CHAPTER 2

THEORETICAL BACKGROUND

AND LITERATURE REVIEW

2.1 Theoretical background

The textile printing by ink jet printing has been predicted to become popular in the near future because it offers a simple process and inevitable benefits [5]. If, comparing with conventional printing processes, ink jet printing has significant advantages. Such advantages include the following [6]

- Ink jet printing process does not require the use of printing plates and therefore, no lead time for plate making/plate mounting operation is needed.

- As no printing plate making is required, there is no need for usually time-consuming color separation process.

- As ink jet printing technology allows direct printing from graphic design software (via microcomputer) to printer, there is no need for the "traditional proofing". Moreover, any modification made to the image can be incorporated into the final print conveniently.

- Ink jet printers are usually much less costly compared to the conventional printing presses.

Following are the several advantages of ink jet printing that are less well known.

- Ink jet printing allows very high degree of reproducibility. There is usually very little variation in image quality of prints from one batch to another.

- Ink jet printing also allows very high degree of printing stability. In other word, there is virtually no variation of image quality of prints from the

beginning to the end of a print run. As such, the cost caused by starting, stopping and re-starting print runs can be eliminated.

- As ink-droplets are created only when required (in drop-on-demand ink jet printing), there is very low ink wastage associated with ink jet printing. Even continuous ink jet printing allows low ink wastage as ink droplets not reaching the substrate are collected, replenished and reused.

- As the whole printing operation is relatively simple, ink jet printers do not usually required any monitoring, provided that adequate fault correction mechanism is incorporated, which is the case for most wide format ink jet printers.

2.1.1 Technology of ink jet printer

Ink jet printing is a non-impact printing process in which ink is ejected through very small orifices to form droplets is that directed to a medium to create an image. The challenge for ink jet printing has been to control this process so that uniformly sized droplet can be produced reliably. The size of print head nozzle can vary from 10-100 micrometers depending on the technology. There are two main technologies have been developed to ink jet printer: continuous and drop-on-demand printing (Figure 2.1) [7].
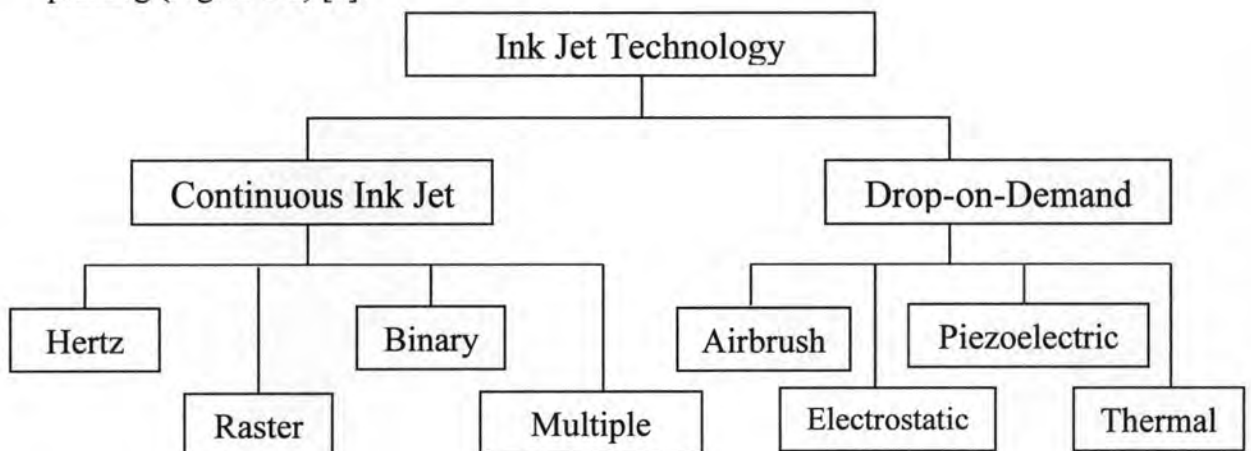
Figure 2.1: Ink jet technology map

2.1.1.1 Continuous ink jet

The continuous ink jet printing process is illustrated in Figure 2.2. Ink is pumped continuously through an orifice plate to generate an array of jet. This plate is attached to a fluid cavity device to which piezoelectric crystals are bonded. The ink's electrical conductivity must be large enough so that the equilibrium charge is readily attained within the duration of the charging voltage pulse, which is approximately the reciprocal of the jet's vibration frequency. Thus it is important that the charging process and drop formation are highly synchronized. The resulting electrostatic force acting on these drops may also be enhanced by passing them between the high-voltage deflection plates. The drops are thus directed into a catcher for disposal or are recycled back to the ink reservoir, which is held under vacuum. This technology can generate drops in the range 15-400 micrometers with a rate of 50-1000 kHz [7].
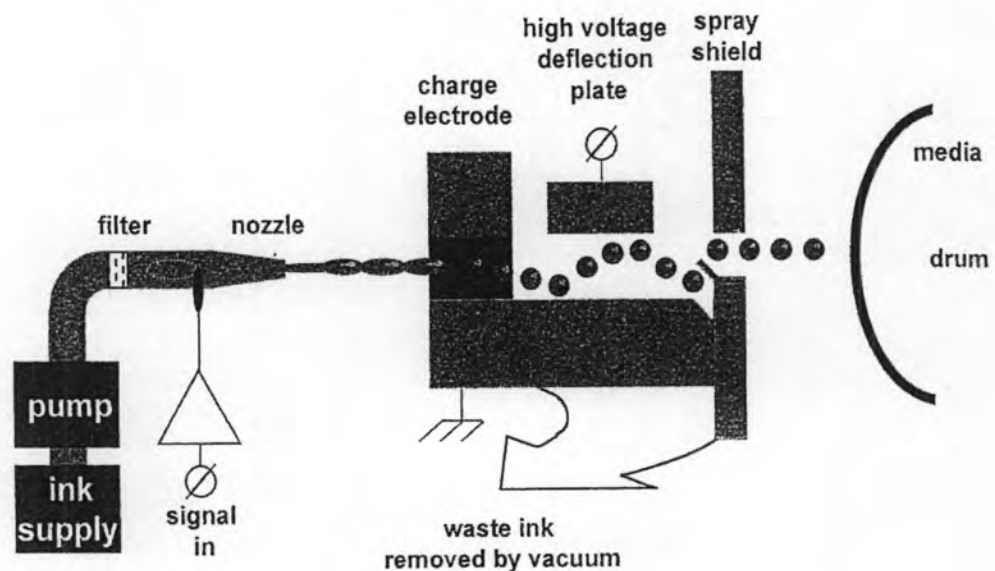
Figure 2.2: Continuous ink jet printing

2.1.1.2 Drop-on-demand ink jet (DOD)

With drop-on-demand (DOD) printing, a droplet is produced only when it is required to form a dot on the medium to create the image. Since there is no deflection of the drops, they are not charged, and they need not be conductive. The two mains methods of ejecting the drop are piezo and thermal or bubble jet. When an electrical pulse of a few microseconds is applied to it, the ink's temperature increases very quickly to around 300°C, approaching its critical temperature. This initiate thermal nucleation, and the bubble of vapor grows, which pushes a column of ink out from the nozzle. Once this heat has been dissipated, the bubble begins to collapse. This process of bubble formation and collapse lasts about 10 microseconds. Capillary action, driven by the ink's surface tension and contact angle, then draws ink from its reservoir to refill the orifice. The momentum of the refill ink can cause the meniscus to bulge out somewhat and then retract due to surface tension in a damped oscillatory motion. This is why DOD printers tent to need more viscous ink than continuous systems to assist in reaching equilibrium as soon as possible. A shear mode piezo electric ink jet design is shown in Figure 2.3 as an example of this technology.
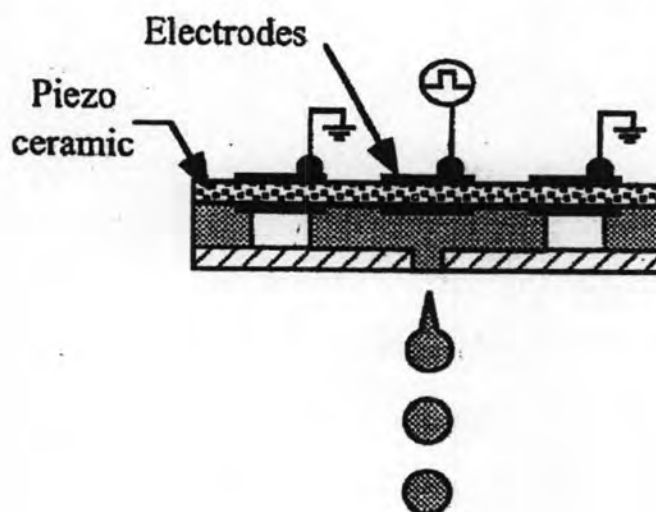
Figure 2.3: A shear mode piezoelectric ink jet design

With the piezo technology, the ink drop is ejected by a pressure wave created by the mechanical motion of a piezoelectric material in place of a bubble. The bend-mode design, the plates are bonded to a diaphragm to form an array of bilaminar electromechanical transducers. Another mode of operation is to contract the walls of the ink channels to squeeze out the ink [7].

2.1.2 Inks for jet printing

Ink jet printing is a non-impact process that uses a stream of minute ink droplets projected onto the stock by a very small nozzle. Drop-on-demand or impulse printing indicates that droplets are only released from the nozzle as they are required. The drops are not charged or deflected in their travel to the substrate. Thus a matrix consisting of a bank of nozzles is required to create the image. The inks used must have physical properties suitable for jet formation and streaming while being capable of producing sharp, dense and permanent images. In addition, they should be stable on storage and must present no long-term health, or short-term chemical, hazard. For accurate and consistent drop formation, the inks must possess a careful balance of rheology, surface tension and (for continuous jet machines) conductivity. Flow should ideally be Newtonian, but viscosity may vary from machine to machine. Impulse jets place more critical requirements on ink viscosity than continuous jets because of their mode of operation which demands that they maintain a stable viscosity during long periods of use. Surface tension is also a critical factor in the formation and maintenance of discrete drops. Water, at 72 dynes cm^{-1}, would provide the optimum surface tension, but because it is blended with dyes, resin and additives. Conductivity, the reciprocal of resistance, is an important property in inks for use in printers which deflect drops. Polar solvents are used to obtain conductivity and water achieves the

highest conductivity. Where inks are to be printed on non-absorbent materials and/or need to be fast drying, organic solvents have to be used [2].

2.1.3 Ink system

The pigmented inks are mainly inorganic powders even though there are few organic pigments. (Figure 2.4) Most dyes are soluble synthetic organic materials, as opposed to pigments which are generally insoluble. Chemically, dyes exist in the ink as individual molecules, while the pigments exist as clusters that consist of thousands of colorant molecules. The disadvantages of the dye-based inks are their relatively poor (long term) image performance which includes light fastness (light fading stability), dark storage stability, humidity fastness, and water fastness.

One explanation to poor image stability for images produced by dye-based inks is that the dye consists of individual molecules which are chemically less stable in terms of light exposure, oxidation, and humidity. Being a cluster of many molecules, the pigment inks have greater resistance to the impact of the environment and therefore possess better light fastness and humidity fastness.

It is necessary to use pigments, when an opaque color is required. The pigment must be extremely well dispersed and often down to a particle size of well under 0.5 μm. Hard and abrasive must not be used, as they might block, unnecessary wear to the fine holes in the nozzle. This would gradually cause the size of the inks droplets to alter and the image to change. The ingredients chosen are specifically selected for their ability to hold an electrical charge for a minimum length of time, as otherwise the process will not work. The average drying time of the inks varies from under one second to over several seconds, depending on the ink formulation and the properties of the substrate being printed [8].
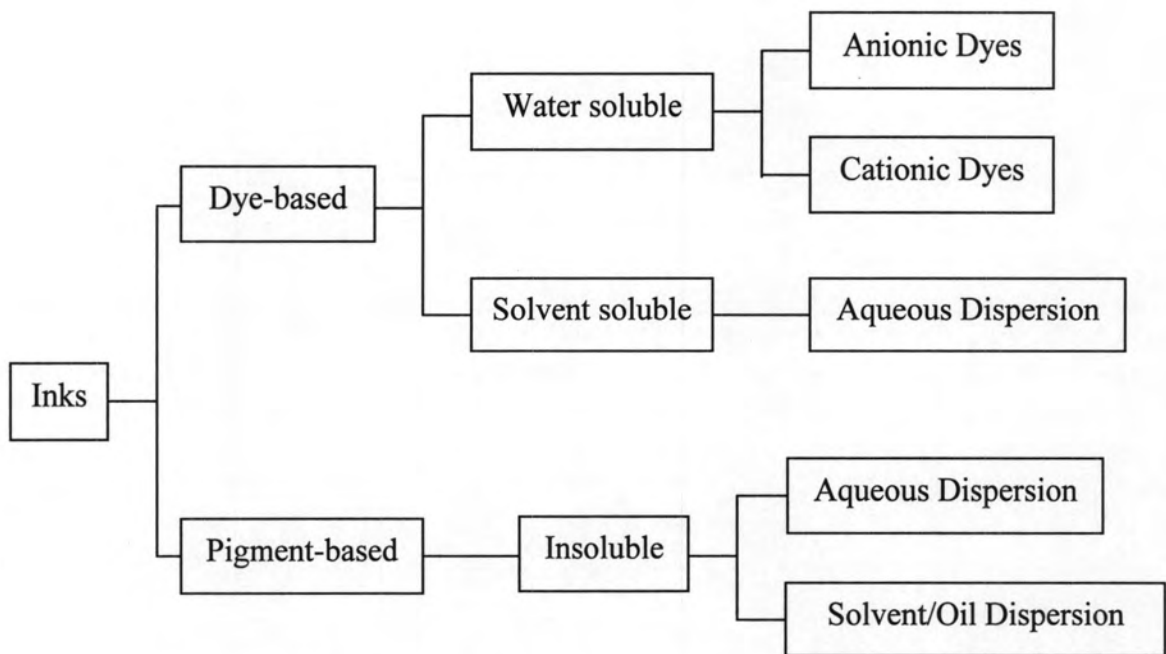
Figure 2.4: Ink system used for ink jet

2.1.4 Ink jet inks requirement

Performance requirements for ink jet inks [7]

I. Print quality   - Match CIE L*a*b* coordinates specifying color

                                     - Minimal show-through

                                     - Controlled dot spread with no inter color bleed

                                     - No feathering

                                     - No splatter

                                     - No misting

                                     - Gloss

                                     - Able to print on a range of media

II. Archival   - Water fastness

                                     - Light fastness

                                     - Dry and wet rub resistance

- Short drying and set time

III. Machine runnability   - Stable drop formation

- No crooked jets

- No nozzle crusting or clogging

- Readily starts up after a shutdown

- If continuous system, also

    - Minimal foaming

    - Sufficiently conducive for deflection

    - Long filter life

    - No shorting of charge plate

    - Wide stimulation voltage window

IV. Machine compatibility   - No corrosion of print head

- No chemical attack of fluid system

- Easily washed off printer parts

V. Stability   - Long shelf life

- Long machine life

- No microbial growth

- No changes with heat/ freezing cycling

VI. Health and safety   - Nontoxic

- Nonflammable

- Material Safety Data Sheet (MSDS)

2.1.5 Properties of Ink jet inks

Inks for digital printing require a special control on parameters like viscosity, conductivity, surface tension, chemical stability, physical stability, pH and foam-free properties. Without the color chemistry base and in-formulation technology, the particle size distribution required for such inks is not possible. A further requirement is an ideal combination of ink and substrate [2].

2.1.5.1 Viscosity

The viscosity is an important property of the ink jet ink. The low viscosity is important not only for transport of the ink through the nozzle, but also for drop formation integrity. The viscosity range of ink jet inks is around 2–8 mPa s [3]. A humectant such as glycol is the primary constituent that affects this parameter. In an ink jet system, the amount of humectant will affect the degree of crusting caused by dye precipitation. Too much humectant would greatly hinder the flow of ink through a 10–μm nozzle. The drop-on-demand printers require a more viscous ink. This is because, instead of high pressure, the drop-on-demand system uses an acoustic wave, usually produced by a piezoelectric transducer, to emit and propel an ink drop.

2.1.5.2 Specific gravity

The specific gravity of the fluid is needed to determine the weight of the mass to be propelled (ink drop) for a velocity control, and to determine other physical properties.

2.1.5.3 Surface tension

Surface tension is one of the primary factors determining where the actual drop will form in continuous ink jet printers. In drop-on-demand printers, it helps to regulate control of the concave meniscus to hold ink in the system. Once the ink has been deposited onto the printing substrate, the interaction of the surface

dynamics of both ink and paper plays a major role in how the final form of the dot will appear.

2.1.5.4 Optical density

The optical density is used in the quantitative evaluation of the contrast of the ink against a known value, that is, the print medium. The optical density results are an inverse tendency by surface tension and viscosity [9].

2.1.5.5 Dielectric properties

The dielectric properties are also primarily important to the continuous flow plotters. The ink drops must be able to accept an applied voltage that will determine where the drops are to be placed. In the Hertz technology, drops are not required to be part of a character receive charge of 200 V. On their way to the printing medium, they pass through a high voltage field of approximately 2000 V. Because same charges repel, these droplets are deflected into a waste receptacle. The drops intended to be part of the plate which does not receive a charge. Therefore, when they go through the high voltage field, there is no effect on their trajectory, and they become part of a printed character.

2.1.5.6 pH

The pH of the ink is critical for several reasons. First of all, the solubility of the dye is greatly affected by pH. The hue of some dyes will change if they go from a low to high pH value. There must be a correlation between the pH values of the ink and of the printing media; otherwise, the archival quality of the print may deteriorate. For example, the ink is as acidic as the paper is, the resulting highly acidic state will cause degradation of the paper and this the finished print. With a low pH ink, therefore, it is advisable to use a high pH paper.

Another reason for controlling pH of the ink is that the orifice of some ink jet systems may be made of a material that is affected by pH. If this is the case, the pH of the ink should be close to neutral to prevent any corrosion.

2.1.5.7 Tristimulus values

To calculate CIE tristimulus values, spectral data of an object, a CIE standard illuminant, and one of the CIE standard observers are required. Tristimulus weights are published for the most common instrument characteristics, CIE illuminants, and the 1931 and 1964 standard observers. Therefore, CIE tristimulus values are calculated by the object's spectral reflectance and a set of tristimulus weights, one for X, Y and Z, which are multiplied together wavelength by wavelength. The products are summed, resulting in tristimulus values with the least amount of error. Tristimulus values, as three variables, can be thought of as a three-dimensional space in which each axis is a primary and a sample's tristimulus values define a position within the three-dimensional space. Two-dimensional map of color can be obtained, called the chromaticity diagram. Because three variables are transformed into two variables, some information is lost. The chromaticity coordinates x, y, and z are obtained by taking the ratio of the tristimulus values to their sum, X+Y+Z, because the sum of the chromaticity coordinates is 1 [10].

2.1.6 Composition of pigmented ink jet ink

Each functional requirement would be uniquely influenced by one component in the ink formulation, but any given component can play multiple roles, both positive and negative. A further complication is that the functional requirements themselves place conflicting demands on the ink, and hopefully the individual operating windows are overlapping and have sufficient latitude. Another part of the formulation work

involves developing a qualification test for the raw materials and any intermediate products [3].

2.1.6.1 Pigment

Pigmented inks are normally prepared in a two-step process. In the first step, a mixture of pigment and water is milled or otherwise mechanically sheared in the presence of a dispersant or stabilizer. During this step, the clumps of as-received pigment particles are broken down into their primary particles. The primary particles become coated with the dispersant molecules and are thereby stabilized against re-aggregation and/or settling. The pigment concentrate thus produced is then diluted in a second step to a working strength ink by addition of co-solvents, called humectants, and other additives, such as surfactants or biocides. Commercially available pigmented inks produced by this method generally result in average particle sizes in the range of 100–200 nm, with particle size distributions often extending to greater than 400 nm. In theory, inks containing these pigment particles with average particle sizes of 50 nm or less, should show improved image quality and improved printhead reliability (i.e., less nozzle clogging) when compared to inks containing significantly larger particles [11].

A pigment junctions by scattering and absorbing light, the relative amounts of which determine the opacity and color of printed pigmented films. These in turn are greatly influenced by the particle size of the pigments and the nature of substrate being printed. The processes, by which they are applied, are useful to examine their required properties for use in printing inks. Pigments should have [8]:

- Good color strength: This is particularly important when thin films of ink are applied, such as in lithographic offset printing.

- Good light fastness: Many pigments, notably from the organic classes, fade in the presence of ultraviolet light. This tendency must be minimized where the printed end product is likely to UV. Posters for display outdoors, for example, are certain to receive high levels of ultraviolet light. Since ultraviolet light is present in the fluorescent tubes used in shops and offices packaging products, magazines, color brochures and so on are also likely targets for fading.

- Stability towards chemical attack: This is a particular requirement of the packaging industry where pigments may have to withstand contact with contents which may be alkaline (detergent, soaps) or acidic (foodstuffs containing citrus acids).

- Fine particle size: This is required to give the correct optical and color properties to the final ink film.

- Dispersibility in normal ink vehicles: The surface energy or wettability of the pigment should be compatible with the solvents and oil used in inks rather than create the expensive need for new vehicle formulations.

There is a universal pigment ink solution as much depending on the print head technology that is being used in the specific textile ink systems. The currently available textile pigment ink jet inks, which contain textile binder, have in general been developed for piezo print heads, which can tolerate higher viscosity inks (>10 mPa s). For low viscosity piezo print heads (<5 mPa s), the pigment ink jet inks generally contain no binder, and the textile binder is applied by a separate post treatment stage [12].

The general properties of organic relative to inorganic pigments include: superior color strength; brighter shades; lower relative densities (less than to

settle in the tin); soft texture (less plate wear); and high transparency (overprinting). Their disadvantages include: a large variation in stability to heat.

Organic pigments are the major source of industrial colorants. Pigments which have multi-molecular crystalline structures, produced to an optimum particle size distribution, insolubility are a key property. When applied in a vehicle to a substrate they either remain on the surface or have a tendency to fill the voids in paper or other irregular surfaces. Each pigment is identified by name in common use, Color Index number. Pigments have been grouped according to their chemical composition with the purpose of indicating their common structure. [13]

Phthalocyanine Blue B NCNF: This is a bright blue treated to prevent flocculation and is a useful cyan in systems where 15:3 suitable for many liquid ink resin systems. (Figure 2.5) Pigment Blue 15:3 represents the most stable crystal, very clean bright green shade, beta copper phthalocyanine. That has slightly more expensive but with increased stability. More stable in tint and strong solvent liquid ink formula account for about 18% of Blue 15 usage.
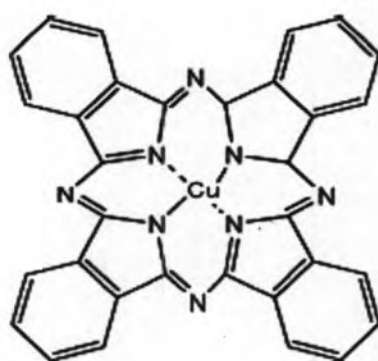

Figure 2.5: CI Pigment blue 15:3.

Quinacridone Magenta Y: A bright blue shade red which is tinctorially weak and difficult to disperse. It is insoluble in organic solvents, unaffected by heat, light, acid, alkali, soap and wax. Owing to its tinctorial weakness and high price, the use of this pigment is limited to the applications which cannot be met in other ways. It works well in most ink systems. The chemical structure of such a pigment is illustrated in Figure 2.6.
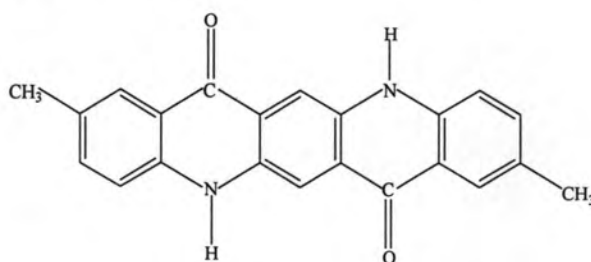

Figure 2.6: CI Pigment Red 122

Quinophthalone yellows: Yellow 138 (Figure 2.7) is bright color, strong coloring power. Its can resist high heat, good light permanency, and acid fastness to alkali and has no migration property.
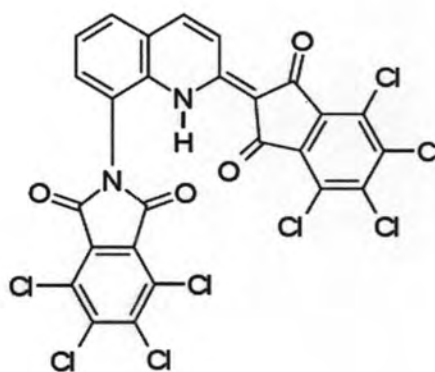

Figure 2.7: CI Pigment Yellow 138

Carbon black: They are pigment of extremely fine particle size, with color varying from a grey masstone with blue undertone to a dense jet masstone with brown undertone, dependent on the method of manufacture. Non-rubber varieties, used in printing ink are produced in pellet, bead, dense or fluffy form. They are chemically inert, extremely fast to heat, light alkali, solvent, and soap. Most grades, however, do contain a small proportion of volatile materials, the effect of which may become apparent on dispersion; account for over 95% black ink usage. It chemical structure is presented in Figure 2.8.
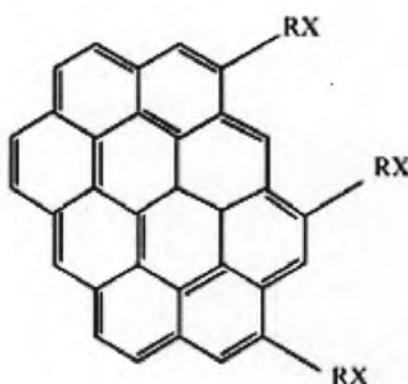

Figure 2.8: CI Pigment Black 7

It is also desirable to use small particles for maximum color strength and gloss. The range of useful particle size is approximately 0.005 μm to 15 μm. preferably, the pigment particle size should range from 0.005 to 5 μm and, most preferably, from 0.005 μm to 10 μm.

2.1.6.2 Binder

The binder of an ink jet ink may contain one or more polymers. The function of the polymer is manifold. It controls the viscosity of the system and promotes droplet formation. The polymer also serves to bind the colorant and

provides the adhesion to the surface. It is also responsible for the properties of the application of the inks. In common with other ingredients in ink, the binder must exhibit good stability upon storage and during use.

The range of chemistry of polymers used within an ink jet formulation is large. This would not only be due to rheological properties influencing on jet break-up but it would also be due to the dichotomy of design for performance in the printer and design for performance on the product to be printed. Among a group of polymer to achieve high end use performance, such as good adhesion, is constrained by the low viscosity requirements of the fluid required for printer operation. When this is combined with the application of a thin film in a form of a dot, it proves to be an extremely demanding set of properties required for the polymer. The ink marked on the product is the whole purpose of the technology and care is need to ensure the fulfillment of an end-user property, and does not compromise performance in the printer [2].

Resins to made binder are of two types, natural and synthetic. A few naturally occurring resins are still used in the preparation of ink vehicles and varnishes, usually after some chemical modification. The ranges of acrylic and methacrylic polymers are based upon monomers of acrylic acid ($CH_2 = CH - COOH$) and methacrylic acid (Figure 2.9).

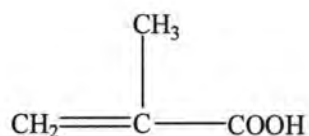$$CH_2 = C \overset{\displaystyle CH_3}{\underset{}{|}} - COOH$$

Figure 2.9: Methacrylic acid.

These are easily polymerized or copolymerized with other comonomer because of their highly reactive double bonds and miscibility with oil-soluble and

water-soluble monomers. Polymerization can be carried out by bulk, solution, suspension or emulsion techniques using a variety of catalysts. The general formula for an acrylic homopolymer is shown in Figure 2.10.
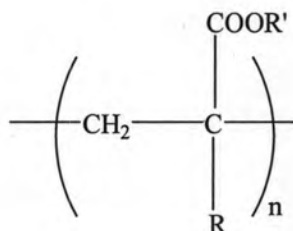

Figure 2.10: Acrylic homopolymer.

where R represents H or CH_3, R' represents H, alkyl, alkoxy, alkenyl or an aryl radical, and n = degree of polymerization. Poly(acrylic acid) in Figure 2.11 and poly(methacrylic acid) in Figure 2.12 are often considered together because of their similarity. Both are soluble in water. They are prepared by direct polymerization of the appropriate monomer [14].
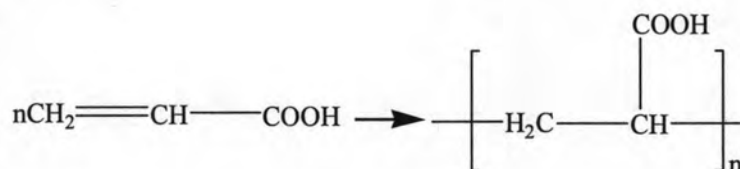

Figure 2.11: Polymerization of Poly(acrylic acid).
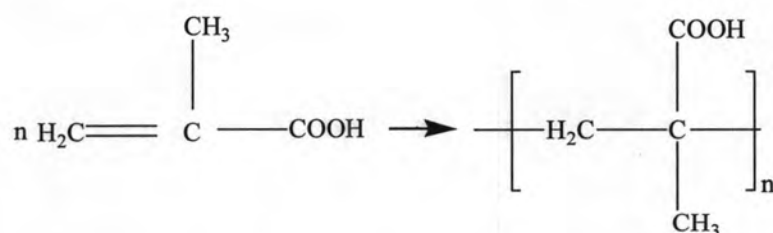

Figure 2.12: Polymerization of Poly(methacrylic acid).

Acrylic resins are characterized by their clarity, chemical inertness, very good lightfastness and resistance to yellowing on stoving. Their softening points

vary widely depending on chemical formula and molecular weight. These polymers also undergo reaction characteristic of carboxylic acids. Recent interest has been shown in the neutralization of aqueous solutions with basic materials such as triethanolamine or ammonia which cause viscosity changes demonstrating the presence of differing molecular conformations. Ordinarily, aqueous solutions of these polyacids have low viscosity because the polymer is tightly coiled, being only slightly ionized. As the pH is raised, more carboxyl groups become ionized. Mutual repulsion of the charges forces the polymer chain to uncoil. In diluted solution extended coils result in higher viscosities (subsequently the viscosity would become lower if hydrochloric acid were added to lower the ionization). The above means that solutions with high solids content can be supplied as stable fluids. When pH is lowered, they become useful vehicles for liquid inks which can then be adjusted for correct viscosity with water or water/isopropanol mixtures.

2.1.6.3 Diethylene glycol

Water-reducible letterpress inks formulated with diethylene glycol have improved press stability, the solvent being more organophilic and less volatile than ethylene glycol, but they have slower setting speeds. Colorless liquid having more viscous and hygroscopic than ethylene glycol is miscible with water alcohols, acetone, glycol ethers and esters. Odour level is low. It is a solvent for high acid value maleic and fumaric resins, nitrocellulose, zein and shellac. It is currently under scrutiny for toxicity.

2.1.6.4 Glycerine

A clear, colorless syrupy liquid with faint odour and sweetish taste, highly hygroscopic, being able to absorb up to 50% of its weight of water. It is

miscible with water, alcohol, glycols and ketones and will dissolve oils, fats and acid dyestuffs. It is used in special water-soluble letterpress inks, e.g. cheque inks, and is a constituent of gelatin rollers. It is too hygroscopic a solvent for formulation of stable moisture-set inks. It can be used as a plasticizer, and it is used extensively in resin manufacture as an esterifying alcohol. Gelatin, sugars and gum Arabic are all soluble in glycerin [11].

2.1.6.5 Water

The majority of inks used in ink jet printers are water-based inks. Exceptions are the inks used in the hot melt or phase change ink jet systems or solvent inks, which are primarily used in commercial ink jet applications. In water-based inks, the liquid portion of the ink, which is referred to as the vehicle, is mostly comprised of water. Water to be used in the makeup of an ink should be as chemically pure as possible. It should be free of calcium, chlorides, sulfates, and heavy metals or contain only minimum trace amounts. The water should be distilled or deionized.

2.1.6.6 Humectants

The ink can dry to a hard, crystalline crust, and this can cause crooked jets or even block an orifice. Thus the ink must exhibit sufficient humectancy that redissolution or redispersion can readily occur [3]. Humectants are added to inks for two purposes: first to retard the evaporation of the ink in the printhead, and second to act as a dye solubilizer. Some typical humectants, used either alone or in combination with one another, are diethylene glycol, glycerol, and poly(ethylene glycol). These chemicals belong to a family called poly(hydric alcohols). If the ink undergoes evaporation, several conditions may occur. The viscosity of the fluid may be increased, thus altering the parameters of the ink.

The proper choice of the grade and quantity of the humectants to be used in the formulation is one of the biggest challenges facing the ink chemist. If the quantity is too high, the ink may take too much time to dry on the printed substrate, even on heavily coated papers. If the quantity is decreased, the ink delivery system may fail as a result of orifice clogging. There is a fine line in determining the percentage of humectants to add to the ink formulation that will allow maximization the ink system so that neither type of failure will occur.

2.1.7 Dispersion technologies in pigmented ink

The technology of ink jet printing progressed very rapidly, but the colorants do not proceed that fast in this decade. There are many pigment dispersion technologies to overcome the coagulation problem of ink jet ink, such as surfactant dispersion, polymer dispersion, micro-encapsulation, and surface modification. These technologies have been developed for the next generation ink jet ink, which provides a significant improvement over the existing inks. In this research, surfactant dispersion for the four color pigments is chosen as the pigment dispersion technique.

Surfactant dispersion: Surfactant molecules consist of structures providing both hydrophobic and hydrophilic characteristics built into the same molecule. A number of reported on the stability of aqueous suspensions of pigments in the presence of the surfactants, which described that a small amount of surfactant markedly affects the stability of suspension. The flocculation and redispersion were explained by the twofold layer adsorption mechanism of surfactants. Adsorption of a second layer of surfactant molecules due to Van der Waals attraction force between the hydrocarbon chains is then possible with the ionized groups of the second layer oriented towards solutions. Therefore, when particles have a twofold layer, they

attained a highly negative charge which causes repulsion between the particles and consequently stabilization of the suspension results. When the pigment dispersion with low molecular weight surfactant, the surfactant is wetting the pigment particles and lowering the interfacial tension, making particle deagglomeration more favorable. The surfactant also displaces occluded air and allows more intimate pigment/ resin contact for maximum efficiency [15].

2.1.8 Silk and silk printing

2.1.8.1 Silk fiber

Silk is a protein fiber and a wide range of dyes can be applied onto it, such as acid, basic, direct, metal-complex, and reactive dyes. Silk is an animal fiber secreted as a continuous filament by a silkworm, and consists essentially of the fibrous protein, fibroin, and in the raw state, is coated with the gummy protein sericin. Fibroin and sericin constitute up to 95% of the raw fiber. The remaining part consists of other proteins, waxes, fats, salts, and ash. It is the only natural fiber available in a continuous filament form [16]. Silk is excreted by *Bombyx mori*, better known as the silkworm. The silk is formed by the polymerization of amino acids with peptide link (-CO-NH-) to give long-chain molecules as shown in Figure 2.13.
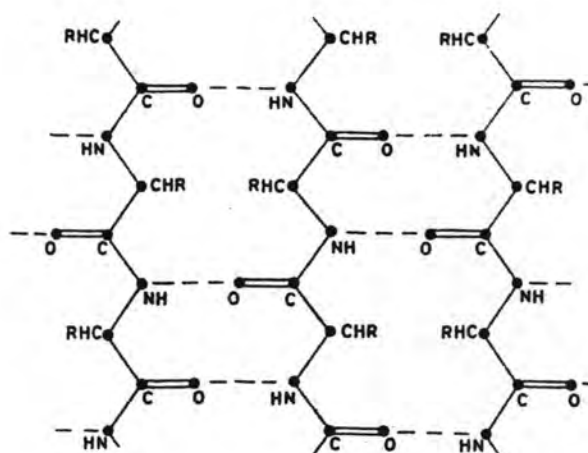
Figure 2.13: Structure of silk molecule.

2.1.8.2 Properties of silk fabric

Physical properties: Silk fibers are strong, with moderate degrees of recovery from deformation. Silk fiber is moderately stiff and exhibits good to excellent resiliency and recovery from deformation, depending on temperature and humidity conditions. Silk has a specific gravity of 1.25–1.30 and a moisture regain of 11% under standard conditions. Silk is soluble in hydrogen bond breaking solvents such as aqueous lithium bromide, phosphoric acid, and cuprammonium solutions. It exhibits good heat insulating properties and is little affected by heat up to 150°C. Silk has moderate electrical resistivity and tend to build up static charges.

Chemical properties: silk is slowly attacked by acids but is damaged readily by basic solutions. Strong oxidizing agents such as hydrochloric acid rapidly discolor and dissolve silk, whereas reducing agents have little effect except under extreme conditions. Silk is resistant to attack by biological agents but yellows and loses strength rapidly in sunlight.

End-use properties appearance: The smooth, translucent surface of silk gives it a high luster, while the triangular shape of the fiber provides highlights that cause silk fabrics to sparkle.

Structure: Silk is a natural continuous filament fiber. It is a solid fiber, smooth but irregular in diameter along its shaft. The filaments are triangular in cross section with rounded corner. Silk fibers are very fine because it has 1.25 denier per filament.

Comfort: The hand of silk is usually considered to be the most pleasant of all of the fibers. It is often described as smooth, crisp, soft, and dry. The pleasant hand comes about through a combination of smooth surface, fineness of fiber, and ability to absorb moisture. The smooth, fine yarns do not trap air well and the protein structure of silk allows a high level of moisture absorption and good wicking. Thus, silk garments are comfortable on all but the most hot and humid days.

Maintenance: The smooth surface of silk fibers prevents dirt from attaching itself readily, so silk fabrics do not soil easily. Fibroin is destroyed by strong acid and alkalies, and even weak alkali in long contact with the fiber will cause some damage. Silk fabrics have good dimensional stability and usually will not shrink or stretch. The resiliency of the fiber assures that it will not wrinkle readily. Silk is damaged by high temperatures and will yellowing.

Durability: Silk is a moderately strong fiber with good resistance to abrasion. It decomposes in strong sunlight and when exposed to atmospheric fumes. The sensitivity of silk to perspiration is of greater concern. Silk has a dry tenacity of 2.8 –5.2 gram per denier (g d^{-1}) and a wet tenacity of 2.5 - 4.5 g d^{-1}.

Care: Silk fibers do not shrink. They swell a bit when wet but the molecular chains are not easily distorted. Crepe fabrics will shrink if washed but this is the result of yarn structure but not fiber content.

Silk fabrics do not soil readily because of the smoothness of the fiber. Silk is harmed less by strong alkalis. Dry cleaning is usually recommended for silk garments because of the yarn structure or non-fast colors.

Silk is resistant to dilute acids and to organic acids. Silk is sensitive to sunlight, which causes white silk to yellow silk and all silk lose strength.

In natural proteins, about twenty different side groups (R_1, R_2, etc.) are found. It is the variation in the order and amount of these groups that determines the properties of the material and gives rise to the large number of natural proteins that play a vital part in animal and plant life. In effect, there is an alphabet of side groups. A complete analysis of insulin and some other proteins has been achieved, but for most proteins the order of the groups is still unsolved.

There are various sorts of cross-links that can form between neighbouring protein molecules:

(a) Hydrogen bonds can form between the –NH– and –CO– groups, linking neighboring main chains together.

(b) Hydrogen bonds may form between hydroxyl groups present in the side chain.

(c) Since there are both acidic and basic side chains, salts may form between them, holding the side chains together by electrovalent forces.

(d) The cystine linkage, deriving from a double amino acid, will form a covalent crosslink between adjacent chains.

The main constituent of silk is one of the simpler proteins, fibroin. Almost all, the side groups are of four simple types:

$$-H, \quad -CH_3, \quad -CH_2OH, \quad -CH_2C_6H_4OH$$
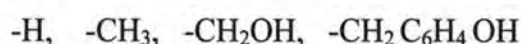
The links between molecules will therefore be mostly main-chain hydrogen bond, with a few hydrogen bonds and salt linkages between side chains.

Silk is essentially used in very expensive luxury goods. It has been able to withstand competition from synthetic fibers in many high-quality textile applications because of its excellent dyeing characteristics, high moisture and absorbency, and heat-preserving property. It has one major drawback that it does not blend easily with other fibers [17 – 18].

2.1.8.3 Pretreatment

In the recent past, there has been an ever-increasing interest for the introduction of enzymes in wool processing. Areas of special interest are increased comfort, increased softness, surface appearance, and reduced pilling performance. Application of enzymes in degumming of silk and best fibers has also been reported. Recent research has shown the effectiveness of enzymatic action on processing of waste-silk fabric. Silk spun from waste silk posses some problems during processing because it contains many impurities in the form of broken chrysalis, straw, lignin, hair, and some cellulosic particles. Conventional processes are not effective in removing all the impurities but protease enzymes that are capable of hydrolyzing the peptide bonds are for silk degumming. Proteases have been reported to give the fabric a softer handle and reduced lousiness. The procedure recommended for scouring and bleaching of the spun silk is: soaping, treatment with enzyme degumming of suitable concentration at 50°C for 3 h, at pH 5.2, and bleaching with hydrogen peroxide. Such a process enhances the surface characteristics, wettability of the fabric, and removes

the impurities as well. Some of the enzymes are used in processing of natural fiber fabrics. Hydrophilic coated and laminated fabrics transmit water vapor selectively by a molecular process, i.e., by absorption, diffusion, and desorption through the solid polymer layer. Such a polymer film or coating shows no evidence of voids or microporous structure, and thus is not susceptible to surface contamination by dirt, dust, etc. Thus, in this research, chitosan pretreatment shall be applied to the silk fabrics [19].

Chitosan: Chitin, a major component of the shell of crab and shrimp, is one of the most abundant natural polysaccharides with a large unexplored commercial potential. Chitosan is partially or completely N-deacetylated chitin, and mainly consists of β-(1,4)-2-amino-2-deoxy-D-glucopyranose (Figure 2.14). In recent years, a number of investigations have been carried out to exploit the potential applicability of chitosan. Since chitosan has unique physiological and biological properties, it is regarded as a versatile starting material for the preparation of various biomedical products when the degree of deacetylation of chitin reaches about 50% (depending on the origin of the polymer), it becomes soluble in aqueous acidic media and is called chitosan. The solubilization occurs by protonation of the $-NH_2$ function on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media. In the solid state, chitosan is a semicrystalline polymer. Single crystals of chitosan were obtained using fully deacetylated chitin of low molecular weight [20]. Chitin, a cellulose-like biopolymer, is widely distributed in nature, especially in marine invertebrates, insects, fungi and yeasts. Its deacetylated derivative, chitosan, is a linear cationic polymer of high molecular weight, readily soluble in acidic solutions. It is also biodegradable, non-toxic, and has been used in the coagulation of suspended solids from various food

processing wastes [21]. Since chitosan is effective in coagulation without any known

disadvantage, it can be a promising substitute for synthetic products. Chitosan has

been applied in the coagulations of bentonite and kaolinite particles in our laboratory.
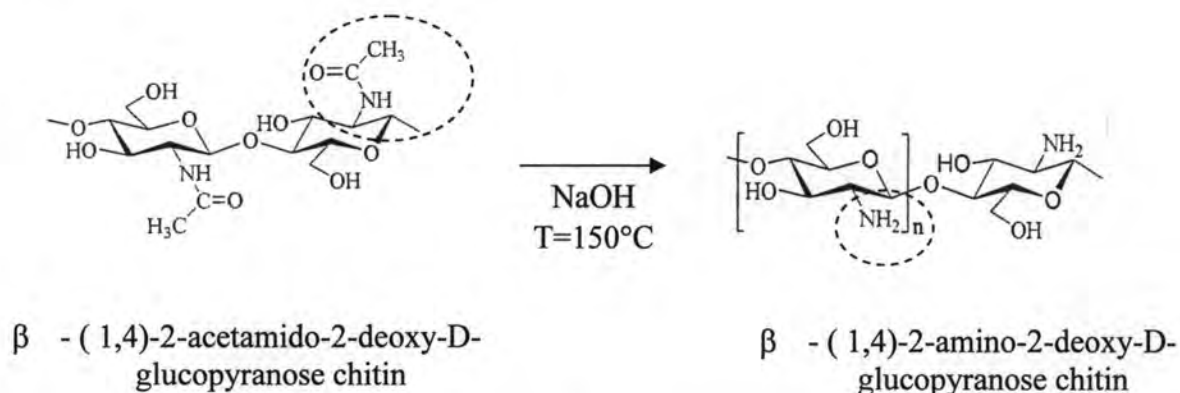
[22]

β - (1,4)-2-acetamido-2-deoxy-D-glucopyranose chitin   β - (1,4)-2-amino-2-deoxy-D-glucopyranose chitin

Figure 2.14: Reaction of chitosan preparation.

Chitosan is dissolved in inorganic acids such as HCl, HNO₃, and

organic acids, preferably acetic acid and formic acid. Chitosan is insoluble in water

and is soluble in acidic solvent below pH 6 to give protonated chitosan as shown in

Figure 2.15. Organic acid such as acetic, formic, and lactic acids are used for

dissolving chitosan and most commonly used is 1% acetic acid solution (pH is about

4.0). Solubility in inorganic acids is quite limited. Chitosan is soluble in 1 %

hydrochloric acid but insoluble in sulfuric and phosphoric acids. Chitosan solution's

stability is poor above about pH 7. At higher pH, precipitation or gelation will occur.

Chitosan solution forms polyion complex with anionic hydrocolloid and provides gel
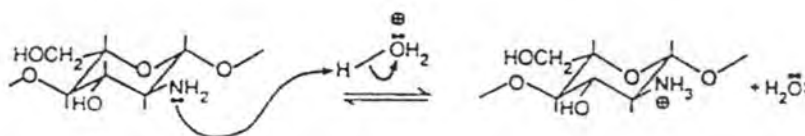
[22].

Figure 2.15: Protonation of chitosan in acid solutions.

2.1.9 Characterization of the printed silks

2.1.9.1 Color measurement

(1) Color gamut

Color gamut is a range of colors achievable on a given color reproduction medium under a given set of viewing conditions. It is a volume in color space [23]. Color spaces or color order systems have been devised to classify colors (Figure 2.16). In this study, the color test chart of printed fabric was evaluated for CIELAB which was measured by a spectrophotometer (Gretag Macbeth Spectrolino, Switzerland), 45°/0°, using illuminant D50 and the 2° observer, based on CIE 1931.

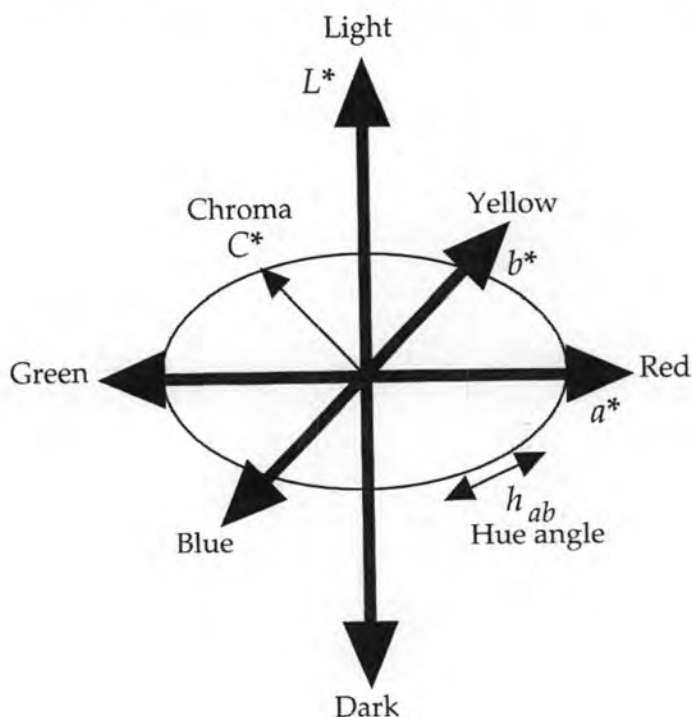**Figure 2.16:** CIELAB color space.

The equations for CIE 1976 L*a*b* (CIELAB color space) are shown in Equations (2.1) to (2.3).

$$L^* = 116(Y/Y_n)^{1/3} - 16 \tag{2.1}$$

$$a^* = 500[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}] \tag{2.2}$$

$$b^* = 200[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}] \tag{2.3}$$

here X_n, Y_n, and Z_n are the tristimulus values of the reference white. For values of X/X_n, Y/Y_n, or Z/Z_n less than 0.01, we obtain Equations (2.4) to (2.6):

$$L^* = 116\,[\,f(Y/Y_n) - 16/116] \tag{2.4}$$

$$a^* = 500\,[\,f\,(X/X_n) - f(Y/Y_n)] \tag{2.5}$$

$$b^* = 200\,[\,f(Y/Y_n) - f(Z/Z_n)] \tag{2.6}$$

where $f(Y/Y_n) = (Y/Y_n)^{1/3}$ for Y/Y_n greater than 0.008856 and $f(Y/Y_n) = 7.787(Y/Y_n) + 16/116$ for Y/Y_n less than or equal to 0.008856; $f\,(X/X_n)$ and $f(Z/Z_n)$ are similarly defined.

(2) Color strength (K/S)

The Schuster-Kubelka-Munk theory depends on the ability to determine K and S values. This can be done by the preparation of calibration panels and their measurement on an appropriate reflectance spectrophotometer. The assumptions of the Schuster-Kubelka-Munk theory are most closely met by instruments that use an integrating sphere measuring head. These devices provide either diffuse illumination or diffuse observation, depending on the details of the optical arrangement. The reflectance of an opaque layer depends on the ratio of K to S and not on the absolute values of the coefficients. Thus the calibration process can be simplified by determining values relative to those of some standard material. It is normal practice to take the scattering power of a standard white formulation. The ratio of K to S is then calculated from the Equation:

$$\text{Color strength, K/S} \quad = \quad \frac{(1-R)^2}{2R} \tag{2.7}$$

$$\text{Relative color strength} \quad = \quad (K/S)_{\text{after washing}} / (K/S)_{\text{before washing}} \tag{2.8}$$

where R = The reflectance of printed silk fabric in the range of the highest absorption [24].

2.1.9.2 Textile testing

(1) Crock fastness

The crock fastness of the printed fabric was evaluated using AATCC Crockmeter (Atlas Electric Devices Corporation, Chicago, USA), and AATCC Test Method 8 – 2001. The amount of color transferred from the printed surface to the other tested surface by a rubbing process, was judged using grey scale (Grey Scale for Staining or the Chromatic Transference Scale). Each printed sample was rubbed with a standard white cotton fabric in back and forth motions for 10 times under both dry and wet conditions. A grade from 1-5 is then assigned [25].

(2) Wash fastness

Wash fastness was carried out by Gyrowash, using ISO 105-C06. A change in color of the staining on the adjacent fabric is compared using the grey scales for staining in accordance with ISO 105 – A03 [26]. Moreover, the color difference in the printed fabrics obtained before and after washing is also reported in terms of color strength (K/S) and relative color strength seen earlier in Equations (2.10) to (2.11).

3) Air permeability

The ability of a fabric to resist air (low air permeability) or allow air to flow freely through it (high air permeability) is dependent primarily on its thickness, porosity, configuration, geometry, type, and the amount of finish and coating. Generally, the fabrics are ranked from the lowest to the highest permeability in an amount of cubic feet of air that passes through a square meter of fabric. Air permeability prediction and measurement are more complex for very porous structures such as nonwoven fabrics than it is for less permeable structures. Air permeability has been related and correlated with numerous other fabric properties. These correlations have usually been made in an attempt to relate them to comfort factors of textiles.

Standard test method for air permeability of textile fabrics is ASTM D 737 – 96. Air permeability is indicated by the rate of air flow passing perpendicularly through a known area under a prescribed air pressure differential between the two surfaces of some material. Air permeability of fabric at a stated pressure differential between two surfaces of the fabric is generally expressed in an SI unit as $cm^3s^{-1}cm^2$ [27].

(4) Bending stiffness

Bending stiffness is generally regarded as the ability of a material to resist deformation (elongation), and is measured in terms of the bending length. In case of a yarn subjected to a tensile force or pull, bending stiffness is the ability to resist elongation. The units for bending stiffness are grams per denier per unit elongation. Average bending stiffness is the bending stiffness of a material from its original state to breaking point. It is the ratio of unit breaking stress to unit breaking strain and thus indicates the average stress for the entire range of extensibility of the

material per unit increase in strain. Average bending stiffness is an indicator of the general character of a material with regard to the bending stiffness quality [17].

JISL 1096:1999 stiffness (45° cantilever method) was used to determine the bending stiffness of the fabric. The cantilever type tester was used to determine the bending stiffness indicated by the length (mm) of the movement of the test specimen. The averages in the warp and weft directions are obtained from 5 measurements [28].

(5) Ink penetration

The penetration of aqueous ink in a fiber can be analyzed with (1) pore absorption of liquid, (2) interaction of anionic and cationic substances, and (3) drying speed of the inks in the fiber. The Lucas-Washburn equation can be described as follows:

$$h = \left(\frac{r \cos\theta}{2} \right)^{1/2} \left(\frac{\gamma}{\eta} \right)^{1/2} t^{1/2} \qquad (2.9)$$

where h is the penetration distance after time, t, r is the pore radius; γ is the surface tension; θ is the contact angle and η is the liquid viscosity. This equation takes into consideration surface tension, viscosity, and contact angle. Based on Equation (2.12), the ratio in square root of the surface tension-to-viscosity ratio, $(\gamma/\eta)^{1/2}$, reflecting the depth or speed of penetration in fabrics, affects solid tone density, color and gamut volume because the low surface tension or low viscosity inks wetted the fabric surface rapidly and penetrated deeper into the fiber and thus gave lower optical density. The optical density results are an inverse tendency predicted by $(\gamma/\eta)^{1/2}$, which was calculated with experimental values [9].

2.2 Literature review

Xue *et al.* [1] prepared the nanoscaled binders suitable for a pigment-based ink jet ink printing on fabrics. The polymer microemulsion with a high content of soft monomer of butyl acrylate (BA) was synthesized via a modified microemulsion polymerization method, where *N*-methylolacrylamide (NMA) served as the cross-linking monomer and monododecyl maleate (MDM) as the copolymerizable surfactant. The effects of the functional monomers (NMA, MDM), the weight ratios of monomers, and the solid contents on the microemulsion properties were investigated by TEM, DSC, particle size analysis, and fabric ink jet printing. The results indicated that the microemulsion had a number-average particle diameter less than 50 nm with a narrow particle size distribution. It was also found that the glass transition temperatures (T_g) of the film formed from the microemulsion could be lower than -30 °C. Fabric ink jet printing application of the pigment-based inks formulated with the as-considered optimum microemulsion as a binder and commercial pigment dispersions demonstrated excellent printability of such inks, and good color fastness and softness of the printed fabrics.

Kiatkamjornwong *et al.* [9] researched on the effects of pigmented ink jet dispersion for printing on silk fabrics. The pigmented ink jet inks were formulated using two types of pigment dispersion techniques: surface modification and micro-encapsulation. Properties of both inks are as follows: viscosity 3.5-5 mPa s, surface tension 38-45 mN m^{-1}, and particle size 0.22-0.23 μm. The stability of the inks was investigated for changes in viscosity and particle size distribution. After 12 weeks, the ink viscosity was increased by 20-40% and the particle size by 2-15%. The surface

modified pigmented inks yielded high optical density, good tone reproduction, better color gamut, and gamut volume.

Daplyn and Lin [6] prepared pigment-based inks for ink jet printing on textile fabrics using three pigments, Cabot Magenta IJX 266, Clariant Toner Magenta E02, and Ciba Microlith Magenta B-WA. The results showed that Cabot Magenta IJX 266 was the most suitable for application via ink jet printing due to its smaller particle size, lower intrinsic viscosity and stability to freeze-thaw cycles and pH changes. While other two pigments possessed lower stability, which could give rise to problems of blocking of print head nozzles. It was found that the prints on cotton fabrics had better image qualities than those on polyester fabrics, mainly due to the greater absorbency offered by the cotton fibers.

Tincher and Yang [29] focused on the silk fabric printing using TOXOT continuous ink jet printer. The fabric was printed with a pigmented ink containing sub-micron particle size polymer latex resins (acrylic resins). Inks with pigment loading of 5-9% and resin content of 15-20% were successfully jetted. The acrylic resins with glass transition temperatures of -10 to 20 $^{\circ}$C gave good fabric hand and acceptable wet and dry crock fastness properties. It was claimed that such pigmented inks appear to be a promising and cost effective approach to ink jet printing of a variety of substrates.

Kiatkamjornwong et $al.$ [5] investigated cotton print qualities that were obtained by ink jet printing and screen printing. The acrylic binder, S-711, with a pigment-to-binder (P/B) ratio of 1/2 (by weight) was used to produce one set of ink jet inks. BR-700 was used in the creation of another set of screen inks. The viscosity and flow behavior of both inks were acceptable. Both ink viscosity and the particle size

distribution were slightly increased during storage at an ambient temperature for two months. The ink jet ink printed fabrics were pretreated with a solution of poly(ethylene oxide) having 2 to 3 million Daltons of molecular weight. The type, concentration, and P/B ratio were exactly the same in both inks using the similar pigment dispersions. Even though the loaded ink volume on fabrics, by ink jet, was turned to be approximately the same in optical density as that given by the screen ink by a multi-pass mode printing, both printed fabrics gave different color saturation, color gamut, and tone reproductions. The color gamut volume, bending stiffness, air permeability, and crock fastness of the ink jet inks are superior to those of screen inks. The print quality of the ink jet printing on cotton fabric was thus better.

Tse and Briggs [30] studied the measurement of the print quality of digitally printed textiles. Print quality in ink jet printing is strongly dependent on the interactions between the ink and the media. For ink jet printing on paper, the significance of ink-media interactions is well recognized and has been extensively researched. Ink jet printing on textiles, however, is a different matter. While the impact on print quality of the fibrous structure of textiles requires further research, a true understanding of ink-fabric interactions and their effects on print quality remains a widely open field for both academic and industrial research.

Bahmani et al. [31] investigated the application of chitosan in pigment printing. The use of chitosan as a combined thickener and binder in pigment printing has been examined in comparison with a commercial printing system (Alcoprint). Padding chitosan onto the fabrics was studied in both uncured and cured samples. The chitosan print system gave only about half the color values of the Alcoprint print system, although apart from one case, the penetrations were very much the same. The

most likely cause for the low color yields is thought to be the aggregation of the pigments in the chitosan paste. The use of chitosan produces a much higher fabric bending length and hence much stiffer fabrics. The fastness of the printed fabric was increased by increasing the curing temperature or time. The major problems with chitosan system were the poor color value and the bending stiffness of the printed fabrics. It is not unusual to add some plasticizing component to reduce the bending stiffness although it is often remarked that the reduced bending stiffness of the print may be accompanied by reduced fastness.

Shepherd *et al.* [32] intended to assess the functional properties of squid pen chitosan in which the chitosan was extracted from squid pens and assessed for comparison. Squid chitosan was colorless, had a low ash content and had significantly improved thickening and suspending properties. The flocculation capacity of squid chitosan was low in comparison with the crustacean sourced chitosans. It was possible to increase the flocculation capacity of squid pen chitosan by decreasing the degree of acetylation. Such chitosan was particularly suitable for medical/analytical applications.