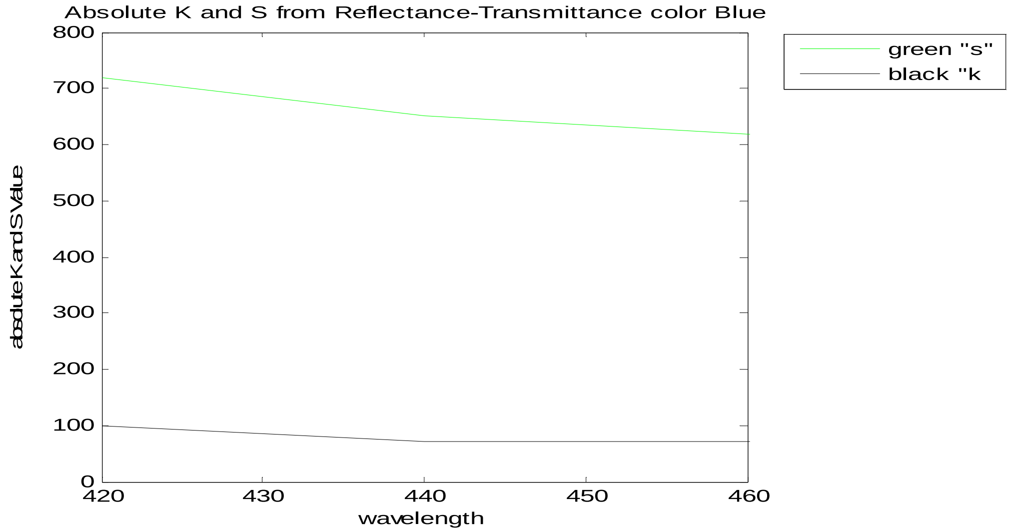
## Type 2 : Blue Colorant Sample

1. Figures of absolute K and S values from different methods:



Approximated Absolute K and S values from reflectance method for different concentrations of colorant blue samples.

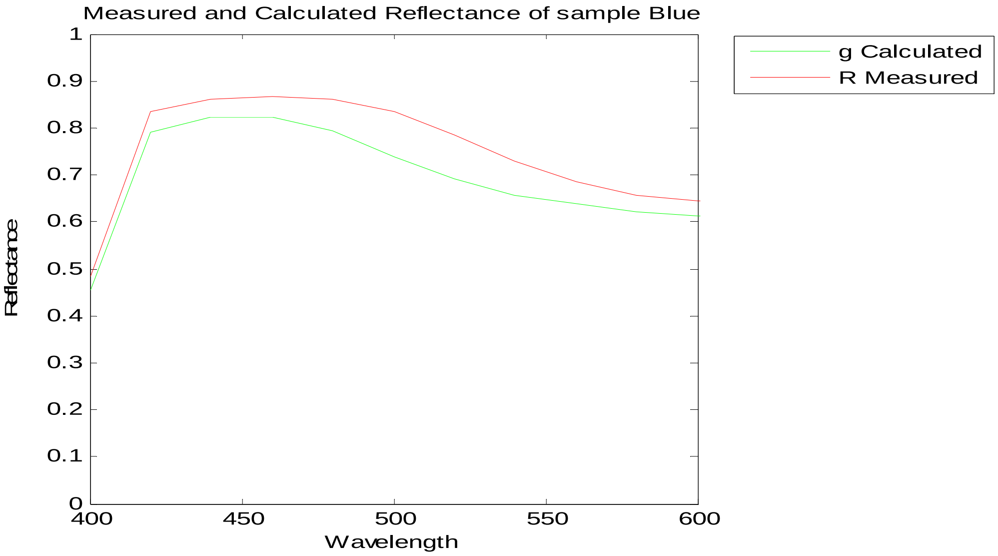
Figure 5.25



Approximated Absolute K and S values from reflectance-transmittance method for different concentrations of colorant red samples.

Figure 5.26

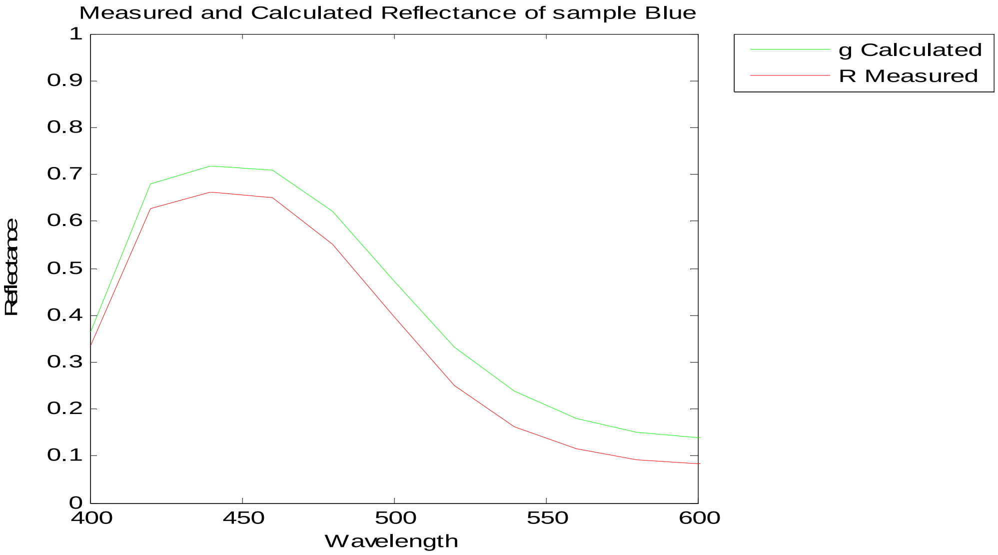
## 2. Figures of reproduced or calculated reflectance curves and measured or original reflectance curves



Calculated and Measured Reflectance curves of blue colorant sample (Concentration of colorant 7%)

(Using Absolute K and S values from reflectance method)

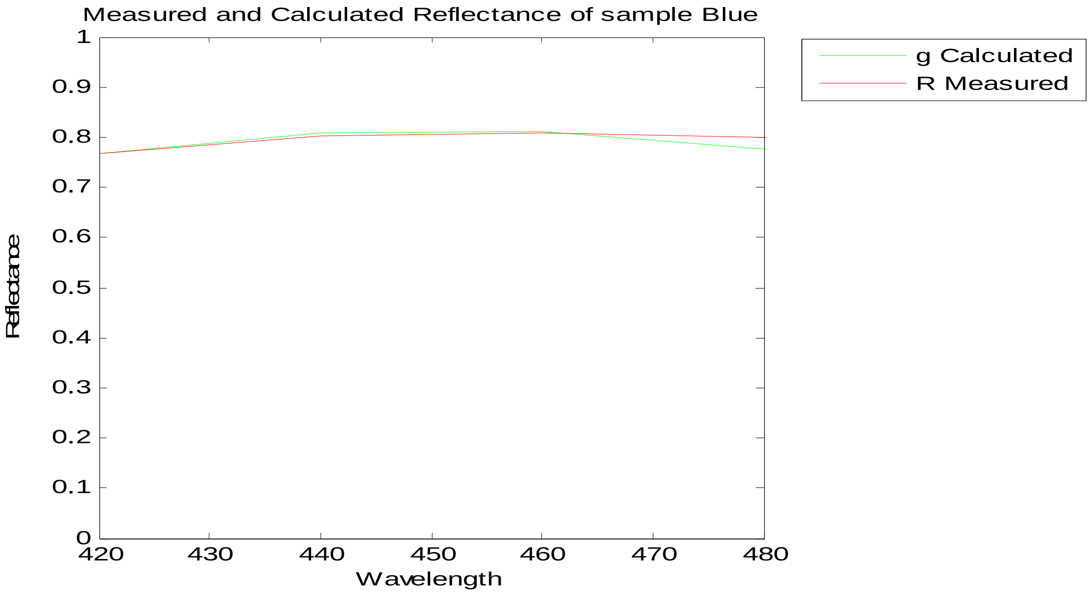
Figure 5.27



Calculated and Measured Reflectance curves of blue colorant sample (Concentration of colorant 79%)

(Using Absolute K and S values from reflectance method)

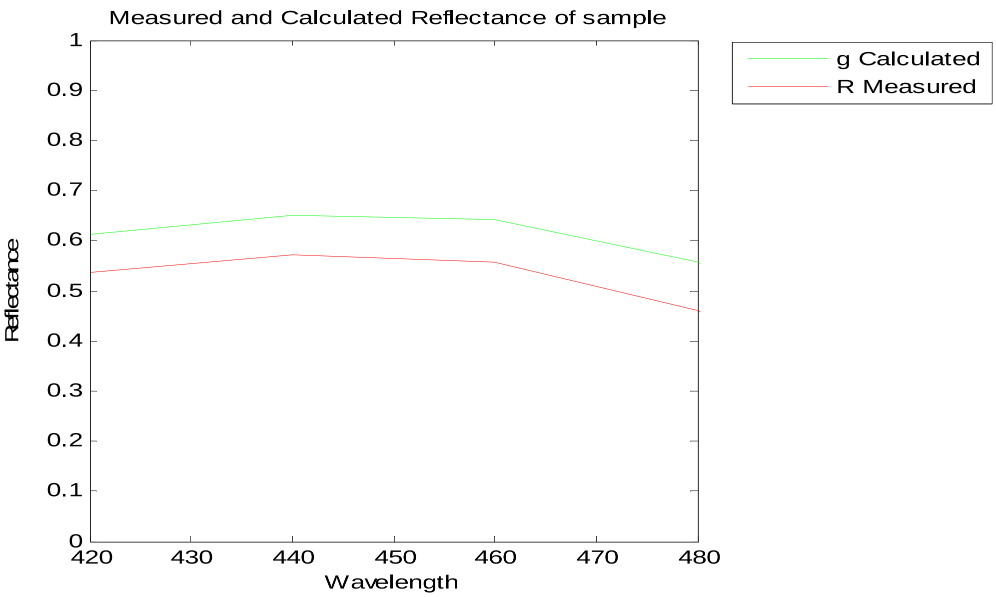
Figure 5.28



Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 7%)

(Using Absolute K and S values from reflectance-transmittance method)

Figure 5.29

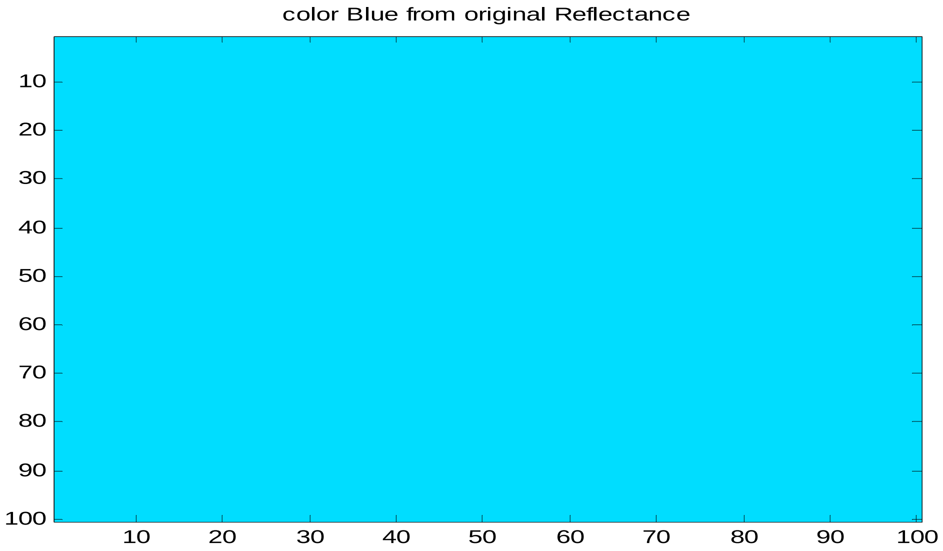


Calculated and Measured Reflectance curves of red colorant sample (Concentration of colorant 79%)

(Using Absolute K and S values from reflectance-transmittance method)

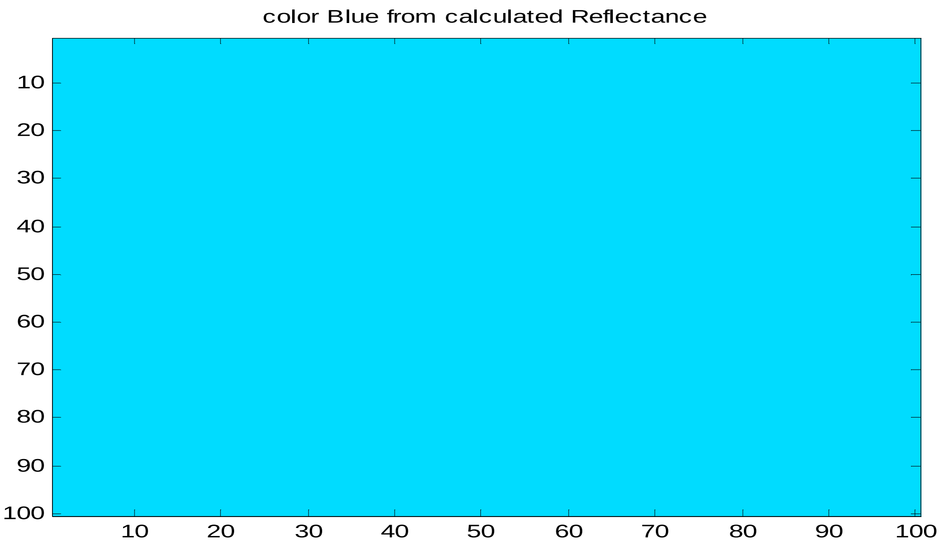
Figure 5.30

## 3. Figures of reproduced RGB image from reflectance



Original RGB image of colorant sample

Figure 5.31

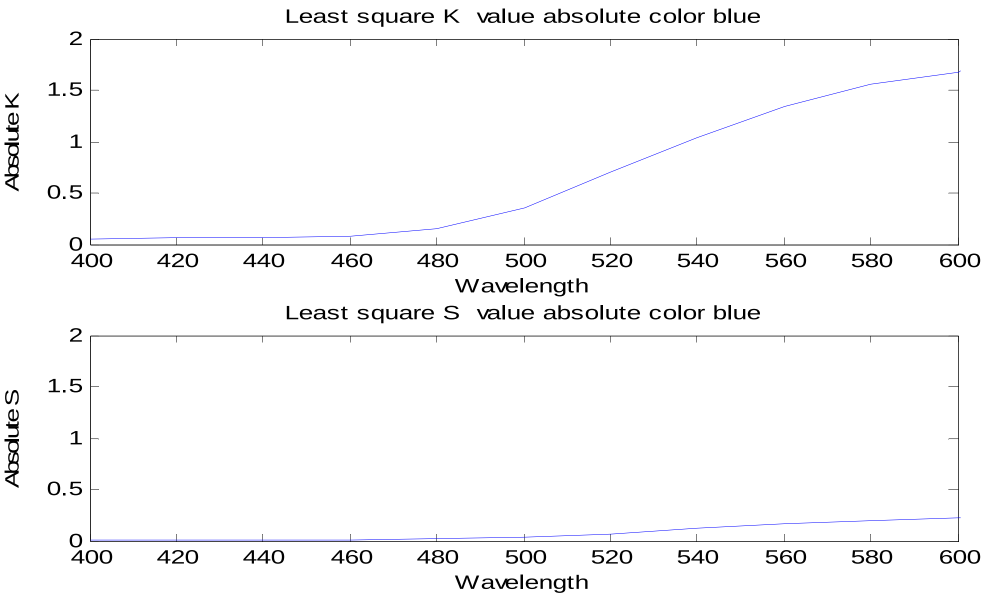


Fi

Reproduced or calculated RGB image of colorant sample

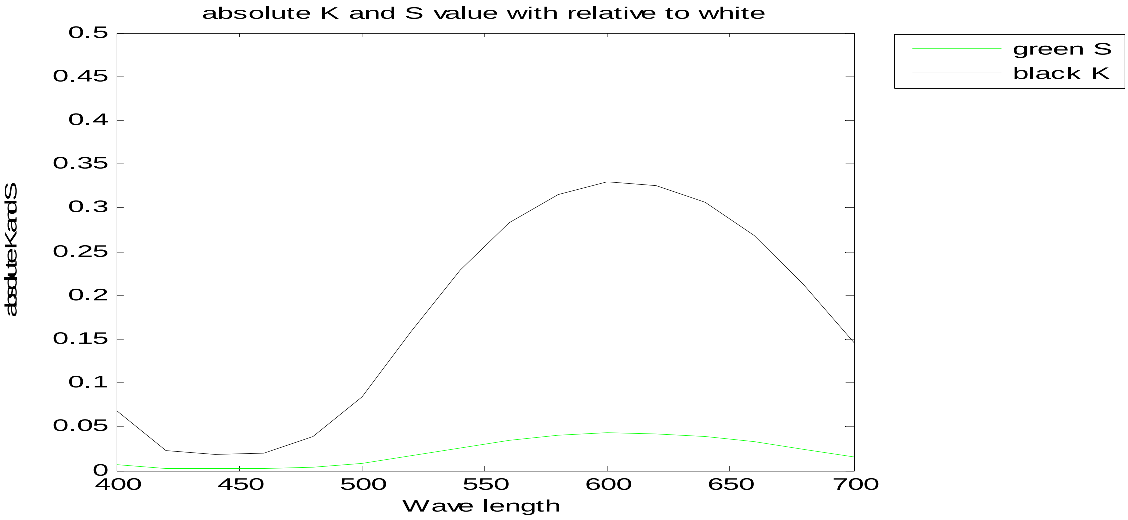
Figure 5.32

4. Figures of K and S values from method least square for opaque panels and with relative white



Absolute K and S values from method least square for opaque panels

Figure 5.34



Absolute K and S values with relative to white colorant for opaque panels

Figure 5.35

# CHAPTER SIX

## 6. FUTURE WORK:

The Kubelka-Munk theory is considered phenomenological where light scattering coefficient is coupled with absorption coefficients, thus gives no information about actual physical light scattering. The physical description of light scattering starts with the scattering and absorption of single particles which includes light scattering at free particle surfaces and their interfaces. Further, Kubelka-Munk theory considers single dimensional light propagation and defines all scattering as back scattering. It does not permit for forward scattering. But, in practice, light scattering in materials such as plastic and paper are multiple scattering processes because of the closely packed structure. Therefore, two flux model used by Kubelka- Munk is not sufficiently correct to do analysis of optical properties, although it has been widely used for the analysis of research problems as well as for industrial applications of color measurements and matching [14, 15, 20,24].

The scattering properties of a material are described in terms of the complex index of refraction. $n = n^{'} + n^{''}$

where, $n^{'}$ is the real part and corresponds to the ordinary ray optics index of refraction. This can be determined easily by according to Snell's law. The imaginary part $n^{'}$ describes absorption and complex to calculate. However, it is possible to calculate efficiently absorption and scattering coefficients from the Mie theory considering the fundamental morphological and optical properties. Several attempts have been done to correlate Kubelka-Munk coefficients with Mie theory but yet no satisfactory results are carried out for industrial application.

On the other hand , studies on many flux theories such as four flux theory , twenty six flux theory as proposed by Mudgett and Richard and revised Kubelka-Munk theory as proposed by Li Yang and Björn Kruse have been shown better performance than two flux Kubelka Munk model. But, very little work has done to study their validity and potential for predicting the reflectance spectra in practical systems. Therefore, future work or study is required to make these existing theories efficiently and accurately useful for practical application or industrial application [15, 23, 24].

# CHAPTER SEVEN

## 7. CONCLUSION:

In color industries, color measurement and color theories are very important to solve coloring process problems as they provide a quantitative evaluation of color. Before applying any theoretical model, it is also necessary to measure the color of objects or colorants with Spectroradiometers and Spectrophotometers in terms of spectral reflectance, transmittance and absorption because all most all color theories use these parameters as the input to do analysis of color or prediction of color of objects. The author also measured spectral reflectance, transmittance and absorption of many samples and materials correctly.

Kubelka-Munk theory that was originally derived in 1931 by P. Kubelka and F. Munk predicts the optical properties of given material or colorants and there by allows the prediction of spectral reflectance. In many industrial applications, the final product is composed of many colorants with different optical properties. It is necessary to predict what result they give when their optical properties are mixed. In many cases, it is also critical to consider the color of a substrate of that material against a given background.

The author calculated successfully the spectral reflectance of industrial samples of opaque and semitransparent types. For opaque system, single constant Kubelka- Munk theory was applied for mixture of different pigments of different concentrations. The concentrations were calculated theoretically by using spline interpolation. Saunderson's correction factors were also applied to the measured reflectance of pigments. The experiment was carried out for three different types of mixtures of pigments and the final result was found to be almost inexact with original measurement. All the reproduced curves were also checked by statistical means and standard deviation. The errors or deviation were found very nominal. Therefore, it can be concluded that single constant Kubelka- Munk theory can be applied to the industrial data of above mentioned opaque nature.

For semitransparent system, double constant Kubelka Munk theory was applied to determine optical properties. Comparisons of optical properties were done fpr each sample calculated by different forms of Kubelka-Munk models such as Reflectance technique, Reflectance-Transmittance technique and Least-squares technique. Analyses were also done for K and S values of different samples with relative to white samples. Further, comparison between reproduced reflectance curves using absolute K and S values obtained from different techniques for different concentrations of colorants were also done. Among the different techniques, Reflectance-Transmittance technique was seen superior than other technique while reproducing reflectance curves. Most of the reproduced curves by Reflectance–Transmittance were very close to measured curves .But, some deviations were also seen in some sample panels especially with those panels having higher concentrations of colorants. In case of reflectance technique, in almost cases some discrepancies were found between the measured reflectance and calculated reflectance. However, the reflectance curves patterns were found very similar to the measured curves. Nevertheless, it can be concluded that double constant Kubelka Munk theory is relevant for translucent materials.

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