

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical background

Comparing with conventional printing processes, ink jet printing has significant advantages. Such advantages include the following [8]:

- Ink jet printing process does not require the use of printing plates and therefore, time-consuming plate making/plate mounting operation is thus eliminated.
- 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.

Followings 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 words, 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. The 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 require any monitoring, provided that adequate fault correction mechanism is incorporated, which is the case for most wide format ink jet printers [9].

2.1.1 Ink jet printing

Ink-jet is a non-impact, dot-matrix printing technology. Ink droplets are emitted from nozzles of the printer directly to a specified position on a substrate to create an image. The operation of the ink-jet printer is easy to visualize, i.e., a print head scans the page in horizontal strips, using a motor assembly to move it from left to right and back, as another motor assembly rolls the paper in vertical steps (see Figure 2.1). A strip of the image is printed, and then the paper moves on, ready for the next strip. To speed things up, the print head does not print just a single row of pixels in each pass, but a vertical row of pixels at a time.

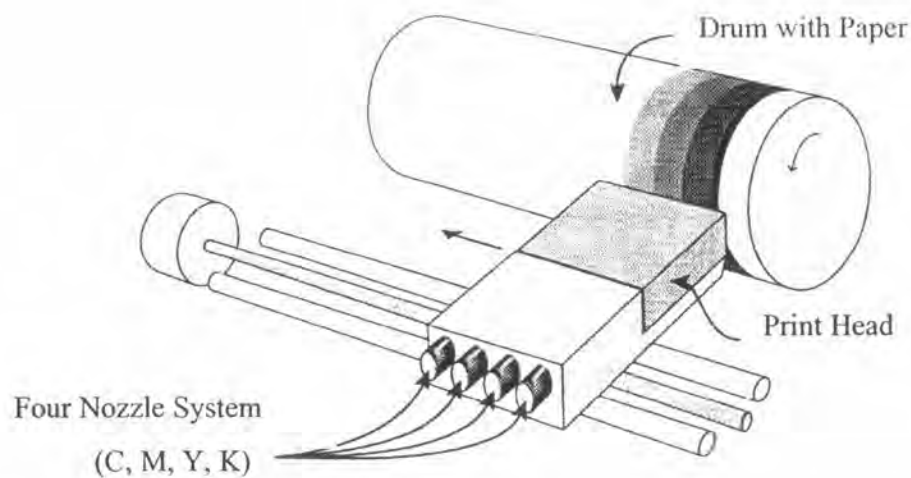


Figure 2.1: A four-color ink-jet printer. [The print head moves along the drum perpendicular to the rotation of the drum facilitating the deposition of ink droplets of all colors in each pixel]

Ink-jet printing has been implemented in many different designs with a wide range of potential applications. Fundamentally, the technologies for ink application are divided into two groups: continuous and drop-on-demand (DOD) as shown in Figure 2.2.

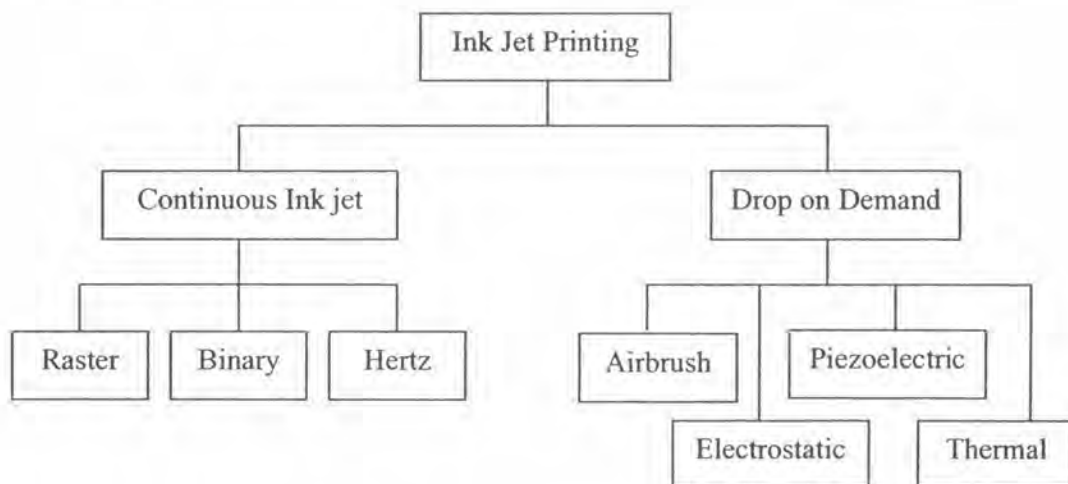


Figure 2.2: Ink jet technology map

In the DOD design, technologies of ink drop formation and ejection can be categorized into four major methods: thermal, piezoelectric, electrostatic, and acoustic. The first two are the dominant technologies for products on market today, while the other two are still in the developmental stage.

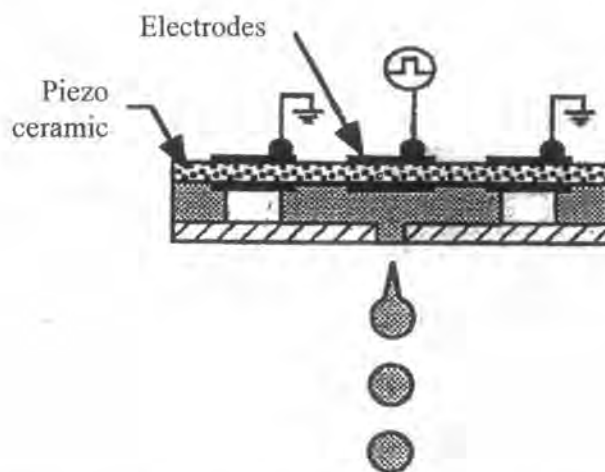


Figure 2.3: A shear mode piezoelectric ink-jet design

In the print head of a piezoelectric ink jet, there are piezo-ceramic plates bonded to the diaphragm (electrodes) as shown in Figure 2.3. Similar to the bubble jet, the piezoelectric material is also controlled by a current pulse. In response to the electric pulse, the piezo-ceramic plates deform in shape which causes the ink volume change in the chamber to generate a pressure wave that propagates toward the nozzle. Consequently, an ink droplet is ejected out. Depending on the mode of shape deformation of the piezoelectric plates, there are different print head designs, such as, push-mode, bent-mode, shear-mode, etc., and Figure 2.3 is an example of the shear-mode design. Piezoelectric ink-jet is also very popular among the ink-jet manufacturers, such as, Epson, Xaar, Tektronix, etc [10].

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 from 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 hazards. For an 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 mN m^{-1} , would provide the optimum surface tension 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 [11].

2.1.3 Ink system

The pigmented inks are mainly inorganic powders even though there are few organic pigments. Most dyes are soluble synthetic organic materials, as opposed to pigments which are generally insoluble (Figure 2.4). 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.

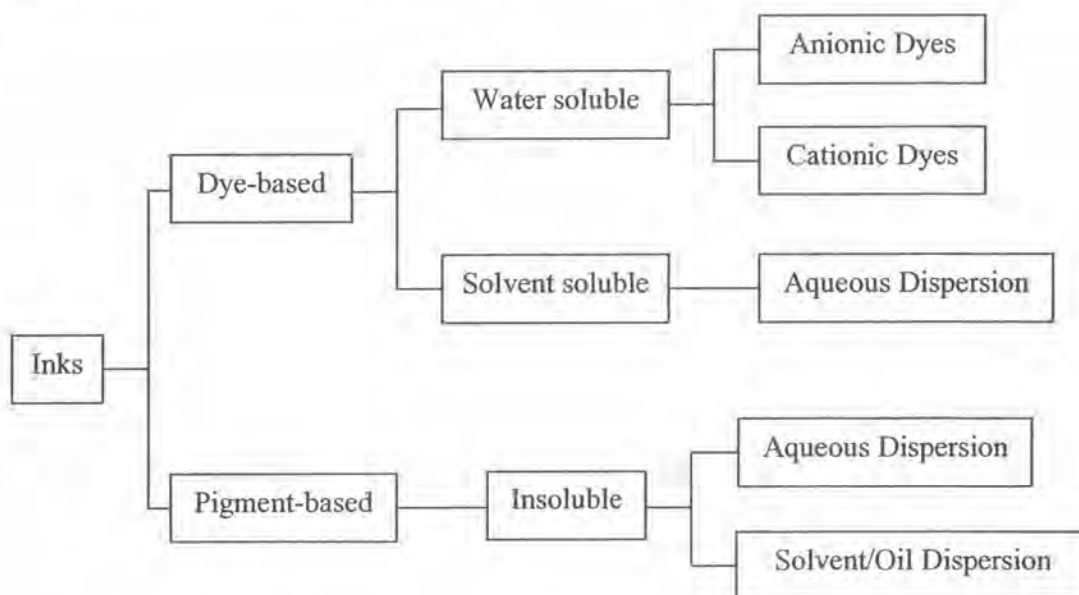


Figure 2.4: Ink system used for ink jet

2.1.4 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 ink formulation technology, the particle size distribution required for such inks is not possible. A further requirement is an ideal combination of ink and substrate. [12]

Viscosity

The viscosity of the ink is of primary importance. A humectant such as glycol is the primary constituent that affects this property. 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.

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.

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.

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.

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 the like charges repel, these droplets are deflected into a waste receptacle. The drops intended to be part of the plate do 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.

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 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 [8].

Tristimulus values

Every color which can be perceived by the normal sighted human eye can be described by three numbers which quantify the stimulation of red, green and blue cones. If two color stimuli result in the same values for these three numbers, they produce the same color perception even when their spectral distributions are different. Around 1930, Wright and Guild performed experiments during which observers had to combine light at 435.8 nm, 546.1 nm and 700 nm in such a way that the resulting color perception matched the color perception produced by monochromatic light at a certain wavelength of the visible spectrum. Evaluation of these experiments resulted in the definition of the standardised RGB color matching functions $\bar{r}(\lambda)$, $\bar{g}(\lambda)$ and $\bar{b}(\lambda)$, which have been transformed into the CIE 1931 XYZ color matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$. These colour matching functions define the CIE 1931 standard colorimetric observer and are valid for an observer's field of view of 2° [13].

2.1.5 Pigments

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 addenda, 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 print head reliability (i.e., less nozzle clogging) when compared to inks containing significantly larger particles [14].

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, it is useful to examine their required properties for use in printing inks, Pigments should have:

- 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 radiation. This tendency must be minimized where the printed end product is likely to expose to UV irradiation. Posters for display outdoors, for example, are certain to receive high levels of ultraviolet radiation. Since ultraviolet radiation is present in the fluorescent tubes used in homes, shops and offices packaging products, magazines, colour brochures and so on are also likely as 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 no universal pigment ink solution as much depends 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 [15].

2.1.5.1 Organic pigments

Organic pigments are the major source of industrial colorants, based on benzene, toluene, naphthalene and anthracene compounds. Typical classes include the azo dyes and pigments giving the Hansa yellow, benzidine yellows, permanent reds, lithol rubines and lake red C. The phthalocyanines give a range of blue to green pigments including that used to formulate the cyan process ink.

The general properties of organic pigments 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 (for overprinting). Their disadvantages include: a large variation in stability to heat

Pigments which have multi-molecular crystalline structures, produced to an optimum particle size distribution, insolubility is 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 names in common use, i.e., Color Index number. Pigments have been grouped according to their chemical composition with the purpose of indicating their common structure.

Phthalocyanine Blue B NCNF: This is a bright blue treated to prevent flocculation and is a useful cyan in systems where C.I. Phthalocyanine Blue 15:3 does not work well and appears weak. All are the resistant properties of the Blue 15s suitable for many liquid ink resin systems; it is used in liquid ink applications more than the C.I. Phthalocyanine Blue 15:3 (Figure 2.5). The C.I. Phthalocyanine Blue is slightly more expensive but with increased stability, very clean bright green shade color, more stable in tint and strong solvent liquid ink formulae, which is accounted for about 18% of the Blue 15 usage.

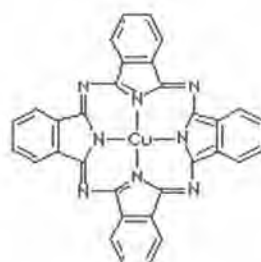


Figure 2.5: C.I. Pigment blue 15:3

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 (Figure 2.6) is limited to the applications which cannot be met in other ways. It works well in most ink systems.

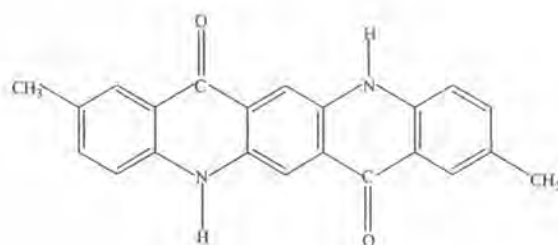


Figure 2.6: CI Pigment Red 122

Mono azo or arylide yellows: They are often commercially known as Hansa, this in fact is a trade name. These yellow pigments (Figure 2.7) are correctly referred to as aceto-acetarylamides. Shades range from a very greenish yellow to a bright warm shade. They are normally fairly opaque pigments but there are some grades that are sufficiently transparent to be suitable for superimposition, acrylamide yellows are widely used for their fastness to light and tinctorial strength as well as resistance to alkali and soap. They are unsuitable for inks that require stoving because they will sublime and bleed strongly in some non-polar organic solvents, paraffin wax and plasticizers. Tinting strength is inferior to diarylides. Arylide yellows are used in both paste and liquid ink formulations [11].

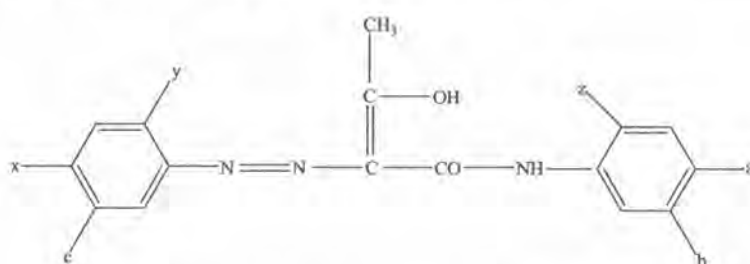


Figure 2.7: CI Pigment Yellow 74

Carbon black: Carbon blacks (Figure 2.8) are powdered forms of highly dispersed elemental carbon manufactured by controlled vapour-phase pyrolysis of hydrocarbons. Most types of carbon black contain over 97 to 99% elemental carbon.

Carbon blacks may also contain chemically bound hydrogen, oxygen, nitrogen and sulfur. The oxygen content is of greatest importance for their application. Oxygen is bound to the surface in the form of mainly acidic or basic functional groups [16].

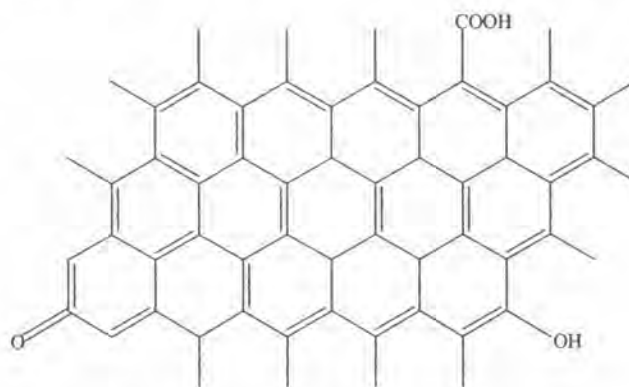


Figure 2.8: CI Pigment Black 7 [16]

2.1.5.2 Composition of Aqueous Pigmented Ink Jet Inks

Each functional requirement would be uniquely influenced by one component in the ink formulation, but any given component can play multiple roles both positively and negatively. 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 [17].

Pigment

A wide variety of organic and inorganic pigments, alone or in combination, may be selected to make the ink. The pigment particles are sufficiently small to permit free flow of the ink through the ink jet printing device, especially at the ejecting nozzles that usually have a diameter ranging from 10 μm to 50 μm . The particle size also has

an influence on the pigment dispersion stability, which is critical throughout the life of the ink. Brownian motion of minute particles will help prevent the particles from flocculation. 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 .

Acrylic resin

Resins used 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 the monomers of acrylic acid $\text{CH}_2 = \text{CH} - \text{COOH}$ and methacrylic acid (Figure 2.9):

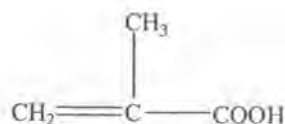


Figure 2.9: Acrylic resin

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 (Figure 2.10) is:

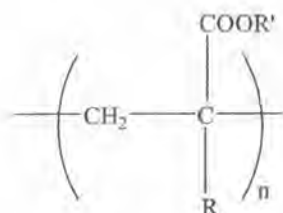


Figure 2.10: Acrylic homopolymer

Where R represents H or CH₃, 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.

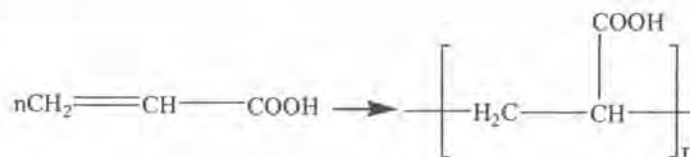


Figure 2.11: Poly(acrylic acid)

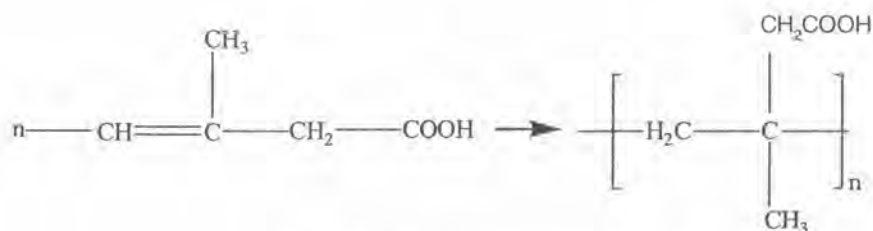


Figure 2.12: Poly(methacrylic acid)

Acrylic resins are characterized by their clarity, chemical inertness, very good light fastness and resistance to yellowing on stoving. Their softening points vary widely depending on chemical formula and molecular weight. These polymers also undergo the reaction characteristics 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 chains 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). This means that the solutions with high solids content can be supplied as stable fluids. When the pH is lowered they become useful vehicles for liquid inks which can then be adjusted for correct viscosity with water or water/isopropanol mixtures.

Diethylene glycol

Diethylene glycol is a colorless liquid with more viscous and hygroscopic nature than that of ethylene glycol. It is miscible with water, alcohols, acetone, glycol ethers and esters. 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. Its odor level is low. It is a solvent for the high-acid value maleic and fumaric resins, nitrocellulose, zein and shellac. It is currently under scrutiny for toxicity.

Glycerin

It is a clear, colorless syrupy liquid with faint odor and sweetish taste, highly hygroscopic, being able to absorb up to 50% of its weight of water. It is miscible with water, alcohols, glycols, and ketones and it will dissolve oils, fats and acidic

dyestuffs. It is used in special water-soluble letterpress inks, e.g. check inks, and is a constituent of gelatin rollers. It is hygroscopic as 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].

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 composed of water. Water 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 containing only minimum trace amounts. The water should be distilled or deionized.

Humectants

Humectants are added to inks for two purposes: first to retard the evaporation of the ink in the print head, 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 polyethylene glycol. These chemicals belong to a family called polyhydric 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 of the ink system so that neither type of failure will occur [18].

2.1.5.3 Surface Modification Dispersion

Many of the inorganic fillers and pigments manufactured for incorporation in paints, plastics, and other organic media are treated with organic reagents to modify the surfaces in the compounding processes. Surface modifications may be used for a variety of reasons that include improvement of the dispersion of the minerals in organic media and modification of the rheology of mineral dispersion. The surface modification dispersion technique is the technique related to chemical bonding and the number of functional groups of the pigment surface. The various surface modifying reactions and interactions are, such as,

- Modification by adsorption of acids, bases, salts and neutral compounds.
- Modification by ion exchange.
- Modification by the adsorption of polymers and the dispersion of minerals.
- Modification by encapsulation polymerization.

Surface-modified organic pigments offer a great freedom to the ink jet ink formulators or developers by providing dispersions with high surface tension, low viscosity, good solvent compatibility, and excellent colloidal stability.[9,10] Cabot Corporation progresses the utilized proprietary technology to modify the pigment surface by attaching functional groups. A wide variety of functional groups enable to modify the surface of pigments. A new generation of ink jet colorants has been using

its proprietary diazonium chemistry to generate pigments with reactive precursors. The secondary and tertiary reactions of these precursors yield products with both unique and useful properties.

The reactive precursor act as a chemical “hook” in order to do secondary and tertiary surface chemistry. The reactive group introduces the desired properties. Therefore it is now possible to attach groups that are not compatible with diazonium chemistry. There are many variants to this chemistry, dependent on the initial treatment path such as condensation reactions, coupling reactions, addition elimination reactions, displacement reactions, etc.

2.2 Pretreatments

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, good surface appearance, and reduced pilling performance. Application of enzymes in degumming of silk and bast 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 poses 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 also used in processing of other 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. The sensitivity of solid polymer to liquid water is extremely variable and depends on their physical and chemical composition. The solid polymer may be completely soluble in water, for example, poly(vinyl alcohol), poly(acrylic acid), etc. They are too sensitive to liquid water and would either dissolve completely or else would not withstand the vigor of normal use. Thus, they are unsuitable for use as permanent, flexible fabric coatings or polymer films. The efficiency of water-vapor diffusion through intermolecular pores can be increased by creating a succession of chemical groups (i.e., amines, hydroxyl, and carboxyl) which are capable of forming reversible hydrogen bonds with water-vapor molecules. These groups thus act "link or conduits", allowing water-vapor molecules to pass through the polymer from an area of high concentration to an area of low concentration. This mechanism is specific for water vapor and does not allow oxygen, nitrogen, and CO₂ molecules, which are incapable of forming hydrogen bonds [1].

2.2.1 Amino Acid and Protein

All proteins are polymers composed of the same building blocks, the amino acids, which are covalently joined together by amide links, known as peptide bonds. They differ only in the number, the nature, and the sequential order of their

constituent amino acids. Amino acids are difunctional; they contain both a basic amino group and an acidic carboxyl group.

The carboxyl and amino groups of amino acids are ionized in solution at neutral physiological pH, with the carboxyl group bearing a negative charge ($-\text{COO}^-$) and the amino group a positive charge ($-\text{NH}_3^+$). The ionization state varies with pH: in acid solution the carboxyl group is not ionized ($-\text{COOH}$) and the amino group is ionized ($-\text{NH}_3^+$). Conversely, in alkaline solution the carboxyl group is negatively charged ($-\text{COO}^-$) and the amino group is not ionized (NH_2). The solubility of proteins is also affected by the pH value.

During protein synthesis, the amino acids are joined end-to-end through covalent linkage. The α -carboxyl group of the first amino acid reacts with the α -amino group of the next amino acid to generate a peptide bond and eliminate a water molecule (Figure 2.13). A consequence of this process is that the amino group of the first amino acid of a polypeptide chain and the carboxyl group of the last amino acid remain intact. A polypeptide chain has thus two different ends, termed respectively the N-terminus and C-terminus. The peptide bond $-\text{CO}-\text{NH}-$ between two successive residues is a relatively rigid planar structure because of its partial double-bond character due to resonance [19].

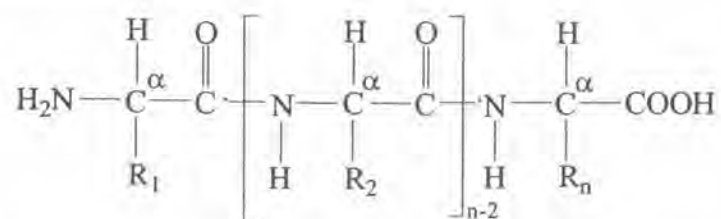


Figure 2.13: Sequence of a polypeptide from left to right

(1) Serine

Serine which contains a primary alcohol group is polar and very soluble in water. Serine is a non-essential amino acid derived from the amino acid glycine. It is important to overall good health, both physical and mental. Serine is especially important to proper functioning of the brain and central nervous system. Serine helps form the phospholipids needed to make every cell in human body healthy. It is also involved in the function of RNA and DNA, fat and fatty acid metabolism, muscle formation, and the maintenance of a healthy immune system. The proteins used to form the brain, as well as the protective myelin sheaths that cover the nerves, contain serine. Without serine, the myelin sheaths could fray and become less efficient at delivering messages between the brain and nerve endings in the body, essentially short circuiting mental function.

(2) Glycine

Glycine is the simplest amino acid and is the only amino acid that is not optically active (it has no stereoisomers). This amino acid is essential for the biosynthesis of nucleic acids as well as of bile acids, porphyrins, creatine phosphate, and other amino acids. Glycine is a nonpolar amino acid. It is the simplest of the 20 standard (proteinogenic) amino acids: its side chain is a hydrogen atom. Because there is a second hydrogen atom at the α carbon, glycine is not optically active. Since glycine has such a small side chain, it can fit into many places where no other amino acid can. For example, only glycine can be the internal amino acid of a collagen helix. Glycine is very evolutionarily stable at certain positions of some proteins (for example, in cytochrome c, myoglobin, and hemoglobin), because mutations that change it to an amino acid with a larger side chain could break the protein's structure.

Most proteins contain only small quantities of glycine. A notable exception is collagen, which is about one-third glycine. Glycine, the simplest amino acid with only a hydrogen atom in its side-chain is poorly soluble in water. Glycine is the smallest of the amino acids. It is ambivalent, meaning that it can be inside or outside of the protein molecule. In aqueous solution at or near neutral pH, glycine will exist predominantly as the zwitterions. The isoelectric point or isoelectric pH of glycine will be centered between the pK_a s of the two ionizable groups, the amino group and the carboxylic acid group. In estimating the pK_a of a functional group, it is important to consider the molecule as a whole. For example, glycine is a derivative of acetic acid, and the pK_a of acetic acid is well known. Alternatively, glycine could be considered a derivative of aminoethane [20 – 22].

(3) Aspartic acid

Acidic or dicarboxylic contains both a second carboxyl group in their side-body; it is largely the charged amino acids that are involved in the buffering properties of proteins. Aspartic acid is alanine with one of the β hydrogens replaced by a carboxylic acid group. The pK_a of the β carboxyl group of aspartic acid in a polypeptide is about 4.0. We note that aspartic acid has an α -keto homolog, oxaloacetate, just as pyruvate is the α -keto homolog of alanine. Aspartic acid and oxaloacetate are interconvertible by a simple trans-amination reaction, just as alanine and pyruvate are interconvertible [23].

(4) Sericin

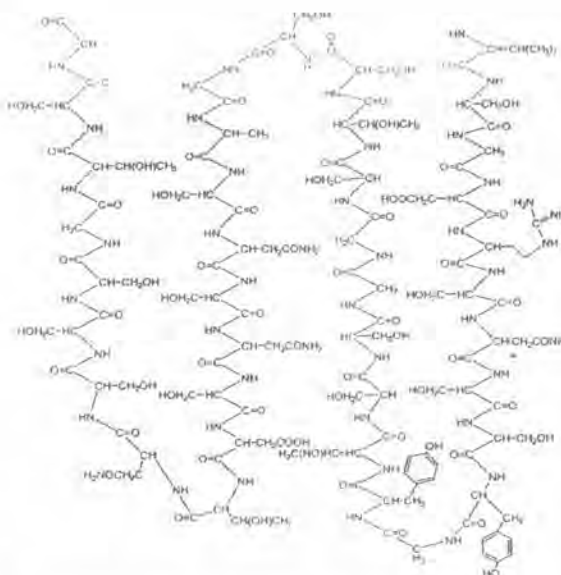


Figure 2.14: Structure of sericin molecule

Sericin in Figure 2.14 constitutes 25 – 30% of the silk protein and it envelops the fibroin fiber with successive sticky layers that help in the formation of a cocoon. Sericin ensures the cohesion of the cocoon by gluing silk threads together. Most of the sericin must be removed during raw silk production at the reeling mill and the other stages of silk processing. Sericin is mostly discarded in silk processing wastewater. If this sericin protein is recovered and recycled. It can represent a significant economic and social benefit. Like fibroin, sericin is a macromolecule protein. Its molecular weight ranges widely from about 10 to over 300 kDa. The sericin protein is made of 18 amino acids most of which have strongly polar side groups such as hydroxyl, carboxyl, and amino groups. In addition, the amino acids serine and aspartic acid constitute approximately 33.4% and 16.7% of sericin, respectively.

Sericin is a water-soluble protein. When sericin is dissolved in a polar solvent, hydrolyzed in acid or alkaline solutions, or degraded by a protease, the size of the

resulting sericin molecules depends on factors such as temperature, pH, and the processing time [24]. The small sericin peptides are soluble in cold water and can be recovered at early stages of raw silk production. The larger sericin peptides are soluble in hot water and can be obtained at the latter stages of silk processing or from processes for silk degumming.

2.2.2 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)-linked 2-amino-2-deoxy- β -D-glucopyranose (Figure 2.15). 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 $-\text{NH}_2$ 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 [25]. Chitin, a type of 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. 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 [26].

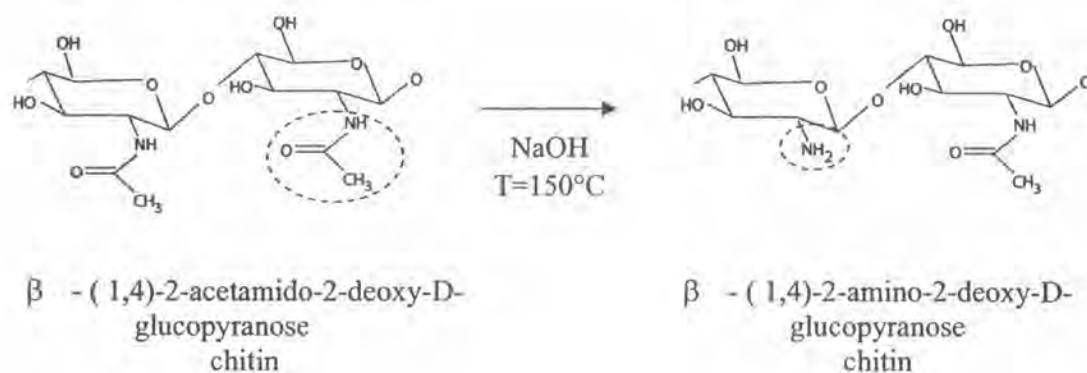


Figure 2.15: Reaction for preparation of chitosan

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. 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, Figure 2.16). 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 [27].

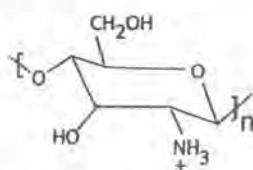


Figure 2.16: Chemical structure of protonated chitosan

2.3 Silk fibre and its properties

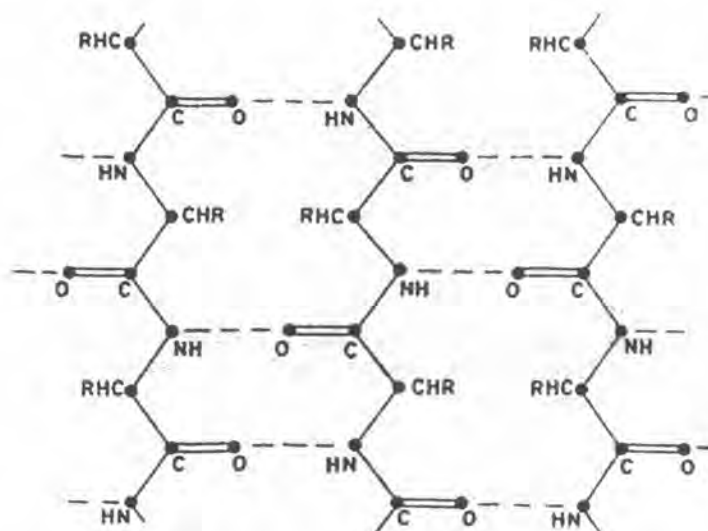


Figure 2.17: Structure of silk molecule

Silk as shown in Figure 2.17 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 the 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 continuous filament form [28]. Silk is natural protein fiber 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.

Physical Properties

Silk fibers are strong, with moderate degrees of recovery from deformation. Silk fiber is moderately stiff and exhibits good to excellence resiliency, 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. 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 (1.25 deniers 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 alkalis, 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 and a wet tenacity of 2.5 - 4.5 gram per denier.

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 not fiber content.

Silk fabrics do not soil readily because of the smoothness of the fiber. Silk is harmed 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 neighboring protein molecule

- (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: $-H$, $-CH_3$, $-CH_2OH$, $-CH_2C_6H_4OH$. 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 [18, 29].

2.4 Characterization of the printed silks

2.4.1 Color measurement

(1) Color gamut

There are several three-dimensional “color space” or “color order” systems that have been devised to classify colors (Figure 2.18). The color test chart of printed fabric was evaluated in terms of CIELAB color space, which was measured by a spectrophotometer (Gretag Macbeth Spectrolino, Switzerland), $45^\circ/0^\circ$, using illuminant D50 and the 2° observer, based on CIE 1931 (Figure 2.19). The color stimulus is dependent on the interaction with proper combination of a light source, an object, and a standard observer [30].

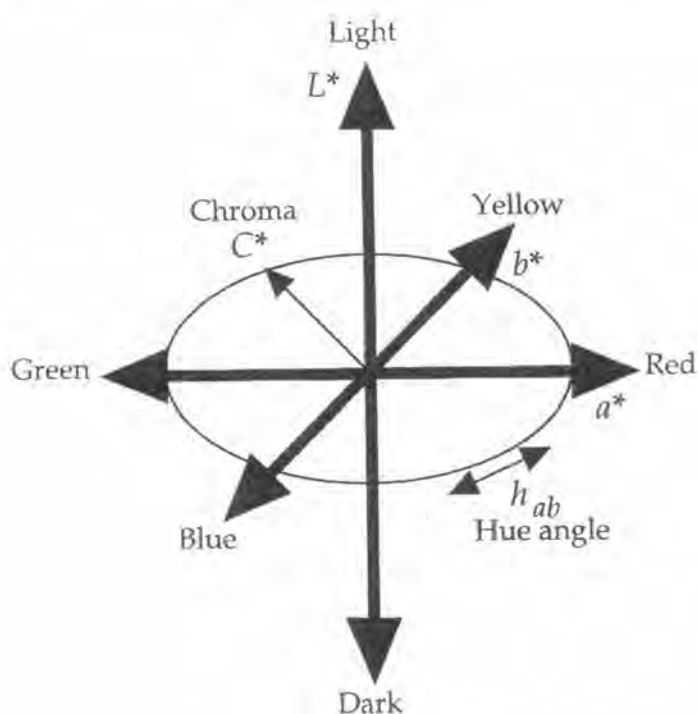


Figure 2.18: The concept of an opponent, rectangular coordinate system using variable L^* , a^* , and b^* to represent lightness, redness-greenness, and yellow-blueness, respectively

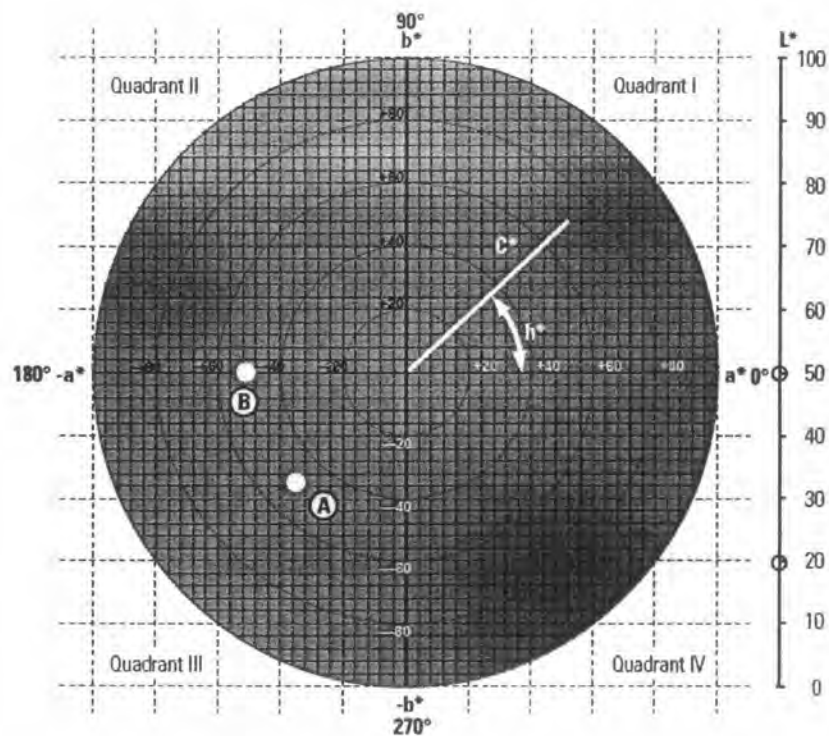


Figure 2.19: CIELab color space

$$L^* = 116 [f(Y/Y_n) - 16/116] \quad (2.1)$$

$$a^* = 500 [f(X/X_n) - f(Y/Y_n)] \quad (2.2)$$

$$b^* = 200 [f(Y/Y_n) - f(Z/Z_n)] \quad (2.3)$$

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. X_n , Y_n , and Z_n are the tristimulus values of the reference white.

$$X = X_n [((L^* + 16)/116) + (a^*/500)]^3 \quad (2.4)$$

$$Y = Y_n [(L^* + 16)/116]^3 \quad (2.5)$$

$$Z = Z_n [((L^* + 16)/116) + (b^*/200)]^3 \quad (2.6)$$

(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 measurement 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 following equations:

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

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

Where R = The reflectance of printed silk fabric in the range of the highest absorption
[31]

2.4.2 Crock fastness



Figure 2.20: AATCC Crockmeter

The crock fastness of the printed fabric was evaluated using AATCC Crockmeter (Atlas Electric Devices Corporation, Chicago, U.S.A. as shown in Figure 2.20), and AATCC Test Method 8 – 2001 (see Figure 2.21). The amount of color transferred from the printed surface to the other tested surface by 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. Later, a grade from 1-5 is assigned [32].

2.4.3 Wash fastness

Wash fastness was carried out by Gyrowash, using ISO 105-C06. A specimen of $100 \times 40 \text{ mm}^2$ in size in contact with the specified adjacent fabric is washed, rinsed and dried. Each printed fabric, sewed with a multifibre strip, was washed at 40°C for 30 min in liquor containing 4 g of standard detergent (without optical brightener) per liter of water at a liquor volume of 150 ml. The multifibre adjacent fabric (DW shown in Figure 2.21) contains wool, acrylic, polyester, polyamide, bleach cotton, and diacetate. A change in color of the staining on the adjacent fabric is compared using the gray scales for staining in accordance with ISO 105 – A03 [33]. Moreover, the

color difference in the printed obtained before and after washing was also reported in terms of color strength (K/S) and relative color strength seen in equations 2.7 and 2.8.



Figure 2.21: HEAL'S Multifibre Adjacent Fabric DW

2.4.4 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 lowest to highest permeability in amount of cubic feet of air that passes through a square meter of fabric. Air permeability prediction and measurement is more complex for very porous structures such as non-woven 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. Air permeability prediction and measurement is more complex for very porous structures such as non-woven fabrics than it is for less structure.

Standard test method for air permeability of textile fabrics is from 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 a material. Air permeability of fabric at a stated pressure differential between two surfaces of the fabric is generally expressed in SI unit as $\text{cm}^3/\text{s}/\text{cm}^2$ [34].

2.4.5 Stiffness

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, stiffness is the ability to resist elongation. The units for stiffness are grams per denier per unit elongation. Average stiffness is the 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 stiffness is an indicator of the general character of a material with regard to the stiffness quality [18].

JISL 1096:1999 Stiffness (45° cantilever method) was used to determine the stiffness of the fabric. Five test specimens each measuring 2 cm × approximately 15 cm are taken in warp direction and weft direction from the sample prepared in accordance with 6 and placed on a horizontal table of smooth surface with 45° slope at one end, so as to align the short side of the test specimen with the base line of the scale. The stiffness indicated by the length (mm) of the movement of the test specimen is obtained by measuring the surface and back of every five sheets, calculating the average values in the respective warp direction and weft direction and rounding off to integral value.

The cantilever type tester was used to determine the stiffness indicated by the length (mm) of the movement of the test specimen. The averages in the warp and weft directions were obtained from 5 measurements [35].

2.5 Literature review

Yu and von Gottberg studied the surface modified color pigments for ink jet ink application. This research studied the modified pigment by attaching functional groups. The conventional dispersants is eliminated for water based applications when ionic and ionizable groups are attached to the surface. This method is analogous to that used in commercially available CAB-O-JET 200 and CAB-O-JET 300 black pigment dispersions, which provides pigments with enhanced formulation flexibility and superior stability. The new dispersion set comprises surface modified Copper Phthalocyanine blue pigment (PB 15:4), Quinacridone red pigment (PR 122), and Monoazo yellow pigment (PY 74). Other examples will be presented as well. The surface modification technology are able to produce a color pigment dispersion set with high surface tension (> 70 dynes/cm), low viscosity (< 3 cP at 10% solids), small particle size, and reliable long term stability. Ink jet inks containing color pigments with surface carboxylate group (COO^-) show improved water fastness over the inks containing a pigment with surface sulfonic acid modifications. When color pigment surfaces are modified with ionic groups, stable pigment dispersions with favorable physical characteristic can be achieved for aqueous ink jet ink [6].

Kiatkamjornwong et al. studied the pigmented ink jet ink dispersion for silk fabric printing. This research concerns the study of the effects of pigmented inkjet dispersion for use on silk fabric. The pigmented inkjet inks were formulated using two types of pigment dispersion techniques: surface modification and micro-encapsulation. Properties of both inks are: 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 examined for changes in viscosity and particle size distribution. The inks were stored at ambient room temperatures for 12 weeks. After storage, the inks viscosity was increased by

20-40 % and the particle size by 2-15 %. The printed silk fabric was analyzed here only for tone reproduction and color. The surface modified pigmented inks yielded high optical density, good tone reproduction, better color gamut, and gamut volume [8].

Kongdee et al. studied the cellulose fiber surface treatment with the silk sericin. Sericin fixation on cellulose fiber was confirmed by Environmental Scanning Electron Microscopy (ESEM) and Fourier Transform Infrared Spectrophotometry-Attenuated Total Reflectance (FTIR-ATR). From ESEM and FTIR-ATR results, it was found that the sericin was successfully coated on the cotton surfaces as a film. Increasing in the sericin content in the finishing solution resulted in the coating enhancement of sericin, and a greater depth of color in the dyed samples. However, the samples with sericin coating were found to have a negligible influence on the tensile strength and the crease recovery angle of the treated fabrics. With increasing in the sericin content, the electrical resistivity of the samples dramatically decreased and water retention increased, indicating that the sericin treated fabrics may be comfortable to wear because of their maintenance of moisture balance with respect to human skin [36].

Jocic et al. studied the interactions that could occur during dyeing of the chitosan treated wool fibers on basis of the spectrophotometric study, by measuring the absorbance values of the solutions containing dye and chitosan. It has been shown that there is a 1:1 stoichiometry between protonated amino groups and sulfonate acid groups on the dye ions in low concentrated chitosan solutions. This interaction forms an insoluble chitosan/dye product. With the excess of chitosan in the solution, the dye can be distributed between the different chitosan molecules and the soluble chitosan/dye products remain in the solution. The mechanism of the interaction is

suggested, that involves the possibility of adsorbed dye molecules to be desorbed and redistributed between other components present in the system, depending on system parameters (pH, temperature and electrolyte presence). The binding of chitosan to wool is due to ionic interactions, such as carboxyl groups in wool forming salts with the free amino groups in chitosan, and hydrogen bonding interactions between hydroxyl and amide groups of the wool with the hydroxyl groups of the chitosan. In acidic solutions, acid dye anions are adsorbed at the cationic acetamido and amino groups of chitosan, presumably rather as by wool fibers. The most probable mechanism of the interaction between chitosan and dye is likely to be ionic interaction of the dye ions with the amino groups of chitosan. At pH 4.2 the sulfonate groups of the dye dissociate and are converted to dye anions ($D-SO_3^-$). The interaction mechanism is based on the formation of the $CHT-NH_3^+ \cdot O_3S-D$ product on a one to one basis (one protonated amino group reacts with one sulfonate group). The attachment of the dye is at one point only (electrostatic reaction between amino and sulfonate groups) It would be expected that the dye molecule is more spatially oriented. This result confirms that, in addition to electrostatic bonding, there is a strong possibility of hydrogen bonding between chitosan and dye molecules [37].

Chen et al. studied the crosslinking of cotton cellulose with DMDHEU in the presence of serine and glycine. Serine and Glycine are selected as coreactants to combine with dimethylol-dihydroxylurea (DMDHEU). The pore structures of DMDHEU-crosslinked cottons are changed when the serine and glycine combine with DMDHEU. DMDHEU alone has lower values of equilibrium absorption, structural diffusion resistance constant, and rate constant, but higher value of activation energy than do DMDHEU-serine and DMDHEU-glycine. The hydroxyl group contained in serine has the higher affinity toward direct dye resulting in the decrease in the value

of activation energy. The expansion patterns of cross section show that the degree of the expansion of the DMDHEU-crosslinked fiber is lower than that of the DMDHEU-serine and DMDHEU-glycine crosslinked fibers. The infrared spectra showed that the -OH group of DMDHEU could react with the functional groups of serine and glycine. Serine has a methylol functional group except one amino group and one carboxylic acid functional group, but glycine has only one amino group and one carboxylic acid group. It is well known that the methylol group is an active functional group for reacting with *N* - methylol group of DMDHEU, and so the condensation between DMDHEU/serine and DMDHEU/glycine and the pore structure are surely different from each other. The surface distribution of crosslinking agent on the crosslinked fabrics for DMDHEU-amino acids is slightly higher than that for DMDHEU alone. The co-reactant amino acids crosslinked fabrics have larger pore structure and slightly higher degree of surface distribution [38].

Oktem studied the surface treatment of cotton fabrics with chitosan. Antibacterial activities of cotton and polyester/cotton fabrics treated with chitosan or chitosan/ DMDHEU have been investigated. The washing durability properties of the aforementioned fabrics were also studied. Another group of fabric samples produced from mature and immature cotton fibers were dyed with reactive dyes and the color yield and color differences of the dyed fabrics assessed. The surface of the treated and untreated cotton fabrics were observed by scanning electron microscopy to compare the morphology. The results showed that sufficient washing durability and a sufficiently high level of antimicrobial effect could be obtained for fabrics treated with chitosan/ DMDHEU. The treatment of cotton with chitosan results in a unique morphological form, having a more textured surface than the unmodified form. This is suggested to be caused by polymer precipitation. Chitosan ability to eliminate the

color differences between fabrics produced from mature and immature cotton fibers is fascinating for the textile finishing industry [39].

Xiao et al. studied the chemical bonding of poly(carboxylic acid) black on cotton and its dyeing and finishing properties. Poly(carboxylic acid) black was applied to dyeing of cotton and acted as wrinkle resistant finishing agent through the bonding between the cotton and the dye. Thermal gravimetry and FT-IR spectroscopy were used to investigate the dyeing mechanism and methods of color stripping, fiber dissolving in cuprammonia and fiber oxidation were employed to indirectly testify the ester linkage of the fiber and the dye. Dyeing properties were examined to show that poly(carboxylic acid) black could realize high fixation, good fastness properties and improved wrinkle resistance on cotton. Carboxylic groups of poly(carboxylic acid) black can react with hydroxyl groups of cotton by dehydrating esterification and the dye was fixed on fiber through ester linkage. The increase of concentration of oxidation agent, more hydroxyl groups was oxidized to aldehyde groups and the fixation of poly(carboxylic acid) black on fiber decreased evidently. This indicated that ester linkage formed during dyeing process, so when some hydroxyl groups were oxidized, they can no longer react with the carboxylic groups of the dye and thus the dye fixation was reduced [40].

Bahmani et al. 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 were noted in both uncured and cured samples. The chitosan print system gave only about half the color value 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 stiffness of the printed fabrics. It is not unusual to add some plasticizing component to reduce the stiffness although it is often remarked that the reduced stiffness of the print may be accompanied by reduced fastness [41].