

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

The theoretical background and ideas for this research are based on the Kubelka-Munk theory, the CIE XYZ colour space and the CIELAB colour space. In addition, the inkjet printing and the dye classification are explained to present all involved information exploited in the research.

2.1 Kubelka-Munk theory

The KM theory is based on Schuster's consideration developed in 1905. Schuster described the interaction of light with the layers in terms of two fluxes of energy. The incident energy flux, i , includes all light directions that have a component travelling towards the illuminated surface, causing the reflectance energy flux, j , which includes all light directions that have a component travelling away from the illuminated surface. The j energy flux, then consequently, causes a number of new incident energy fluxes. Therefore, consequently these i energy fluxes cause another number of new reflectance energy fluxes. These i and j energy fluxes are termed as the down flux and the up flux respectively.

In inkjet printing, we use a dye to generate the colour. Printed layers are usually semitransparent. The light reflected from the printed surface includes light directly scattered from the colorants in the ink layer and light that has been transmitted through the layer, reflected by the substrate and transmitted back out of

the system. The KM theory does provide a solution for semitransparent and it can be developed by first establishing the optical properties of a layer in isolation as shown in Figure 2-1.

The optical properties of the isolated layer can be described by the reflectance R_0 and transmittance T of energy as defined in Equations 2-1 and 2-2:

$$R_0 = \frac{\text{Energy flux reflected by layer}}{\text{Energy flux incident on layer}} \quad \text{Equation 2-1}$$

$$T = \frac{\text{Energy flux transmitted through layer}}{\text{Energy incident on layer}} \quad \text{Equation 2-2}$$

The reflectance of the composite is obtained by imaging the coating layer split from the substrate (Figure 2-1). A flux I is assumed to be incident on the top surface of the layer. This causes an amount of IR_0 reflected back at the surface and IT transmitted through the coating layer to the substrate layer. A second flux J is assumed to be reflected back from the substrate and is incident on the bottom surface of the coated layer. The amount JR_0 is reflected and JT transmitted through the coated layers.

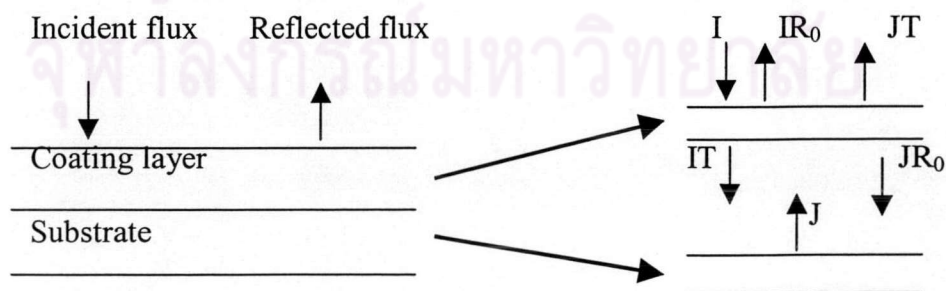


Figure 2-1 Imaginary splitting of the coating from a substrate to form an isolated layer.²

The reflectance ratio of the system can be defined as follows:

$$R = \frac{\text{energy flux reflected by system}}{\text{energy flux incident on system}} \quad \text{Equation 2-3}$$

In order to determine the properties of the substrate, two more reflectance expressions need to be defined:

$$R_g = \frac{\text{energy flux reflected by substrate}}{\text{energy flux incident on substrate}} \quad \text{Equation 2-4}$$

The relationship of R can be expressed more simply by defining the new term (Equation 2-5):

$$R = \frac{\alpha \cdot R_g + \beta \cdot R_\infty}{\alpha + \beta} \quad \text{Equation 2-5}$$

where R_∞ is the reflectance of the ink film that is sufficiently thick to be opaque. α is a function of the opaque reflectance, R_∞ and the reflectance of the substrate, R_g (Equation 2-6)

$$\alpha = \frac{1 - R_\infty^2}{1 - R_g R_\infty} \quad \text{Equation 2-6}$$

and β is a function of K, S and D via the variable Z as defined in Equation 2-7 :

$$\beta = e^{2Z} - 1 \quad \text{Equation 2-7}$$

where $Z = D\sqrt{K(K+2S)}$ and D is the thickness of the layer.

The coefficients K and S of the layer material then can be calculated from reflectance values by Equation 2-8, Equation 2-9, Equation 2-10 and Equation 2-11 respectively.

$$R = \frac{\text{energy flux reflectance by system}}{\text{energy flux incident on system}} \quad \text{Equation 2-8}$$

$$Z = \frac{1}{2} \ln(\beta + 1) \quad \text{Equation 2-9}$$

$$K = \frac{Z}{D} \left[\frac{1 - R_\infty}{1 + R_\infty} \right] \quad \text{Equation 2-10}$$

$$S = \frac{Z}{D} \left[\frac{2R_\infty}{1 - R_\infty^2} \right] \quad \text{Equation 2-11}$$

However the KM theory is limited in the sense that it does not take into account the partial reflection of light at the air to layer interface as the light enters and leaves the layer. Therefore the Saunderson correction is needed to correct the true reflectance R to the measured reflectance ρ .

2.1.1 Saunderson correction

The Saunderson correction is derived by considering the interaction of two energy fluxes with the boundary. An energy flux I is assumed to be travelling from the air to layer and flux J travelling from layer to air (Figure 2-2). The fractions of the

incident flux I are reflected and transmitted by the interface are r_e and t_e respectively. The fractions of the incident flux J that are reflected and transmitted by the boundary are r_i and t_i respectively.

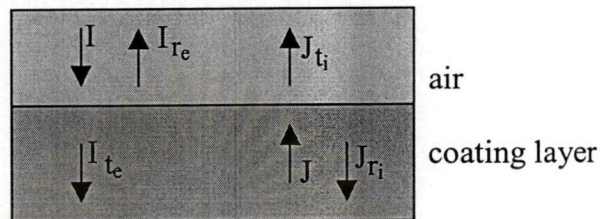


Figure 2-2 Diagram of energy flux at the boundary of air and coating layer.²

Therefore, the relationship of the measured reflectance ρ and the true reflectance R is expressed by Equation 2-12

$$\rho = r_e + \frac{t_e t_i R}{1 - r_i R} \quad \text{Equation 2-12}$$

This equation is often known as the Saunderson equation. It can be rearranged to calculate the true reflectance.

$$R = \frac{\rho - r_e}{t_e t_i + r_i (\rho - r_e)} \quad \text{Equation 2-13}$$

The measured reflectance is corrected by Equation 2-13 that is used to calculate K and S in the KM theory.

2.1.2 Determination of R_∞ for a semitransparent layer

R_∞ is the reflectance of an opaque layer of the ink. Determination of R_∞ seems to be difficult because the layer of the printing ink is not a fully opaque layer. Therefore, a value of R_∞ may be determined from the reflectance of prints over a white and over a black substrate. Assuming that T_w and R_b are the reflectance of the layer over the white substrate and over the black substrate respectively and $R_{g,w}$ and $R_{g,b}$ are the reflectance of the white and black substrates, then the value of β can be obtained by Equation 2-14 and Equation 2-15. The value of Z and consequently β are independent of the substrate of the semitransparent layer. Therefore, β_{black} equals β_{white}

$$\beta_{black} = \left[\frac{R_{g,b} - R_b}{R_b - R_\infty} \right] \left[\frac{1 - R_\infty^2}{1 - R_{g,b} * R_\infty} \right] \quad \text{Equation 2-14}$$

$$\beta_{white} = \left[\frac{R_{g,w} - R_w}{R_w - R_\infty} \right] \left[\frac{1 - R_\infty^2}{1 - R_{g,w} * R_\infty} \right] \quad \text{Equation 2-15}$$

Since $\beta_{black} = \beta_{white}$.

$$\left[\frac{R_{g,b} - R_b}{R_b - R_\infty} \right] \left[\frac{1 - R_\infty^2}{1 - R_{g,b} * R_\infty} \right] = \left[\frac{R_{g,w} - R_w}{R_w - R_\infty} \right] \left[\frac{1 - R_\infty^2}{1 - R_{g,w} * R_\infty} \right]$$

Rearranging produces a quadratic equation for R_∞ :

$$R_{\infty} = B - \sqrt{B^2 - 1} \quad \text{Equation 2-16}$$

where B is given by Equation 17 :

$$B = \frac{(1 + R_b R_w)(R_{g,w} - R_{g,b}) - (1 + R_{g,b} R_{g,w})(R_w - R_b)}{2(R_b R_{g,w} - R_{g,b} R_w)} \quad \text{Equation 2-17}$$

2.2 CIEXYZ Colour space

The CIEXYZ is built on a spectroscopic foundation together with the human colour matching ability. These values describe the colour perception. These amounts are called tristimulus values X, Y, Z. The calculation of the tristimulus values relates the spectral power distribution $S(\lambda)$ of the light that illuminates a sample, and its composition is generally unknown. To get comparable values, the CIE has recommended the use of only a few standardized power distributions (standard illuminants). These are used to calculate the numbers that describe colours. The light that is reflected or transmitted by the sample is measured. This provides the values of $R(\lambda)$ or $T(\lambda)$. Each colour sensation can be described by calculating the amount of light that must be sent from the three imaginary primaries to the eye to get the same perception as that induced or stimulated by the light from the sample. The calculation of the tristimulus values is the first step for solving every task with the help of colour measurement.³

Shown below are the equations for calculating the tristimulus values corresponding to the description above.

$$X = \sum S(\lambda) \times R(\lambda) \times \bar{x}(\lambda)$$

$$Y = \sum S(\lambda) \times R(\lambda) \times \bar{y}(\lambda) \quad \text{Equation 2-18}$$

$$Z = \sum S(\lambda) \times R(\lambda) \times \bar{z}(\lambda)$$

Where $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ are colour matching functions.

The tristimulus value Y has a special significance. It is a measure that relates to the lightness of the sample. By establishing the colour matching functions of the eye $\bar{y}(\lambda)$ was determined to be equal to the luminous efficiency of the eye. This is exactly true only for the 2° standard observer. The tristimulus value Y is called therefore also the luminance factor. The tristimulus values are standardized so that ideal white has the value $Y = 100$ for every illuminant and every observer (Table 2-1).

Table2-1 Tristimulus values of ideal white samples for standard illuminants D65 and A and for 2° and 10° standard observers. ⁴

| Tristimulus values | Illuminant D65 | Illuminant A |
|--------------------|----------------|--------------|
| X ₁₀ | 94.81 | 111.14 |
| Y ₁₀ | 100.00 | 100.00 |
| Z ₁₀ | 107.30 | 35.20 |
| X | 95.04 | 109.85 |
| Y | 100.00 | 100.00 |
| Z | 108.88 | 35.59 |

2.3 CIE 1976 L*a*b* Colour System

In the CIELAB system, the value of a colour is described by three parameters L*, a* and b*. The L* is the lightness axis along which are located neutral gray tones from white to black. Hue and chroma are described by the relationships of a*, red-green, and b* , yellow-blue. The CIE chromaticity diagram is plotted from ratios of XYZ values, the formulas for L*, a* and b* contain cube roots ($x^{1/3}$) and are thus known as nonlinear transformations. The value of L*, a*, b* are derived from X, Y, Z by the following equations

$$L^* = 116(Y/Y_n)^{1/3} - 16$$

$$a^* = 500[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}]$$

Equation 2-19

$$b^* = 200[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}]$$

with the constraint that $X/X_n, Y/Y_n, Z/Z_n > 0.008856$.

In calculating L*, a* and b* values of $X/X_n, Y/Y_n, Z/Z_n < 0.008856$ may be included if the normal formulae are replaced by the following modified formulae:

$$L^* = 903.3(Y/Y_n)^{1/3}$$

for $Y/Y_n \leq 0.008856$

and

$$a^* = 500[f(X/X_n) - f(Y/Y_n)]$$

$$b^* = 200[f(Y/Y_n) - f(Z/Z_n)]$$

$$\text{where: } f(X/X_n) = (X/X_n)^{1/3} \quad X/X_n > 0.008856$$

$$f(X/X_n) = 7.787(X/X_n) + 16/116 \quad X/X_n \leq 0.008856$$

$$f(Y/Y_n) = (Y/Y_n)^{1/3} \quad Y/Y_n > 0.008856$$

$$f(Y/Y_n) = 7.787(Y/Y_n) + 16/116 \quad Y/Y_n \leq 0.008856$$

$$f(Z/Z_n) = (Z/Z_n)^{1/3} \quad Z/Z_n > 0.008856$$

$$f(Z/Z_n) = 7.787(Z/Z_n) + 16/116 \quad Z/Z_n \leq 0.008856$$

X, Y and Z are the tristimulus values of the surface colour, and X_n , Y_n and Z_n are the tristimulus values of the reference white under the appropriate illuminant.

This was completed in an effort to get a perceptually uniform colour space that could be correlated with visual colour appearance. In other words, distances between colours correspond more closely to differences in appearance in CIELAB space than in CIE xyY space. CIELAB colour values are often used in quality control, such as for comparing the differences in printed colours or the difference between a printed reproduction and original item.³ A measure of colour difference in CIELAB space, ΔE^*_{ab} is calculated using the distance formula (Equation 13) to determine the distance in colour space from one colour to another.

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad \text{Equation 2-20}$$

where:

L_1^* , a_1^* , b_1^* = CIELAB coordinates of reference colour

L_2^* , a_2^* , b_2^* = CIELAB coordinates of comparison colour

2.4 Inkjet printing

This subject consists of the history of inkjet printing, a characteristic of inkjet printing and classical inkjet printer.

2.4.1 The history of inkjet printing

The first use of inkjet as a graphic patterning or recording device is generally attributed to Lord Kelvin in about 1873. However, it was not until the 1960's that inventors and manufacturers began to realize the potential for inkjet as a character printer. The first inkjet recording device, which was based on the continuous inkjet technology of Elmquist and Hertz at the Lund Institute in Sweden (generally referred to as Hertz continuous inkjet technology), was introduced by Siemens Elema in 1952. Printing speed, quiet operation, non-contact imaging and all points addressability were some of the perceived advantages of these early inkjet printers. However, most of these printers were plagued with reliability and maintenance problems. These problems were primarily the result of being on the early part of the learning curve for inkjet component and ink manufacturing. In addition, the maturing development of impact dot matrix and band printers made the successful marketing of the inkjet products very difficult. As a result, only the industrial marking and document processing segment of the printer market, which highly valued the non-impact printing capability and was accustomed to preventative maintenance, was quick to pick up on this new technology.

The generation of inkjet products for character and image printing began to appear in about the mid 1970's. This time period saw the introduction of both industrial and office continuous inkjet printers.

The next major event in inkjet technology was the announcement of the Hewlett Packard Thinkjet Printer in 1984. This product was the result of HP's implementation of thermal or bubble inkjet technology which was independently invented and developed by both HP and Canon in the late 1970's and early 1980's.

2.4.2 A characteristic of inkjet printing

Inkjet printing is a direct printing process. Image information in the form of electronic signals is converted to a latent charge on a stream of ink droplets. The droplets pass through a constant electrostatic field which cause deflection of the droplets to the proper location on the paper surface. Unwanted, uncharged droplets pass through the deflection field to a return path for reuse.

Inkjet printing has been developed using electrostatic and magnetostatic method although the electrostatic method has been received much more attention. Within the electrostatic class of printing, the process has been developed using proportional charge and binary charge. Generally the proportional charge method has been used in lower cost, lower speed machines where a droplet stream is deflected in one or two directions by controlled deflection plates similar to the techniques used in cathode ray tubes (Figure 2-3). At higher print speeds, the deflected beam technique is too slow because individual jet streams are provided for each dot position in the raster line. A single value charge is placed on the droplets not used for printing, a fixed field

then deflect, those droplets to a return path while the uncharged droplets continue on to the substrate (Figure 2-4). Both of these methods involve a transient latent charge image on the liquid droplet.

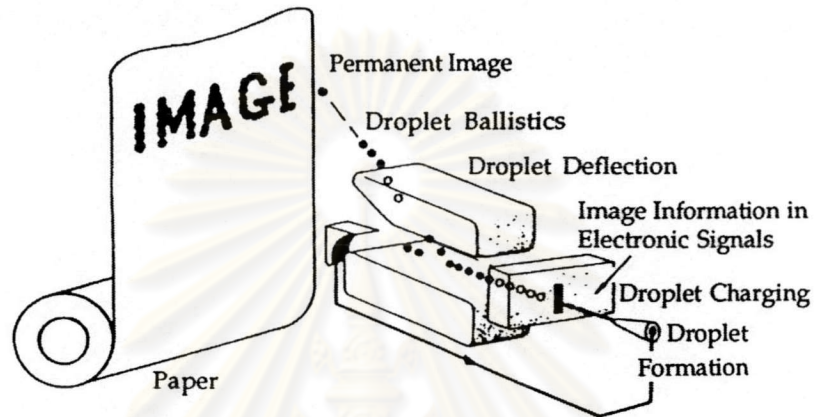


Figure 2-3 Proportional charge inkjet deflection. ⁵

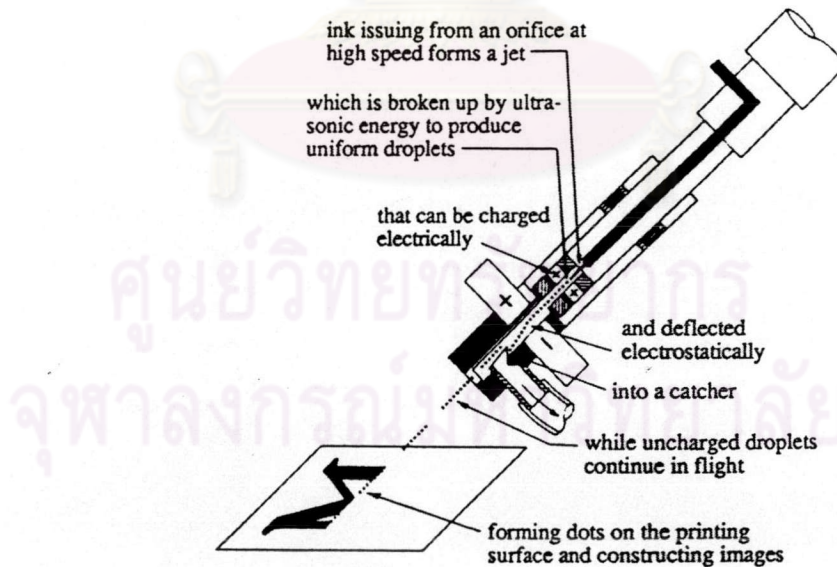


Figure 2-4 Binary charge inkjet deflection. ⁵

This process can be used to print on a variety of substrates, including corrugated board, plastics, fabric and paper.

2.4.3 Classification of inkjet printing

All inkjet processes rely on computer input to form a dot matrix image made up of individual drops of ink. The major difference between the different systems available is whether the ink spray is continuous or drop-on-demand.

2.4.3.1 Continuous-spray systems

In continuous systems, each ink orifice sprays ink drops continuously toward the printing surface. Ink drops not needed to form the image are deflected so that they do not hit the printing surface, and are accumulated in an ink recycling unit for reuse. The most common continuous inkjet printing unit in use is the Videojet system. The Videojet print head consists of an ink chamber which continuously emits a small stream of ink through a single ink orifice. When forced through a small orifice at high speed, liquid ink tends to break up into a spray containing drops of various sizes. To control individual drop size and direction, the ink is given a frequency by a vibrating piezoelectric crystal. This frequency makes the emitted drops regular in size, shape, and spacing. As the drops leave the jet orifice, they are subjected to electric charges, which vary in strength, based on digitized information sent from the computer. The electric charges of various strengths deflect the ink drops from a straight path, and move them in the appropriate directions to produce the desired dot

matrix image. Drops not needed in the matrix are given a charge, this deflects them into the ink recycling system.

2.4.3.2 Drop-on-demand System

A drop-on-demand, or impulse, printer produces a drop from the ink orifice only when a drop is needed to form the matrix image. The ink drops are given a frequency in a manner similar to that of continuous drops. However, instead of being continuously sprayed, electrical impulses, based on digitized information from the computer, cause individual drops to be squeezed out of the ink orifice and propelled towards the printing surface. On-demand units have the advantage of being less complicated because they do not require a dot deflection system for dot placement or to remove unwanted drops. They are also economical because ink is only provided where it is needed to form the image. Their major disadvantage is that they are much slower than continuous spray systems.

2.5 Dye based ink

Dyes are materials that can dissolve in solvents or water to form clear, coloured solutions. The individual dye molecules are separated during dissolution to give colour centres that are very small.

Because they are finely dispersed, they have the advantages of being bright, with high colour strengths and transparencies. As a family of colourants, they cover a greater colour gamut than do pigments, partly because the family of dye is bigger than

that of pigments. The main disadvantages of dyes for printing application arise from their small molecular size. The reason cause of their high transparency they lack the covering power of inorganic and many synthetic organic pigments. This is a disadvantage in certain applications, particularly in the field of packaging where it may be necessary to coat transparent film or kraftboard. High transparency, however, is a key requirement for the successful multicolour over-printing of process colours. Unfortunately, the low physical density of dyes in molecular solutions results in the need for very thick ink films in order to give high optical densities. Moreover, their high degree of dispersion presents a huge surface area for attack by hostile environments such as heat, light and solvent activity. Their fastness to these agents is therefore low.

Although dyes are far more important in the textiles than in the printing industry, they do find applications in certain printing inks and this has increased with the growth of electronic imaging technologies. They are now used for inkjet printing, dye sublimation and dye diffusion thermal transfer processes. They have long been used to produce lakes for printing ink pigments and as toners to improve the colour rendering of pigments.

For a colorant to function it must have both the required colour and the ability to stick to the surface to be coloured. In the case of printing inks, where solid pigment particles are used, a binder is usually required that takes the form of a natural or synthetic resin. However, dyes often have the ability to attach themselves to the material being coloured but, for this to occur, the overall colorant system must be compatible. For example, an inkjet dye must be able to adhere to the substrate being printed which could be paper (cellulose fibres), plastics or metals. The mechanism by

which the dye molecule attaches itself to a substrate type can be classified by the following processes.

2.5.1 Direct dye processes

This depends upon the dye molecules and those contained in the surface of the substrate (or its fibres) being mutually attracted. This can occur if both contain polar molecules of oppositely induced charge, resulting in physical attractions between the molecules and thus leading to adhesion.

Consequently, most fibres comprising polar molecules can be coloured simply by immersing them in a solution of the dye. Since most water-soluble dyes dissociate in solution, the electrically charged dye component liberated can deposit itself onto a suitable substrate, direct from solution.

Dyes of the direct class are often suitable for use as water-based inkjet colorants. Cellulose fibres are rich in hydroxy groups and form polar entities capable of hydrogen bonding. Non-cellulose substrate, including many of the plastic films may be non-polar and will not provide a fast surface for these dyes. Therefore, the surface molecules either came to be modified chemically during synthesis or by physical treatments, such as heat or corona discharge, that modifies the chemical nature of the surface by creating polar groups.

2.5.2 Disperse dyes

These are insoluble in water and are used as colloidal aqueous dispersions. They are often applied as suspensions in a soap solution which wets the substrate, bringing the colloidal particle into contact with the fibres into which they become dispersed. Such dyes are only useful in conjunction with fibre networks, such as those found in textiles and paper.

2.5.3 Mordant dyes

A mordant is that which provides a chemical link or bridge between the dye and the fibre. In the paper making industry alum (potassium aluminum sulfate) has long been used to fix rosin size to paper fibres in order to improve their water and ink control properties, and also to fix dyestuffs in paper. A commonly used mordant dye is alizarin, which relies on a metal complex, of trivalent chromium, to bond the dye molecule to the side groups of the fibre molecule.⁶

2.5.4 Vat dyes

These are often very fast dyes which are usually incorporated into the fibre in a form that is insoluble in water. To render it soluble, the dye is chemically reduced in the vat; dye molecules attach to the fibre. It is then exposed to air (oxygen) or an oxidizing agent when it takes on its final colour by reverting to the insoluble form. These dyes are applied in this way for colouring textile, particularly denim jeans

2.5.5 Reactive dyes

Some dyes have the ability to react chemically with a fibre to produce a permanent bond. These dyes combine covalently with the fibre. During the coloration process the dye is first absorbed by the fibre and then reacts with it by either a substitution reaction or an addition reaction between the reactive system in the dye molecule and a suitable group in the fibre molecule. Reactive dyes are of outstanding importance for colouring cellulosic fibre, alone and in blends.

2.5.6 Acid or anionic dyes

Acid dyes are water-soluble anionic dyes. These dyes are applied primarily to fibres such as wool, silk and nylon, all of which contain basic groups. Although some acid dyes stain cellulosic fibres considerably, none are sufficiently substantive to be of commercial value for colouring cellulosic materials.

The Colour Index includes 1:1 and 1:2 metal-complex acid dyes in the general acid dye classification; they are not listed separately.⁷

Chemically the acid dyes consist of azo (including metal-complex azo), anthraquinone, azine, triarylmethane, xanthen, ketonimine, nitro and nitroso compounds. The colour range is complete, many dyes being very bright, although the metal-complex types are relatively dull.

As far as chemical structure is concerned it is convenient to divide the acid dyes into two groups, non-metallised acid dyes and metal-complex acid dyes.

2.5.7 *Non-metallised acid dyes*

These are largely azo and anthraquinone compounds. Many are characterised by brilliance of colour and good to very good fastness to light.

2.5.8 *Metal-complex acid dyes*

These are co-ordination complexes in which one metal atom, chromium or cobalt, is complexed with one or two molecules of a monoazo compound containing hydroxy, carboxy, amino or methoxy groups, or combination of these, in the o,o'-positions relative to the azo linkage, complex in which one atom of metal is associated with one molecule of the co-ordinating compound are known as 1:1 complexes and those in which one atom of metal is co-ordinated with two organic molecules of the organic compound as 1:2 complexes.

2.5.9 *Basic or cationic dyes*

These dyes are defined as one that dissociates in aqueous solution to give a coloured cation. Basic dyes generally contain a quaternary ammonium group. Their great attraction lies in their brilliance, but their poor fastness to light.⁸

2.6 Literature Reviews

Kang, 1991,⁹ studied a colorant mixing model for highlighting colour inkjet printing on paper. Inkjet printer was a continuous-stream inkjet, using water-based dye inks. Computer models of colour mixing were examined by comparing among Beer-Bouguer law, Kubelka-Munk (KM) theory, and its variations with measured values. The results indicated that the calculated spectra from the single-constant KM model is closely with the measured spectra. Thus, KM theory was used to determine the colour gamut of ink-paper systems. It also made colour matching easier and faster, since a preliminary colour matching could be done in a computer simulation.

Parton and Berns, 1991,¹⁰ developed a model for predicting the spectral reflectance factor properties of printed inkjet ink on paper using single-constant KM theory. Two criteria that were used to determine the effectiveness of the model were being representative of all concentration levels of characteristic curve shape and linearization between K/S and concentration. The model predictions indicate both systematic and random errors. The random errors are due to process-control variations, the systematic errors are mainly attributed to fluorescent quenching. The claim that the single-constant KM theory which has a less complex form was adequate for use in product development.

Katemade, 2001,¹¹ studied colour matching in printing ink systems. The method used in this study involved the calibration of the sets of printing inks to determine their optical properties. Two-constant KM theory, which has a more complex form, was used for simulating a colour gamut. The results indicated that an

average of colour difference between the measured reflectance and the predicted reflectance was about 6 for the lithographic ink.



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