DEVELOPMENT OF AN OPTIMUM PRINTING SYSTEM FOR DIGITAL INK-JET PRINTING

A Thesis Submitted in Partial
Fulfillment of the Requirements for the
Degree of Master of Philosophy

By
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TO MY PARENTS AND SISTERS

CERTIFICATE OF ORIGINALITY

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Submitted by **CHOI Pui-shan**
for the degree of **Master of Philosophy**
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ABSTRACT

The thesis is concerned with the study of the development of an optimum printing system for digital ink-jet printing using reactive ink on the cotton fabric. Based on the experimental results, it was found that both the contents of pre-treatment print paste, i.e. alginate, urea and alkali, and the post-treatment of steaming time after ink-jet printing played the major role in affecting the final colour yield of the printed cotton fabric. The optimum content of pre-treatment print paste and the proper condition of post-treatment after ink-jet printing were developed to achieve higher colour yield for three primary colours and one black colour with the aid of the response surface experimental design technique. The colour fastness results of the cotton fabric pre-treated by the newly developed ink-jet printing system were similar to those of the commercially available pre-treated cotton fabric.

Orthogonal design had been used to determine the effect of pre-treatment print paste and steaming time on the colour yield of ink-jet printed cotton fabric. In addition, fractional factorial design had also been used to study the factors, i.e. sodium alginate, urea, sodium bicarbonate and steaming time. According to the results of the highest colour yield obtained on the cotton fabric, it was found that urea was the dominant factor when compared with other factors. On the other hand, the final colour yield was not only influenced by an individual factor, i.e. amount of alginate used, amount of alkali used, amount of urea used and duration of steaming time, but also due to an interaction effect among these factors.

Characterisation of the reactive inks had been experimentally conducted using various instrumental techniques such as Ultraviolet-Visible Spectroscopy (UV/VIS), Thin-Layer chromatography (TLC) and Infrared Spectroscopy (IR). Based on the results of UV/VIS absorption spectra, the maximum absorbance of the reactive inks studied was determined and hence the respective colour was found. TLC had been used to separate various dye components present in the reactive ink for dye analysis and confirmation. Furthermore, the functional groups and chemical composition of the reactive inks had been deduced by using the IR analysis technique and compared with the chemical structures of known reactive dyes.

The feasibility of using chitosan to replace sodium alginate as a thickener in the pre-treatment print paste was studied with the aid of orthogonal design. According to the results of different colour fastness tests and colour appearance measurement, chitosan in principle could work as a pre-treatment print paste thickener after modifying the pre-treatment procedures. In addition, it was found that chitosan could also impart higher anti-bacterial property onto the cotton fabric.

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CHAPTER 1.

INTRODUCTION

1.1 Background

In recent years, there are increasing interests in the application of digital ink-jet printing in the textile market. The ink-jet printing technique stands out benefits like speed, flexibility, creativity, cleanliness, competitiveness and also eco-friendliness [1, 2]. However, the production process of ink-jet printing for cotton fabric with reactive inks was different from that of the conventional printing process [3-5].

For long length, conventional printing method like rotary screen printing is fast (30 – 70 m/min.), continuous and economical. The colour gamut is wide and no special fabric pre-treatment is needed before printing. For short run, however, conventional textile printing process is uneconomical owing to high wastage of fabric and inks, high engraving cost, high labour cost and spent a lot of time spent on colour-matching, print paste making, sampling design and registration etc. Design sampling or proofing is particularly a very lengthy and expensive process.

Nevertheless, ink-jet printing offers distinct advantages. For short runs, sampling or proofing, there are no screens; consequently, all costs pertaining to screen engraving, print paste making, strike-offs, downtime and wastage are eliminated. There are no registration problems and unlimited choice in terms of repeat size is available as all the dyes go onto the fabric. Hence, no thickener or print paste is needed and water as well as energy consumption are low. The technology is amply suitable for just-in-time delivery and mass customisation.

The ink-jet technology, however, is still limited by low production speed, low availability of fast and low-viscosity dyes, and small size of colour cartridges. Fabric must be specially prepared to be able to run on the ink-jet printers in open width condition and absorbs dye quickly. Many pigments like pearl, metallic and white are not yet available for printing through the ink-jet printers. Material handling is also limited, stretch knits and performance fabrics are not printable as yet.   In addition, durable solution for post printing operations like print fixation and finishing are yet to emerge.

In the conventional textile printing of cotton fabric, the reactive dye is applied with alkali and other additional chemicals in the form of a print paste. The print is then normally steamed to fix the dye onto the cotton fabric and then washed thoroughly to remove any unreacted dye, chemicals and thickener. However, due to the requirement of purity and specific conductivity requirements for ink-jet printing [3, 4, 6, 7], none of the conventional printing chemicals such as alkali, urea and sodium alginate thickener can be directly incorporated into the ink formulation. As a result, the cotton fabric should be pre-treated with those printing chemicals used in the conventional textile printing. The chemicals necessary for fixing reactive dye should be padded onto the cotton fabric prior to the ink-jet printing stage.

For the ink-jet printing of cotton fabric with reactive inks, the contents of pre-treatment print paste, i.e. sodium alginate, urea and alkali, together with the steaming time after ink-jet printing play the major role in affecting the final colour yield of the printed cotton fabric [4]. In order to achieve the maximum colour yield, the combination of these four factors must, therefore, be studied in depth. Hence, a detailed study of these factors that influence the colour yield of ink-jet printed cotton fabric should be conducted.

The findings obtained from this study can provide a better understanding of the effect of pre-treatment print paste and steaming time on the final colour yield of ink-jet printed cotton fabric. Furthermore, the optimum conditions used for the ink-jet printing process can also be determined and provided.

1.2 Objectives

This thesis is concerned with the optimisation of printing systems for ink-jet printing. The principle objectives of the thesis are summarised as follows:

1. To determine the present status and characteristics of the existing ink-jet ink for utilisation in ink-jet printing including chemical, physical and biological properties by means of modern instrumental techniques. To determine the general properties of ink that are suitable for ink-jet technology in textile industry.
2. To determine the effect of pre-treatment and post-treatments processes by means of colorimetric attributes using fractional factorial experimental design in ink-jet printing.
3. To develop an optimum printing model system using response surface modeling for pre-treatment and post-treatment processes in ink-jet printing.
4. To study the modification of cotton surface using various chemical techniques in order to increase the colour yield of ink-jet printing.

1.3 Methodology

In order to achieve the objectives, the following methodologies have been adopted:

1. To determine the present status and characteristics of the existing ink-jet inks for utilisation in printing including chemical, physical and biological properties by means of modern instrumental techniques such as Spectrophotometry, Ultraviolet-Visible Spectroscopy, Infrared Spectroscopy and Tin-Layer Chromatography.

2. To conduct physical and chemical pre-treatment processes as well as post-treatment processes for increasing both ink uptake and ink fixation on fabric surface in ink-jet printing.
3. To optimise the pre-treatment print paste recipe with the help of fractional factorial experimental design and response surface modelling.
4. To apply chitosan to the pre-treatment process using different chemical techniques.
5. To examine the colour printout properties by means of colour fastness properties, and anti-bacterial tests.

1.4 Scope of Thesis

The thesis comprises six chapters which are outline as follows:

Chapter 1 introduces the background information, objectives, methodology and scope of the thesis.

Chapter 2 summarises the comprehensive literature survey of ink-jet printing development including hardware (printer), ink formulation media (substrate), software and chitosan application.

Chapter 3 studies the characterisation of reactive ink using. A serial of analytical methods namely UV Ultraviolet-Visible Spectroscopy, Thin Layer Chromatography and Infrared Spectroscopy were used to examine the reactive ink properties, including respective colour and chemical structure.

Chapter 4 determines the effect of pre-treatment print paste and steaming time on the colour yield of ink-jet printed cotton fabric with the aid of the orthogonal design. Furthermore, the interaction effect between each printing factor was studied using the fractional factorial design. Based on the results of the highest colour yield on the cotton fabric, it was found that urea was the dominant factor when compared with the other factors. Optimisation of ink-jet printing system for cotton fabric was studied using response surface design.

Chapter 5 evaluates the feasibility of using chitosan to replace sodium alginate as a thickener in the pre-treatment print paste with the aid of the orthogonal design. Two-bath method had been developed for the modification of pre-treatment procedures. Based on the results of different colour fastness tests and colour appearance measurement, chitosan in principle could work as thickener in pre-treatment print paste, and impart higher anti-bacterial property onto the cotton fabric.

Chapter 6 states the major results and findings obtained from the present work research work and draws the final conclusion. The remaining ink-jet printing problems are outlined and some future research works are recommended.

CHAPTER 2.

LITERATURE REVIEW

2.1 Ink-jet machine development

Digital ink-jet printing is developed to replace or cooperate with conventional printing in textile industry. Ink-jet is a non-contact technology that uses nozzles to spray drops of ink directly onto the substrate [8]. Digital ink-jet printing is a process that enables the direct transfer of a design onto fabric from a computer file, without the need for the production of screens or run heavy-duty machinery.

Ink-jet printing was pioneered in Japan in the 1980s with but limited development due to high price. Companies such as Sophis began to modify the existing paper printing machines for use in textiles and the price started to come down. Companies started to provide paper-backed fabric that had the necessary preparation treatments [9-11].

As chemical companies such as Ciba, BASF and Dystar started to develop textile dyes specifically for use in the ink-jet printing machines, the technology became more accessible and further alleviated the cost [12]. The first commercially available ink-jet printing system on textile introduced in 1991 was a continuous stream type which used the Procion P (monochlorotriazinyl) reactive dyes in the ink formulations for printing cellulosic fabrics.

At ITMA 1995 there were few ink-jet printing machines on view with slow production speed and hence limited to sampling or very small lot printing [10]. A major change in the development of ink-jet systems specifically for textile printing was evident at ITMA but the major limitation was low production speed. At ITMA 2003, one of the ink-jet printing machines demonstrated could operate at printing speeds of 150m^2/ hour [13]. This printing speed was only suitable for short to medium production run lengths, but it was still far from the requirement of long production run length [14-19].

Within these ten years, ink-jet printing has been regarded as the most advanced technology in textile printing since it is integrated with computer technology such as CAD system. Ink-jet textile printing has a great comparative advantage than other traditional textile printing methods. It is believed that ink-jet printing may become a favorable kind of textile printing method in the future [9-11].

2.1.1 Current applications

Ink-jet printing is used in some domestic scales with short run textile printing. It includes the printing of curtains, decorative and furniture fabrics, home textiles, roller blinds, table and bed linen, wall paper, carpets, woven ribbons and labels, banners and flags, ties and scarves and so on. Ink-jet printing can produce small quantities of high quality products, for example, products with rich colour content and specific design in a less expensive way [15, 20].

2.1.1.1 Problem associated with ink-jet printing

In the previous 10 years development, ink-jet printing is mainly used for sampling, but in only a few cases for print production. The slow development of ink-jet printing is due to a number of restrictions which are summarised as follows:

2.1.1.1.1 Production speed is low

The printing machines are limited in speed by their low drop ejection frequency and by the frequent need for maintenance operations like wiping the nozzle face or discharging a small amount of ink outside the textile printing area at each scan [15, 21-23]. Hence, it limits them to sampling or low volume production for certain niche markets.

2.1.1.1.2 Material cost is high

Although digital print technology carries a relatively modest price tag in relation to the screen print operation, the cost of the materials for ink-jet printing remains high [24, 25]. Fabric needs extra preparation steps prior to printing and the ink must be highly purified. Many of the commercial inks for ink-jet printing offer the price around to $1000 per litre while the pre-treated fabrics commonly cost around $100 per metre [21, 26, 27].

2.1.1.1.3 Colour gamut and accuracy

The range of colours that can be obtained through four-colour process is smaller than that of spot colour, and the colours are often less vivid and inconsistent. The problem is due to the mixing of process colour dyes on the fabric and uniformity in flat tint printing. Colour accuracy is limited by the ability to place small enough amounts of ink together to match the right colour [5, 8, 21, 28-36]. In addition, colour representation is different under various textile substrates.

2.1.1.1.4 Technological restrictions with regard to nozzles

Technological restrictions include excessive wetting or drying on the nozzle plat, nozzles not printing after periods of inactivity, nozzles not firing consistently during periods of high usage, or ink/print-head interactions causing mis-directed nozzles [33]. While each of these failures can cause inconsistent colour performance and poor image quality, well-designed inks matched to the print head/printer system will eliminate these issues as a concern [21, 32].

2.1.1.1.5 Limited choice for customers

Many textile customers are required to purchase special pre-treated fabrics and do not have an option to use their own fabrics. Printers that allow customers to use their fabrics limited the type of fabrics that can be used.

Sharp outlines are obtained in ink-jet printing, but problems of uneven printing and difficulties in attaining deep shades are experienced, presumably because drop volumes of Cyan (C), Magenta (M), Yellow (Y) and Black (K) inks are so low that they do not blend on the fabric surface [28, 37].

For a successful adoption of ink-jet textile printing, a number of aspects still need to be improved. These include the developments in chemical systems for colouration, integration of the information technology workflow through production planning, digital integration of printing and cutting, new creative routes and colour management [20]. It is also necessary to integrate the concept with flexibility in dye and substrate combinations, appropriate methods of fixation and finishing, and the end-use properties required.

2.2 Historical development

Ink-jet printing of fabrics is a relatively new technology in textile printing area. In recent years, the research and development of ink-jet print mainly focus on increasing the printing speed in order to increase the production output for larger quantities [5, 6, 10, 11, 19, 22, 27, 38-49]. However, there is lack of detailed study concerning the relationship between the pre-treatment and post-treatment processes of ink-jet printing aiming to get better colour quality of the ink-jet printed fabric.

Schneider published a paper about the improved colour quality of ink-jet printing in 2002 [38]. The aim of this research was to investigate the influence of the contents of pre-treatment print paste on the ink-jet printing but the published paper did not consider the important factor of post-treatment process.

Fan studied the effect of pre-treatment on the print qualities in 2002 [50], and the research was mainly dealt with the relationship between the pre-treatment and colour quality. However, the factors of urea, alkali and sodium alginate that affected the colour yield were all neglected.

Subsequently, Yang particularly evaluated the effect of steaming condition on colour consistency in 2004 [51]. He confirmed that the post-treatment by means of steaming time was one of important factors that affected the colour quality. Nevertheless, the interaction between the contents of pre-treatment print paste and steaming process was still lack of systematical study.

Chitosan has been developed as a possible substitute for synthetic polymers in a variety of textile dyeing and finishing applications. According to Bandyopdhyay, chitosan could reduce the amount of electrolyte addition during dyeing with reactive dyes and enhance dye fixation in 1998. Another research of chitosan was conducted on cotton fabric dyeing in 2004 [52]. It was found that the pre-treatment of cotton textile with chitosan could yield higher colour strength. Furthermore, chitosan pre-treatment could reduce the required amount of dyestuff for a given percentage shade [52].

Chitosan can also be applied to textile printing, mainly as the pre-treatment print paste. Bahmani conducted a research on the application of chitosan in pigment printing in 2000 [53]. In this research, printing paste made up from the mixtures of chitosan, pigment and acetic acid at the appropriate viscosity gave satisfactory prints on the polyester and polyester/ cotton woven fabrics. It was found that fabrics printed with only pigment, chitosan and acetic acid could give satisfactory colour fastness to rubbing, washing and light [54].

2.3 Structure of ink-jet printing system

Basically, ink-jet printing system consists of four components, namely (i) hardware; (ii) ink formulation, (iii) media and (iv) software. These components can influence the printing quality in ink-jet printing [15, 21].

2.3.1 Hardware

In the ink-jet printing system, the hardware normally refers to the ink-jet printer. In the case of ink-jet printing on textiles, the printing speed and print head life are the critical hardware issues for commercial and technical considerations. Normally, there are two types of ink-jet printers available namely (i) coarse resolution type and (ii) fine resolution type. The coarse resolution type printer has a maximum resolution of 40 lines per inch while the fine resolution type printer offers fine resolution up to 300 lines per inch.

Coarse resolution ink-jet printer

These printers are normally based on valve technology and have been only accepted by the carpet industry in the field of textile printing. There are two commercially available systems, i.e. Millitron system and Chromojet system, but the resolutions of all these system are relatively coarse and are not acceptable in the field of textile printing [15].

Fine resolution ink-jet printer

In the recent research of ink-jet technology in textile printing, focus has been confined to the area of fine resolution with the printers being sub-divided into two bases of technologies, namely (i) Drop-on-Demand (DOD) and (ii) Continuous ink-jet (CIJ). The development of these two technologies is summarised in Figure 2-1.

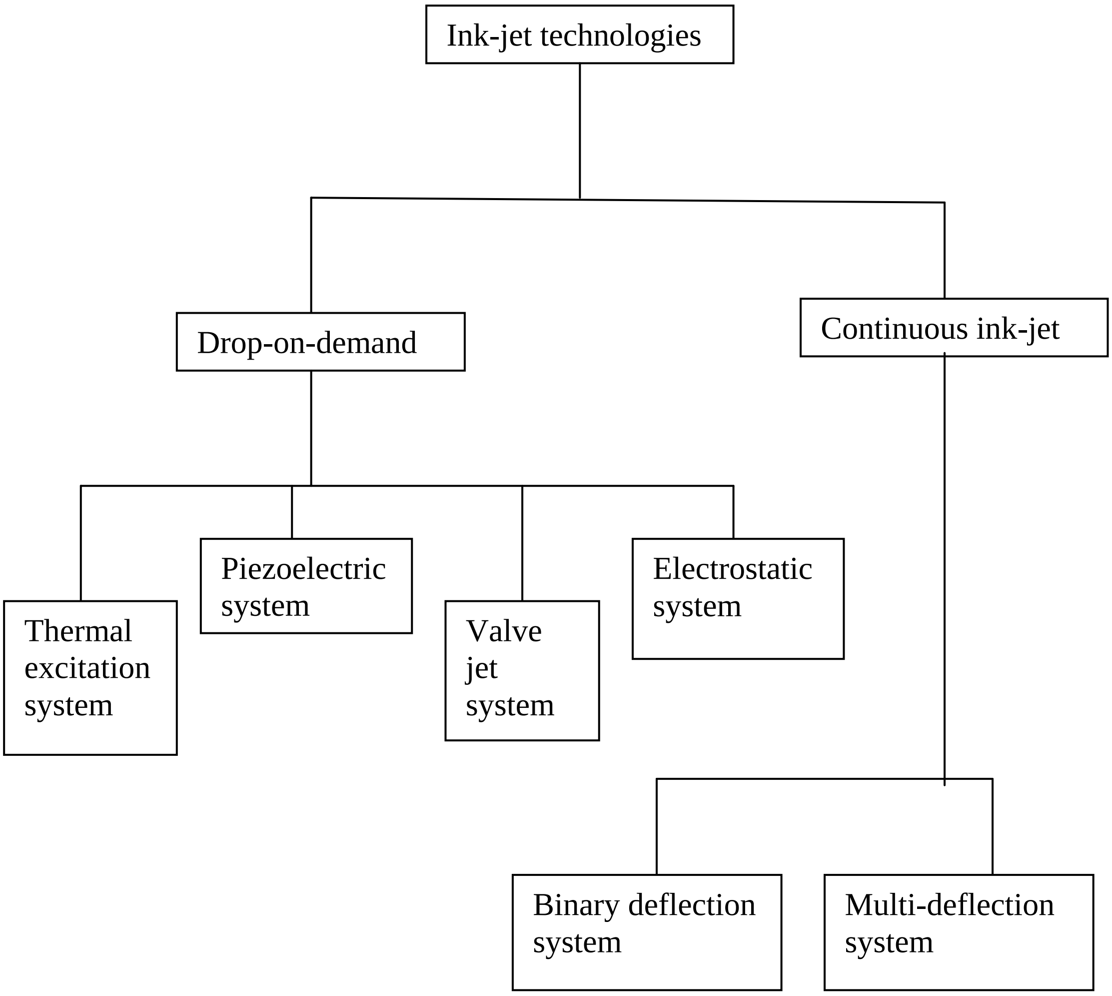


Figure 2-1 The ink-jet technologies for textiles

2.3.1.1 Drop-on-Demand (DOD) printers

This type of printer uses the technology of producing a droplet of ink only when required for printing and delivering it onto the substrate. The ink droplets are not charged. The DOD printer utilises four different systems which have been developed to generate a drop of ink on demand from the control computer. Details of such systems are summarised as follows [15]:

2.3.1.1.1 Thermal excitation system

Most of the DOD printers (about 85%) generally employ thermal excitation principle to generate the ink drop. The signal given by computer heats a resistor to a high temperature (>350°C) which causes the volatile component of ink to form a vapour bubble, and ultimately a drop of ink is ejected from the nozzle as shown in Figure 2-2. Approximately 10000 drops are produced in one second and the volume of a single ink droplet is about 150-200 picolitres. The main advantage of this system is low cost of nozzle fabrication. However, the system suffers from several drawbacks such as (i) high nozzle failure rate, (ii) decomposition of ink components on the resistor due to high temperature required for ejection of drop which leads to poor heat transfer and/or nozzle clogging, and (iii) resistor failure due to rapid heating.

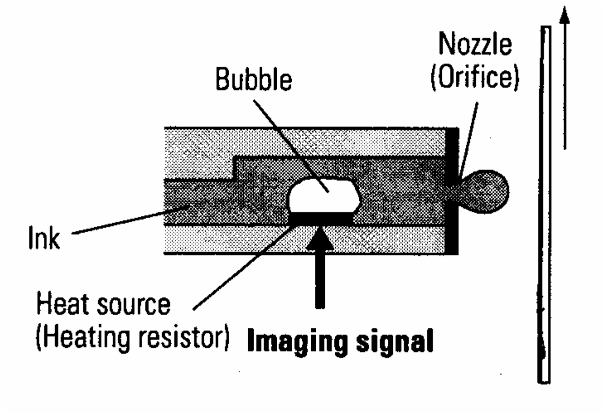


Figure 2-2 Thermal excitation system of DOD ink-jet printer

2.3.1.1.2 Piezoelectric system

In this type of printer, a droplet of ink is produced using a piezoelectric transducer as shown in Figure 2-3. The computer imposes an electrical potential across a piezoelectric material, causing a contraction in the direction of electric field and an expansion in the direction perpendicular to it, which ejects the ink drop. When the electrical potential is removed, the piezo comes backs to its original dimension and the ink chamber is filled up from an ink reservoir by capillary action. The cycle time is somewhat higher (14000 drops per second) than normal ink-jet, but the volume per drop of ink is smaller (150 picolitres). This allows the piezo-based printer to produce a very high resolution print (1440 dpi).

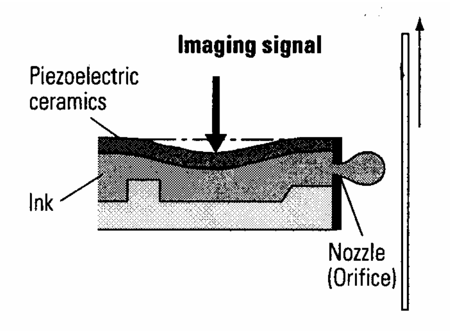


Figure 2-3 Piezoelectric DOD ink-jet printer

2.3.1.1.3 Valve jet system

The valve jet system which is not much used in textile printing utilises solenoid valves to control the flow of ink to an air stream which takes the drop to the substrate. The system can produce a resolution of only 25 dpi, but the amount of ink deposited at each spot in the image can be properly controlled and hence a continuous tone can be obtained.

2.3.1.1.4 Electrostatic jet system

Figure 2-4 shows the electrostatic jet system. In this system, an electrical potential is developed between the nozzle and a valving electrode causing a drop of ink to be pulled out from the nozzle.

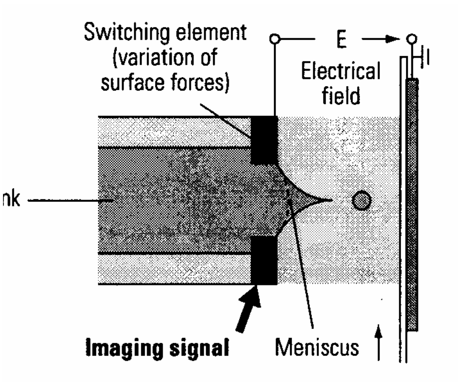


Figure 2-4 Electrostatic DOD ink-jet printer

2.3.1.2 Continuous ink-jet (CIJ) printers

In the CIJ printers, ink is forced at a high pressure through a small nozzle. The emerging stream of ink is broken into small droplets which can be selectively charged and deflected while passing through high voltage deflection plates. The design can be produced by two techniques, i.e. (i) binary deflection system and (ii) multi-deflection system.

2.3.1.2.1 Binary deflection system

In the binary deflection system, droplets are either charged or uncharged by the charging plates as shown in Figure 2-5. The uncharged droplets will be unaffected by the deflection plates which carry a charge opposite to that of the charging plates. The undeflected droplets then strike the substrate to form the image. Droplets carrying a charge are deflected to a catcher or gutter by the deflection plates for recycling [25].

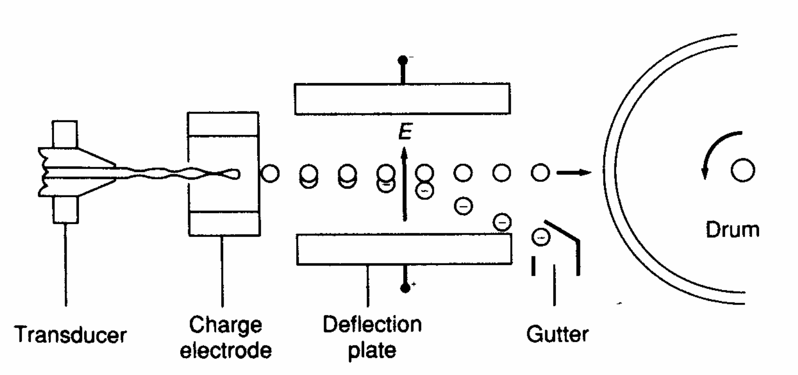


Figure 2-5 CIJ binary deflection system [25]

2.3.1.2.2 Multi-deflection system

The multi-defection system shown in Figure 2-6 uses the same basic principle as binary deflection system but with more control. This approach differs from the binary deflection system in which the droplets are given a variable charge that gives different deflections on the droplet passing through the deflection plates. This allows multiple positions on the substrate (up to 30) to be printed from a single jet.

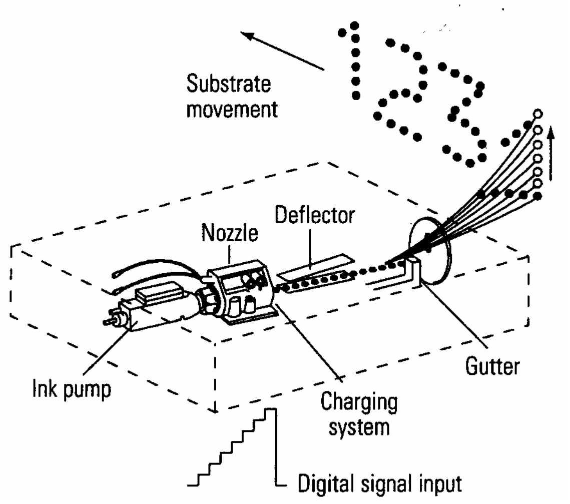


Figure 2-6 CIJ multi-defection system

2.3.1.3 Critical hardware issue between DOD printers and CIJ printers for textile printing

When comparing the two types of printer, perhaps the most obvious discussion point is that the speed is one of the major issues. The need for increased speed probably favours CIJ printers over DOD printers. Both the number of drops per second and the drop volumes are limited by basic design parameters in the DOD printers. These design limitations are much less restrictive in the CIJ printers.

Conversely, the cost of CIJ heads is significantly higher than that of the DOD heads. The general approach for DOD printer developers is to add larger and larger numbers of nozzles in order to increase the printing speed. The difficulty with this approach is that each additional nozzle increases the computer capacity and data handling rate needed for the control of the printer, thereby increasing the probability that one of the nozzles will clog or fail [15, 55].

Print head life is already a critical issue for DOD printers. No commercial printing system based on this technology has the nozzle life expectancy required for textile printing. In this respect, CIJ printers will have the second major advantage over the DOD printers. The continuous flow of ink tends to give fewer problems with clogging or air bubble ingestion that are experienced in the jets of DOD printers. The disadvantages of the CIJ printers is that ink recycling systems must be provided for recovering and reusing the inks that are not required for image formation.

2.3.2 Ink formulation

The ink-jet colourants must possess essentially some characteristics such as high purity, high chroma, clear tone of the colour, high solubility in water and acceptable wet and light fastness properties on the printed fabric. Therefore, when developing the colourant system for ink-jet printing, the system should fulfill these basic requirements [3, 9, 15, 30-32, 46, 56]. Various important colourant systems selected for ink-jet printing are summarised in the following sections:

2.3.2.1 Reactive ink

Inks based on reactive dyes can be used for printing cotton, viscose or cellulosic fibres. The dyes react with the cellulose to form covalent bonds chemically. It is this bond that gives reactive dyes their high level of fastness to washing. In order to achieve full chemical reaction, alkali and heat are required. In ink-jet printing, the alkali must be first applied by a pre-treatment process as it will interfere with reactive dyes and the nozzle components if it is placed inside the ink. The heat is applied after printing by a steam or hot air fixation process. A separate wash process must be required to wash off any unfixed reactive dye and to ensure optimum fastness [26, 57, 58].

2.3.2.2 Disperse ink

Disperse inks are based on a special type of disperse dye that can be printed onto paper and then transferred to textiles using a heat press. These inks can also be printed directly onto substrate. There are also disperse inks that have particular fastness properties, which can be applied directly to the substrate and high temperature steam is generally used to fix the dye [58].

2.3.2.3 Acid ink

Acid dyes are used for printing nylon, wool, silk or polyamide fibres. Although acid dye occupies only a small sector, it is still quite important for ink-jet printing as many high quality designs are printed on luxurious fabrics such as wool and silk. A pre-treatment is generally necessary to prevent wicking of the ink on the fabric. A post-treatment such as steaming is necessary in order to get fixation, and a separate wash-off process is required to ensure the complete removal of unfixed dye [58].

2.3.2.4 Pigmented ink

Pigment printing accounts for almost half of all printed textiles and is, therefore, an important colouration system [46]. The coloured pigment is bound to the substrate using a binder system. In ink-jet printing system, it must be applied in the ink either, by separate nozzle system or by application after ink-jet printing. The advantage of these types of ink is that they can be applied to many different substrates. The application route is shorter than that of any dye-based inks as it does not employ a pre-treatment or washing process [58].

2.3.2.5 Control factors of ink for ink-jet printing

Inks are the control factor for efficiency and economy of ink-jet printing. To ensure fault-free printing, the factors such as viscosity, surface tension and conductivity are required to be controlled.

2.3.2.5.1 Influence of viscosity

It is recognised that low viscosity ink does not work on the ink-jet printer [3]. It is not caused by a high ink viscosity or by particles in the inks, because these are filtered out. Low viscosity ink also gives the same results. There must be an additional parameter which causes the blocking of nozzles [32, 59, 60]. This may be the surface tension or some other undiscovered parameters. In order to explain these results, it is necessary to take a closer look at the function of a piezo print head as shown in Figure 2-7.

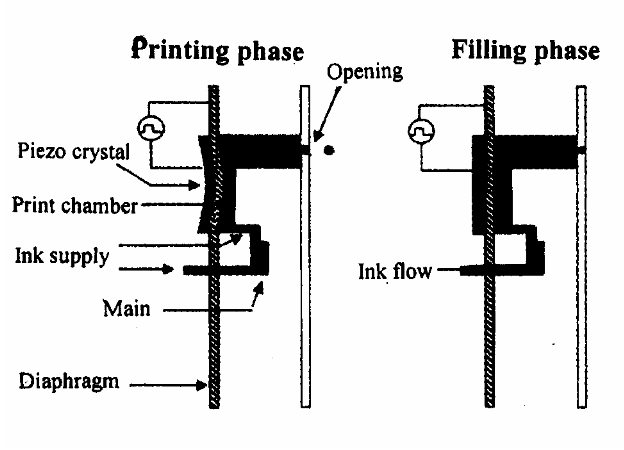


Figure 2-7 Ink flow within a piezo print head

Figure 2-7 shows that the piezo print head is an open push-pull-system. The deformation of the piezo crystal causes a pressure wave. The pressure wave overcomes the pressure lost at the nozzle and the forces of surface tension at the meniscus. A drop is formed at the nozzle. The pressure shock is also large enough to shoot the formed droplet onto the fabric. This process should work better with a lower viscosity and lower surface tension of the ink but this is not really the case. Low viscosity ink does not work. To explain this, the complete system must be considered.

The ink chamber is an open system with two exits. Instead of being pressed through the tiny nozzle, the ink can also flow back into the pipe system. The force which prevents the reflux of the ink is the viscosity. A minimum viscosity is therefore necessary to prevent the reflux of the ink into the tube system. In this way, the ink works like a valve meaning that the ink is a part of the printing system itself. On the other hand, if the viscosity is too high, the suction force of the piezo crystal is too small to pump the ink into the ink chamber and printing is thus not possible [60].

During the suction phase of the piezo crystal, the pressure in the ink decreases. If there are any dissolved gases in the ink, they will form bubbles like those formed while opening a bottle of mineral water. This gas bubbles interrupt the ink flow in the tubes and block the nozzles. It is therefore necessary to de-aerate the inks using ultrasonic treatment before filling the ink tanks.

2.3.2.5.2 Influence of surface tension on printing quality

Surface tension plays an important role during the formation of ink droplets. The surface tension of commercial inks varies between 21 to 48 mN/m. It is noted that the surface tension of ink is influenced by the amount of surfactant inside the ink. Improvement in printing behaviour is only possible with high concentration of surfactants.

One reason for this is that the static method used for the measurement of surface tension is too slow for effect which determines the behaviour during the very quick process of droplet formation [32, 60]. Another reason is that the surface tension is less important than the viscosity as viscosity is a decisive factor. Furthermore, it is possible that a higher surface tension reduces the risk of satellite droplets during droplet formation and this can be an advantage for ink with high surface tension.

2.3.2.5.3 Influence of conductivity

Conductivity of ink influences the printing behaviour depending on the salt content of ink. A salt content of more than 1-1.5% has a negative effect on the printing behaviour. Blocking of nozzles also occurs with high salt content. In addition, only high purified dyes are suitable for ink formulation in ink-jet printing [32].

2.3.3 Media

2.3.3.1 Fabric pre-treatment

Similar to conventional printing process, the success of ink-jet printing depends mainly on the fabric preparation process [13, 35, 45]. Textile substrates generally need some pre-treatment and post-treatment in order to ensure proper ink absorption and fixation. The fabrics, e.g. cotton fabric, have to be properly desized, scoured and bleached. Singeing improves not only the quality of prints but also the process of reproducibility. In the case of unsinged fabric, the projecting hairs can block the ink-jet or cause the missing of colour.

Depending on the dye class applied and the substrate on which the print is being made, the textile material needs a certain pre-treatment before being ink-jet printed [15]. For the printing of cotton fabric with reactive dye, the cotton fabric has to be pre-padded with chemicals such as alginate, urea and alkali. Those chemicals are used for controlling the sharpness of borders, increasing the depth of colour and maximising the shade development.

2.3.3.2 Fabric hairiness

Owing to the construction of the print head and the transversal movement along the width of the fabric, there is a small static charge being built on the print head. This causes an attraction of all loose fibres which cling onto the print head. The closer the print head moves to the fabric, the bigger will be the problem of blocking the nozzles [61].

2.3.3.3 Warp and weft alignment

It is not only important to keep the fabric feeding flat into the printer. The cloth needs to remain straight during the printing process so that a line remains a line and does not become curved after fixation and washing off. If the fabric warp and weft alignment is not straight during printing, even the best stenter operator cannot get it straight again during the drying operation in the post-treatment. Therefore, it is very important to print on straight fabric and to keep the fabric straight on the printer [61].

2.3.3.4 Fabric tension

It is commonly known that the fabric needs to be flat during printing. In ink-jet printing, this is mainly done by putting a bit of tension on the substrate when guiding it through the machine. Many elastic fabric constructions are not allowed to be stretched during printing. Therefore, attention needs to be paid to minimise the tension and to keep the fabric as flat as possible. Since ink-jet printing is a printing method in which there is a movement each time followed by a pause, thus there is a risk in the formation of printing stripes coming from tension followed by relaxation. To minimise this, the question of tension control comes up again [61].

2.3.3.5 Shrinkage during printing

Ink-jet printing is a non-contact printing method which allows the fabric being printed but without being touched. This eliminates the image distortion and does not put a lot of strain on the material being printed. Hence, ink-jet printing does not require an aggressive fabric hold down method as encountered in the conventional screen printing. Nevertheless, when the pre-treated fabric is printed, this comes down to a local wetting of the fabric. The deeper the colour being printed, the wetter the fibres get and the more the shrinkage phenomenon becomes visible [61].

2.3.4 Software

Software includes printer drivers, image processor and colour management system which can convert computer-based designs into the electronic signals to control the scanning ink-jet head and machine. These systems can also ensure faithful and reproducible results for different batches of fabric, and provide a total interface with the other components of a digital design, sampling and production environment [24, 30, 35, 48, 62].

2.4 Role of chemicals in pre-treatment paste

In conventional printing, the reactive dye is applied with alkali and other additional chemicals in the form of a print paste [35, 63]. The print is normally steamed to fix the dye to the cotton and then washed thoroughly to remove any unreacted dye, chemicals and thickener. Due to the requirements of purity and specific conductivity, most of the conventional printing chemicals such as alkali, urea and sodium alginate thickener can be incorporated into the ink formulation [3, 15, 19, 25, 57]. As a result, the cotton fabric should be pre-treated before printing. The chemicals necessary for fixing reactive dyes to cotton can be padded onto the fabric prior to the ink-jet printing stage.

It is a common practice that most of the commercially pre-treated cotton fabrics available in the market for ink-jet printing have been padded with pre-treatment print paste. However, due to commercial reasons, the content of such pre-treatment print pastes used for the commercially pre-treated fabric was not disclosed resulting in very expensive price for this fabric type.

2.4.1 Alkali

Sodium carbonate or sodium bicarbonate is generally used in the pre-treatment paste for in ink-jet printing of cellulosic fibre when dealing with reactive dyes, aiming to help the development of final shade [57]. Alkali is essential to produce ionisation of accessible cellulose hydroxyl groups which can react with the reactive dye [64].

Sodium bicarbonate has been the preferred alkali medium because it is cheap and can give sufficient print paste stability with reactive dyes. During steaming or baking, sodium bicarbonate loses carbon dioxide followed by the increased ionisation of cellulose. When the high stability of the dye is required, sodium carbonate may be preferred because the more stable dyes will give higher colour yields under more alkaline conditions [64].

For the dyes of high reactivity the concentration of sodium bicarbonate may be reduced or sodium trichloroacetate is used. The latter decomposes during steaming to form sodium carbonate and allows the use of neutral print pastes or even pastes slightly acidified with acetic acid.

2.4.2 Sodium alginate

Sodium alginates are natural thickeners suitable for use in printing with reactive dyes [45, 57, 64, 65]. All other carbohyydrates react with the dye and this results in low colour yield or unsatisfactory handle due to insolubilities of the thickener. Sodium alginate also contains hydroxyl group but it reacts very little, presumably because the ionised carboxyl groups on every ring of the polymer chain repel the dye anions. The function of sodium alginate in the pre-treatment paste is aimed to control the sharpness of borders of the final print [65].

2.4.3 Urea

Urea is necessary for optimal fixation of reactive dyes in hot air or superheated steam [57]. Urea also reduces the yellowing of cellulose under hot, dry, alkaline conditions, and thus helps in the production of bright colours. It acts as a solvent for the reactive dye and accelerates migration of the dye from the thickener film into the cellulosic fibre [64]. The hygroscopic properties of urea not only control penetration but also have a significant impact on the sharpness of the printed pattern.

2.5 Chitosan application

2.5.1 What is Chitosan?

Chitosan is the derivative of chitin produced by alkaline deacetylation. Chitin is the second most abundant natural polymer after cellulose, and it is recovered at present as a by-product of the sea food industry, typically from the crab shell. The structures of Chitosan and Chitin are shown in Figure 2-8.

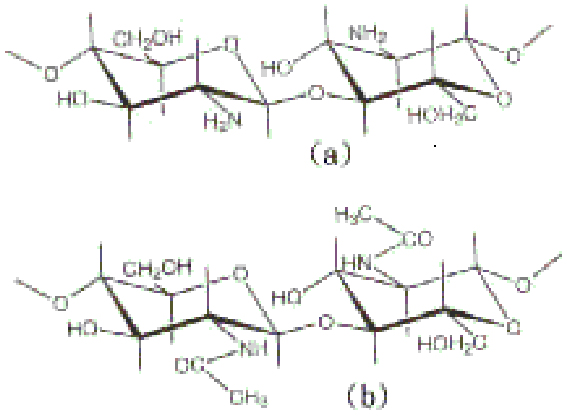


Figure 2-8 Chitosan (a) and Chitin (b) structures

The structure of Chitosan is very similar to cellulose except that amino groups replace the secondary hydroxy groups at C-2 position in the cellulose chain. It is soluble in 1% acetic acid solution while it is insoluble in water, soap solution or dilute alkali. It has the properties of anti-microbial, anti-tumor, biodegradability, biocompatibility, non-toxicity and wound healing. It makes chitosan attracts more and more scientific and industrial interest from diversified fields such as chemistry, medicine, food and textile sciences.

2.5.2 Applications in textile

Currently, sodium alginate is a common and an important thickener used for preparing the pre-treatment print due to its ready solubility and excellent stability even after high-temperature fixation treatments [66]. In addition, the extent of interaction of sodium alginate with reactive dyes is very small. Similar to sodium alginate, chitosan has also found widespread used as novel biomaterial.

As a natural polymer, sodium alginate and chitosan are biocompatible, biodegradable and non-toxic [67]. Previous research reported that chitosan could be applied to different textile areas [54], and one of the areas was to apply it to the conventional textile printing for improving the dye uptake and colour fastness.

CHAPTER 3.

CHARACTERISATION OF INK-JET PRINTING INK

3.1 Introduction

In the analysis of four unknown commercial ink-jet printing inks, three instrumental techniques were involved namely:

1. Ultraviolet-Visible Spectroscopy (UV/VIS)
2. Thin-Layer Chromatography (TLC)
3. Infrared Spectroscopy (IR)

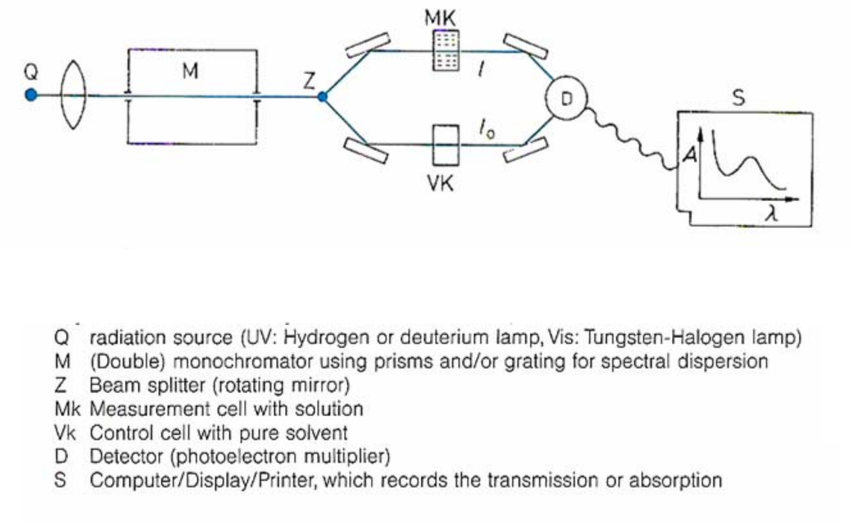
UV/VIS can be used to analyse the colour range of the dye existing in the four unknown commercial inks. By analysing the UV/VIS absorption spectra of the inks, their maximum absorbance can be found and hence the respective colours will be known.

TLC is widely used in dye analysis. TLC possesses the same fundamental mechanism as HPLC. The result of TLC can show the separation of dye or dye mixtures and help find out the number of dye components existing in the four unknown commercial inks. If there is only one dye in each ink after TLC separation, this means that the ink is pure.

IR is used as a means of identifying the chemical composition of inks. By obtaining the IR spectra of the inks, the functional groups and the dye class of the unknown dyes can be deduced.

3.2 Ultraviolet-Visible Spectroscopy (UV/VIS)

UV/VIS combined with other spectroscopic methods can be used as a valuable method for qualitative analysis and structure determination [68]. UV/VIS is valuable for the determination of the colour of dye present in inks. By analysing the UV/VIS absorption spectrum of the ink, the maximum absorbance of the ink was determined and hence the respective colour was known. The principle of UV/VIS is shown in Figure 3-1 [68].



Q	radiation source (UV: Hydrogen or deuterium lamp, Vis: Tungsten-Halogen lamp)
M	(Double) monochromator using prisms and/or grating for spectral dispersion
Z	Beam splitter (rotating mirror)
Mk	Measurement cell with solution
Vk	Control cell with pure solvent
D	Detector (photoelectron multiplier)
S	Computer/Display/Printer, which records the transmission or absorption

Figure 3-1 Ultraviolet-Visible Spectroscopy

3.2.1. Instrumentation

UV/VIS Spectrometer Lambda 18 shown in Fiqure 3-2 was used to produce the spectral absorbance curve for the four unknown commercial ink-jet printing inks.

Figure 3-2 UV/VIS Spectrometer Lambda 18

3.2.2 Experimental procedures

3.2.2.1 Sample preparation

Four unknown commercial ink-jet printing inks namely Cyan (C), Magenta (M), Yellow (Y), Black (K) were studied. The ink samples used for generating the UV/VIS spectra were measured in solution form. The solvent used must be in optically pure state. In the experiment, deionised water was used as a solvent for the dilution of inks and reference cell measurement. The use of the dilution of inks was to increase the optical transmittance of the light source of the UV/VIS, otherwise the inks in too high concentration would affect the spectra obtained.

Three different ink concentrations, i.e. 0.25%, 0.1% and 0.05%, were prepared for the scanning of spectra. Totally, twelve ink samples were generated for the scanning of spectra. Before scanning the sample, the reference solvent (deionised water) was scanned with the following scanning conditions:

1. wavelength range: 800nm – 200nm
2. number of cycles: 5
3. scanning speed: 120nm/min
4. resolution: $1cm^{-1}$

The twelve ink samples were scanned under the same scanning conditions as the reference solvent. After the ink samples were scanned, their absorption spectra were generated and the maximum absorption peaks were labelled. Two spectra of every ink sample were scanned and totally twenty-four spectra were produced.

3.2.3 Result and discussion

3.2.3.1 Characterisation of the colour range by UV/VIS

The precise description of colour range is depending mainly on the wavelength position of the absorption band or the maximum absorption peaks, partly on the band width and partly on the overall shape of the absorption curve.

The general relationship between the observed hue and wavelength region where the maximum value lies is illustrated in Table 3-1. This table is used to evaluate the colour of the four unknown commercial inks. The resultant UV/VIS absorption spectra measured from the four unknown commercial inks are shown in Figures 3-3 to 3-6. Only 0.05% of each ink sample is shown in these figures.

Table 3-1 Absorption band and colour relationship

Colour	**Colour of light absorbed and wavelength region of light absorption**	
Yellow	Violet-blue	400-430nm
Orange	Blue	430-470nm
Orange-red	Blue-green	470-500nm
Red-purple (magenta)	Green	500-540nm
Purple	Yellow-green	540-570nm
Violet	Yellow	570-590nm
Blue	Orange	590-610nm
Greenish-blue (cyan)	Orange-red	610-700nm

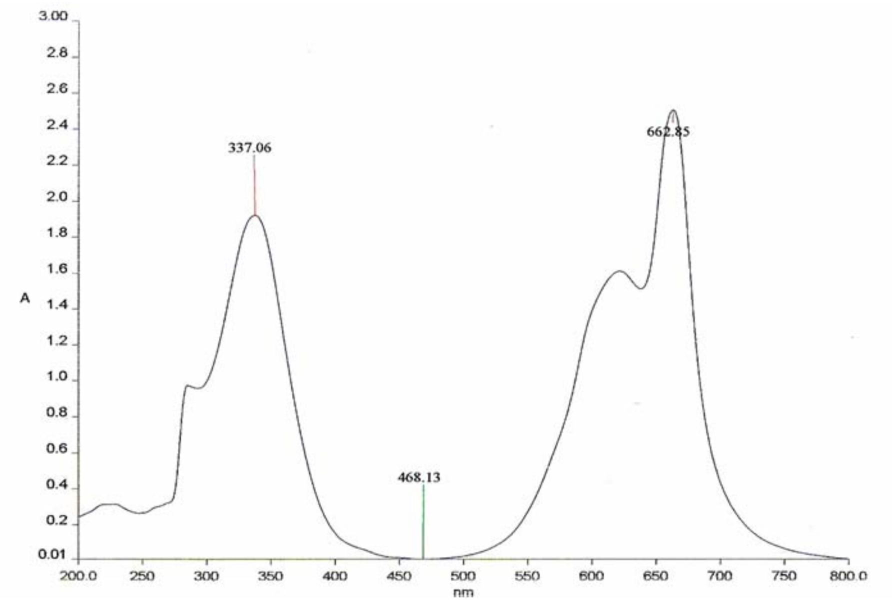


Figure 3-3 Absorption Spectrum of 0.05% Cyan

Figure 3-3 shows that a sharp peak was found within the visible region (400nm-700nm), and the maximum absorption peak was located at 662.45nm. By referring to Table 3-1, the maximum absorption peak of 662.45nm was located within the absorption region of orange-red light (610-700nm). As a result, the colour of this ink was regarded as Cyan (greenish-blue).

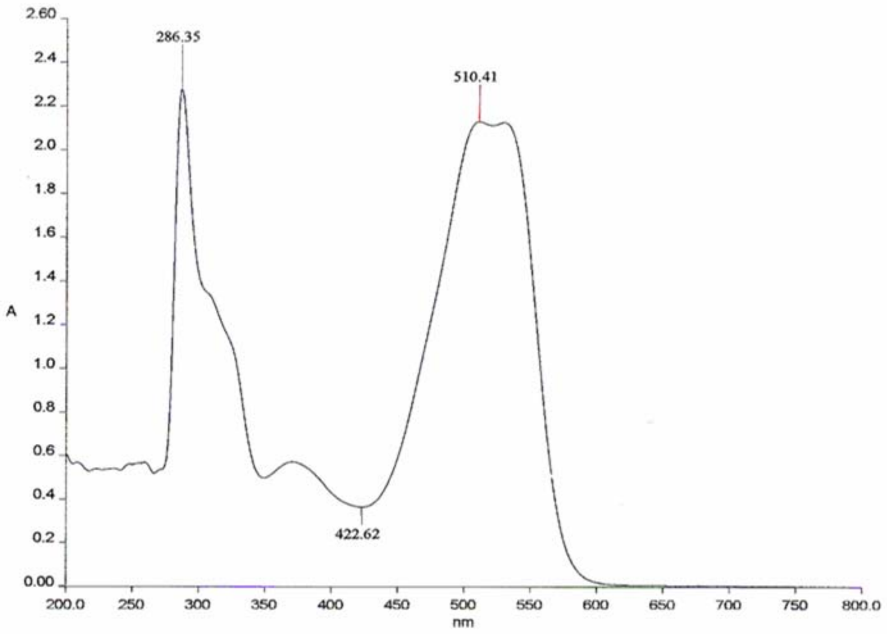


Figure 3-4 Absorption Spectrum of 0.05% Magenta

Figure 3-4 shows that a sharp peak was found within the visible region (400nm-700nm), and the maximum absorption peak was located at 510.41nm. By referring to Table 3-1, the maximum absorption peak of 510.41nm was located within the absorption region of green light (500-540nm). As a result, the colour of this ink was regarded as Magenta (red-purple).

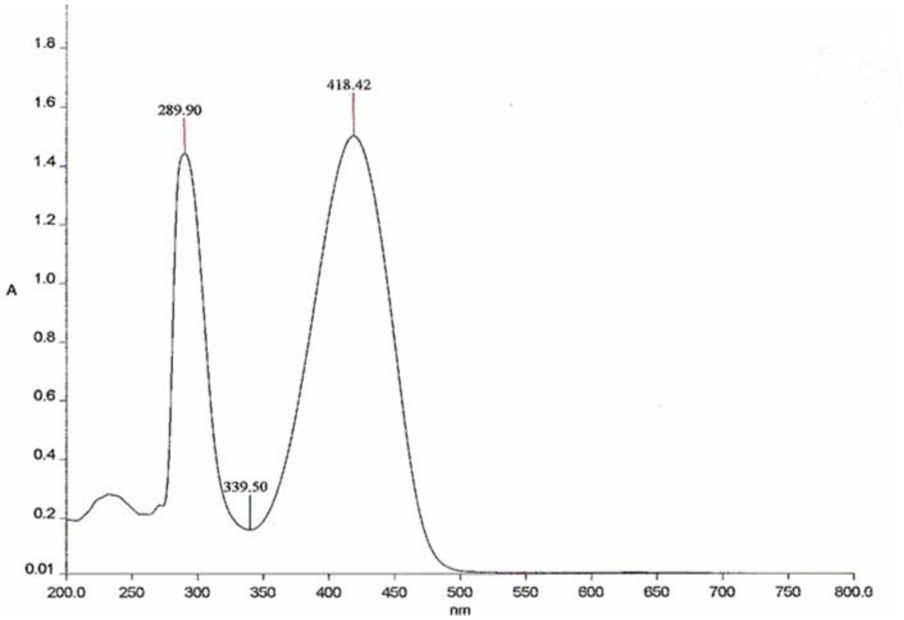


Figure 3-5 Absorption Spectrum of 0.05% Yellow

Figure 3-5 shows that a sharp peak was found within the visible region (400nm-700nm), and the maximum absorption peak was located at 418.42nm. By referring to Table 3-1, the maximum absorption peak 418.42nm was located within the absorption region of violet-blue (400-430nm). As a result, the colour of this ink was regarded as Yellow.

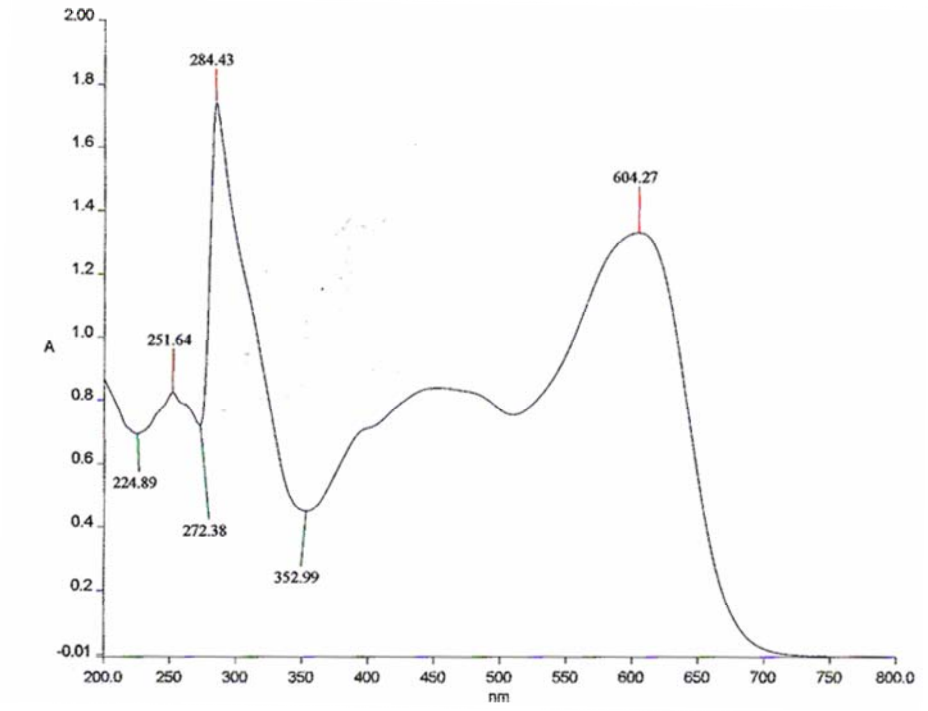


Figure 3-6 Absorption Spectrum of 0.05% Black

Figure 3-6, shows that a broad band of absorption was found within the 400nm-650nm region, and a relatively sharper absorption peak was located at 604.27nm. As a result of a broad absorption band of light, the colour of this ink was regarded as Black.

3.3 Thin Layer Chromatography (TLC)

TLC is widely used in many fields including dye analysis [69]. It is a mode of liquid chromatography in which the sample is applied as a small spot or streak to the origin of a thin solvent layer supported on a glass, plastic, or metal plate. It is a method of analysis in which a mobile phase passes over a stationary phase in such a way that a mixture of substances is separated or resolved into its components. The separation mechanism of TLC is the same as HPLC.

TLC can be used as both an analytical technique and preparative technique [70]. The separated substances that are tentatively identified by TLC can be eluted for further characterisation by other micro-analytical techniques such as Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Ultraviolet-Visible Spectroscopy (UV/VIS), Infrared Spectroscopy (IR), Nuclear Magnetic Resonance (NMR), Mass Spectrometry (MS) and electro analysis.

3.3.1 Experimental procedures

3.3.1.1 Detection and visualisation

Ascending development of TLC was used in this experiment. After the application of ink samples, the TLC plate was placed in a beaker and held vertically. The solvent was then allowed to rise by capillary action. There was no pre-treatment or dilution of inks and so the four unknown commercial of ink-jet printing inks C, M, Y and K colours, were applied directly onto the TLC plate. As the ink samples were coloured substances, thus it could be viewed in daylight without any treatment. The resultant TLC plates were visually assessed in the light box using D_{65} illuminant.

3.3.1.2 Materials and apparatus

Ink-jet printing inks: Four commercially available printing inks (C, M, Y, K)

Commercial TLC plates: Merck Aluminum Silical gel 60 (no fluorescent) 20x20 cm

Solvent: Acetonitrile, chloroform, methanol, n-hexane and water

Apparatus: 1000 ml beakers (substitute for TLC development chamber) and micro-pipettes

3.3.1.3 Sample preparation

The TLC plate was cut into 6 pieces with each size of 11cm x 7 cm. A line of 1.5cm was slightly drawn away from the bottom on the plate with a pencil, and this should be the only area to be handled in order to avoid placing fingerprints on the plate. Small crosses were marked on each with 1 cm away from each other along the line for placing the sample spot. The micro-pipette filled up with the ink sample was held vertically, and the ink sample was dropped onto the marked cross by layer contact. A round spot or zone of ink sample was formed.

The plate was dried using a dryer for 10 minutes to assure that all the inks were completely dried. 100ml solvent was poured into the breaker. The plate was dipped into the beaker vertically and the solvent was then allowed to rise by capillary action. The level of solvent must not be above the application of the ink sample. After 1 hour, the plate was taken out from the beaker and dried for 15 minutes using a dryer. The resultant TLC plate was assessed visually in a light box using D_{65} illuminant. The whole experiment was done in the fume board because the solvents were highly flammable and volatile. The 6 trail of TLC plates with different solvents used are shown in Table 3-2.

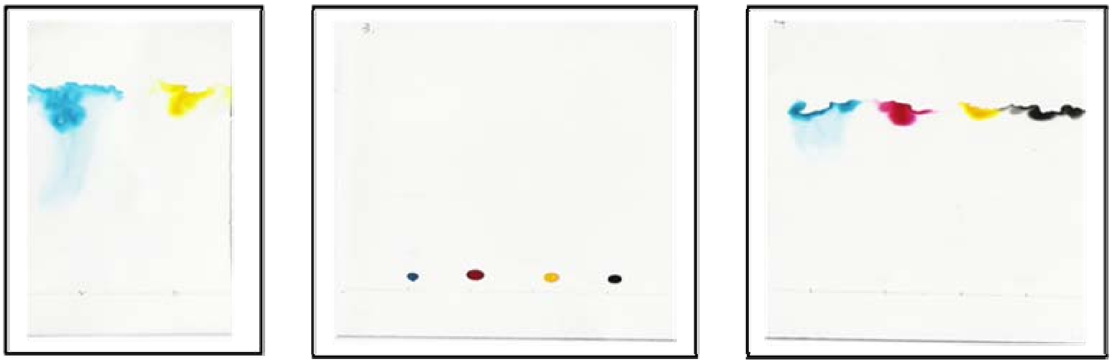
Trial	**Ink sample**	**Solvent used (Mobile phase)**
1	Cyan, Yellow	100% methanol
2	Cyan, Yellow	100% n-hexane
3	Cyan, Magenta, Yellow, Black	100% chloroform
4	Cyan, Magenta, Yellow, Black	100% methanol
5	Cyan, Magenta, Yellow, Black	acetonitrile: water (65:35)
6	Cyan, Magenta, Yellow, Black	Methanol: acetonitrile: water (50:32.5: 17.5)

Table 3-2 Different solvents used for the development of TLC plates

3.3.2 Result and discussion

3.3.2.1 Analysis of commercial ink-jet printing inks by TLC

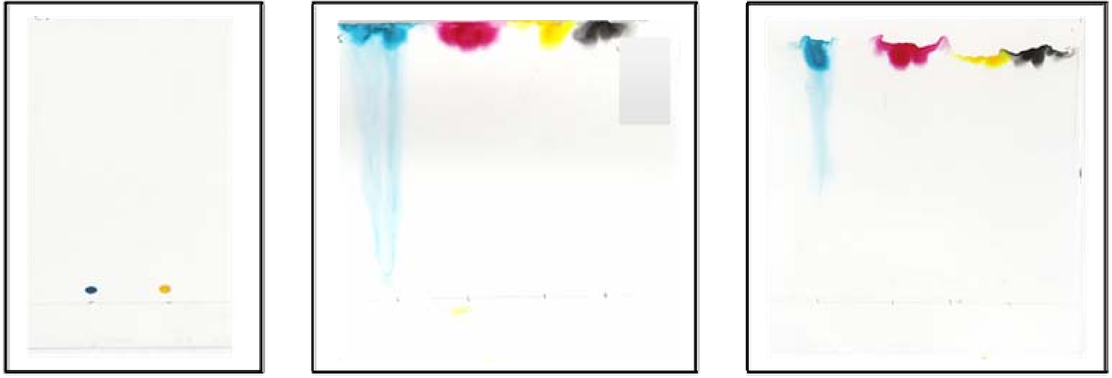
The results of ink separation on the TLC plates was presented by means of photographs as shown in Figure 3-7.



Trial 1
Solvent: 100% methanol

Trial 3
Solvent: 100% chloroform

Trial 5
Solvent: acetonitril/water (65:35)



Trial 2
Solvent: 100% n-hexane

Trial 4
Solvent: 100% methanol

Trial 6
Solvent: methanol/acetonitrile/water

Figure 3-7 The results of ink separation on TLC plates

According to the TLC results shown in Figure 3-7, it was found that trails 1, 4, 5 and 6 showed positive results while trails 2 and 3 showed negative result. For the positive result, the ink spot moved up to the top part of the plate. As for the negative result, the ink spot remained at the original position. This meant that the solvents used for trails 1, 4, 5 and 6 were suitable for separating the four different ink-jet printing inks of C, M, Y and K colours using Aluminum Silical gel 60 TLC plates.

The solvents or solvent mixture used for these four trails were 100% methanol, acetonitrile/ water mixture (65:35), and methanol/ acetonitrile/ water mixture (50:32.5:17.5) respectively.

With regard to the TLC chromatograms of trails 1, 4, 5, and 6 shown in Figure 3-7, only one ink sample spot moved up to the plate and no other spot was separated and found. As a result, it was primarily concluded that the four different commercial ink-jet printing inks of C, M, Y and K colours were composed of only one dye component.

3.3.2.2 Analysis of commercial ink-jet printing inks by HPLC

HPLC was used to separate the components of dyes present in the ink-jet printing inks of Cyan, Magenta, Yellow and Black colours in order to identify the purity of inks. The solvents chosen were based on the results obtained from TLC. Due to the time constraint, the relatively less influencing parameters such as flow rate and concentration of ink sample would not be studied thoroughly in the investigation. Details of HPLC instrumental parameters are summarised in Table 3-3. In general, pure ink can be identified by the formation of single peak in the HPLC chromatogram.

Table 3-3 HPLC instrumental parameters

Instrumental parameters	**Choice of relative parameters**
Column	Alphabond C18 125A 10U i.d.3.9mm 300mm
Solvent	100% Methanol
Wavelength selection of UV absorbance detector	254nm
Flow rate	0.5 ml/min
Concentration of ink sample	0.5%

Methanol was chosen as a representative solvent to study the test. HPLC chromatograms obtained by four different ink-jet printing inks namely Cyan, Magenta, Yellow and Black with the detection wavelength of 254nm were selected for discussion as shown in Figures 3-8 to 3-11 respectively.

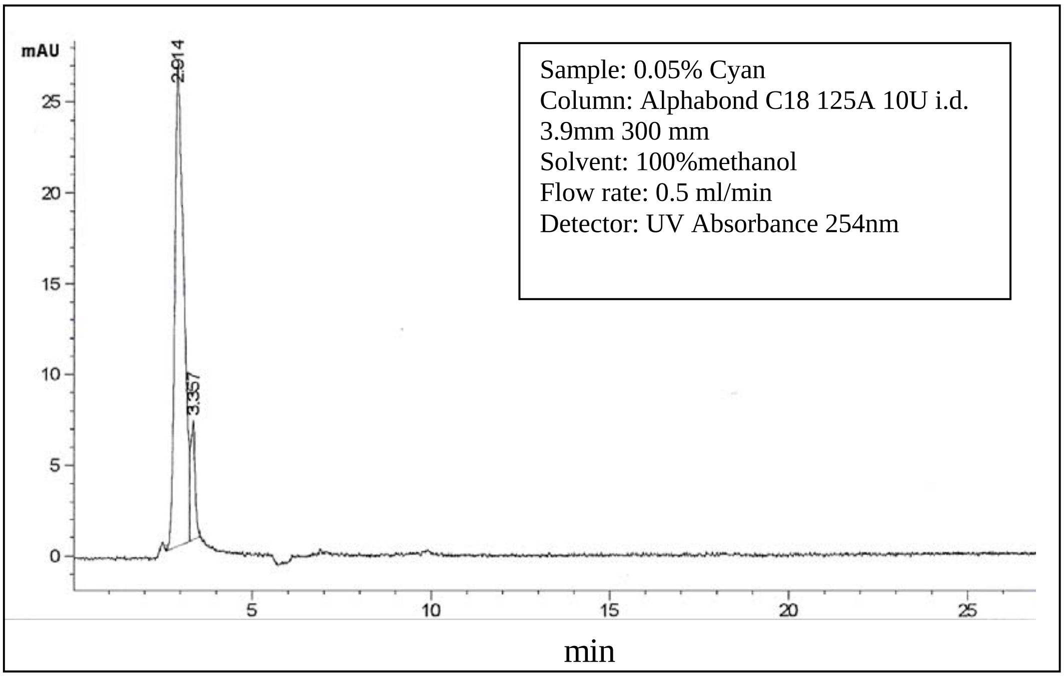
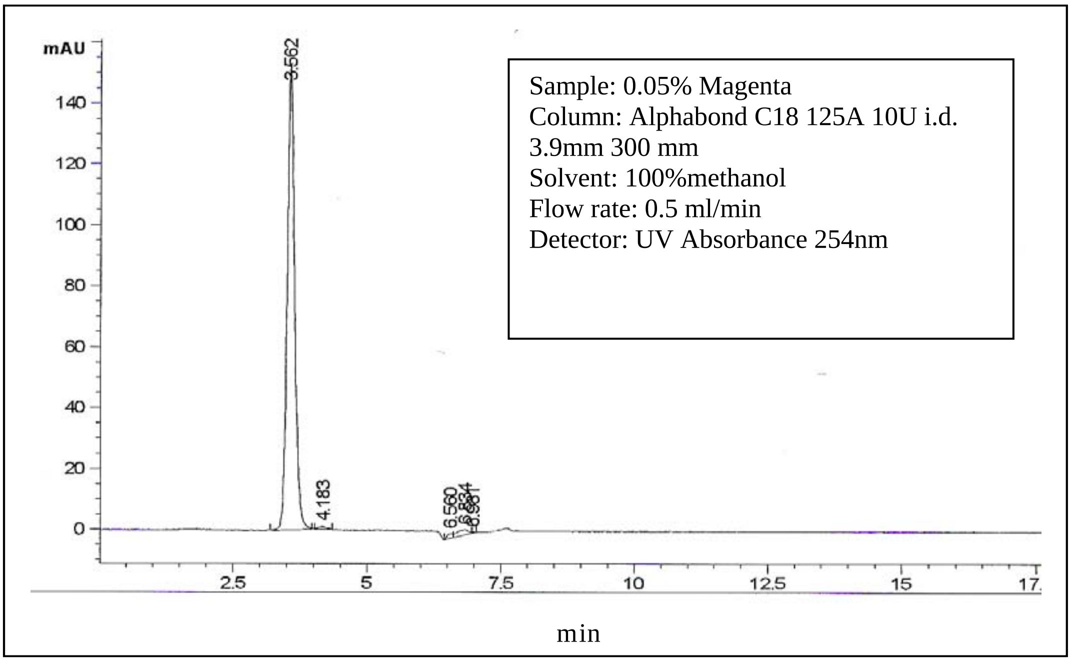
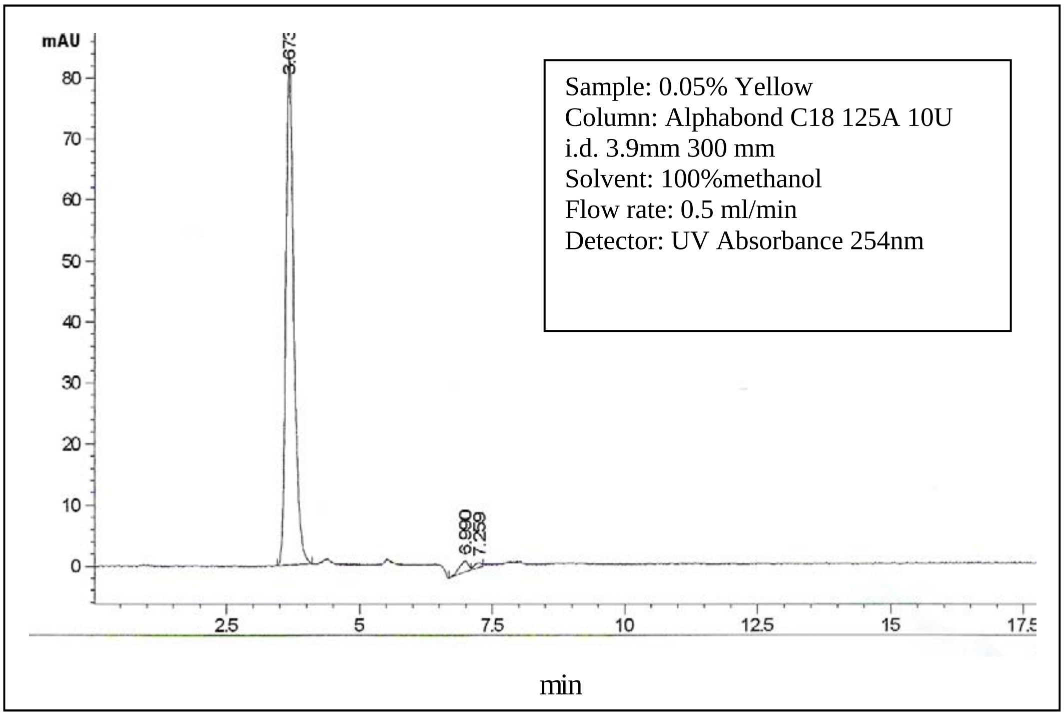

Sample: 0.05% Cyan
Column: Alphabond C18 125A 10U i.d. 3.9mm 300 mm
Solvent: 100%methanol
Flow rate: 0.5 ml/min
Detector: UV Absorbance 254nm

Figure 3-8: HPLC Chromatogram of Cyan



Sample: 0.05% Magenta
Column: Alphabond C18 125A 10U i.d.
3.9mm 300 mm
Solvent: 100%methanol
Flow rate: 0.5 ml/min
Detector: UV Absorbance 254nm

Figure 3-9: HPLC Chromatogram of Magenta



Sample: 0.05% Yellow
Column: Alphabond C18 125A 10U
i.d. 3.9mm 300 mm
Solvent: 100%methanol
Flow rate: 0.5 ml/min
Detector: UV Absorbance 254nm

Figure 3-10: HPLC Chromatogram of Yellow

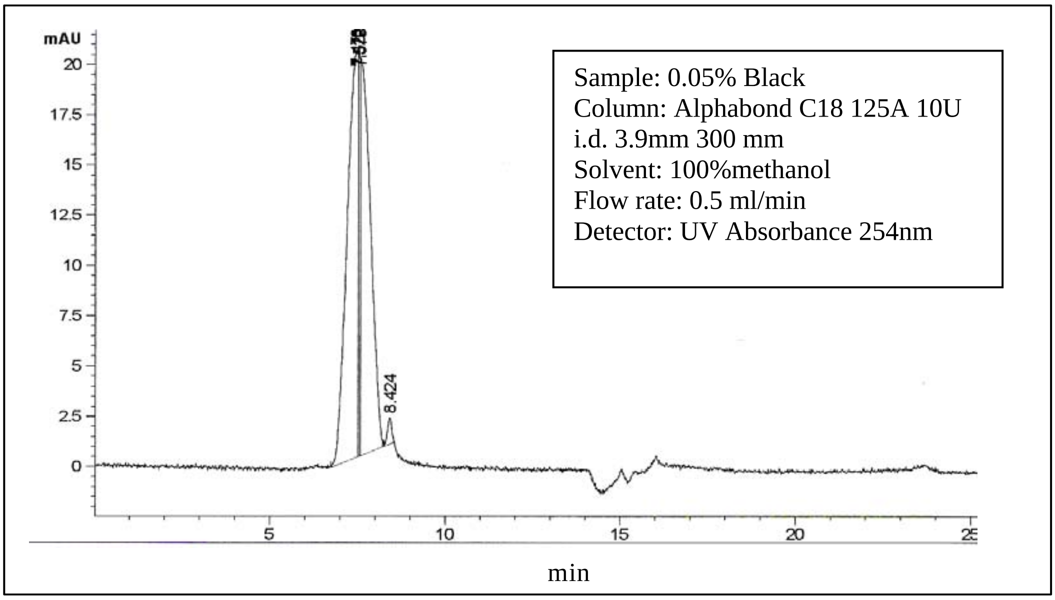


Figure 3-11: HPLC Chromatogram of Black

According to the results of Figure 3-8 to 3-11, it was found that the chromatograms of four different ink-jet printing inks namely Cyan, Magenta, Yellow and Black with the wavelength detection of 254nm exhibited only one sharp peak. This indicated that there was only one dye componet present in the ink. In addition, the results also showed that the use of Alphabond C18 column of HPLC instrument and 100% methanol was capable of completely separating ink components.

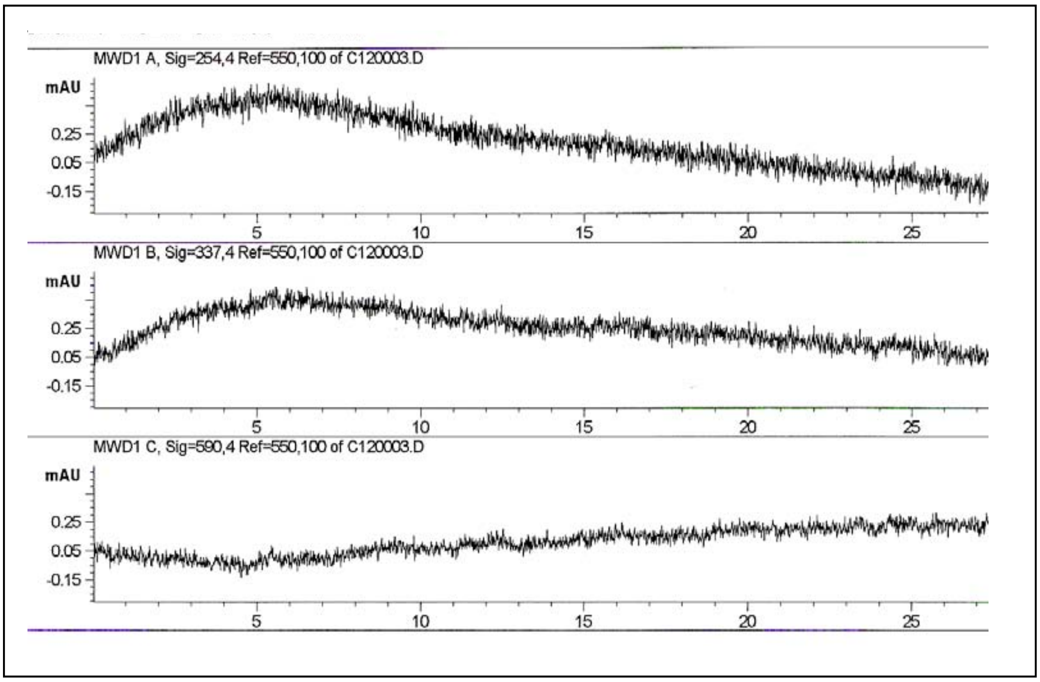


Figure 3-12: HPLC Chromatogram of Cyan

On the contrary, the chromatogram shown in Figure 3-12 confirmed that no peak could be obtained from the detection wavelengths of 254nm. The column used for this HPLC chromatogram was RSLC-CN 250*4.6mm while the solvent used was 100% hexane. This proved that the RSLC-CN column and 100% hexane solvent were incapable of separating Cyan. As for TLC, it was found that 100% hexane was also incapable of separating the ink.

The overall results of HPLC obtained were similar to those of TLC mentioned in Section 3.3.2.2. Hence, this confirmed that the four different ink-jet printing inks namely Cyan, Magenta, Yellow and Black contained only one dye component.

Based on the results of HPLC, it was further confirmed that the TLC test results obtained was correct for all four different ink-jet printing inks.

3.4 Infrared Spectroscopy (IR)

Infrared (IR) spectroscopy is a technique used for identifying the structure of chemicals based on the interaction of atoms with infrared radiation. Molecular vibration and rotation can be excited by the absorption of radiation in infrared region. Such molecular vibrations and rotations can be directly measured as absorbance in the infrared spectrum.

When infrared radiation interacts with an organic compound, certain frequencies of energy are absorbed while others are transmitted or reflected. The frequencies absorbed or transmitted are determined by the functional groups present in the substance. The molecular vibrations are localised within the functional groups and do not extend over the rest of the molecules. Such functional groups can be identified by their absorption bands [68].

In general, IR can be used as a means for identifying the chemical composition of the material. On one hand, the IR spectra can indicate certain specific functional groups present in a dye molecule. On the other hand, it can be combined with the instrumental analysis technique to identify the actual chemical composition of a material [71, 72]. As a whole, IR is a simple and convenient analytical technique that can provide basic and valuable information about the chemical composition of a material [71-73].

In textile ink-jet printing, the chemical structures of the reactive dyes present in the ink were not disclosed due to commercial reasons. As a result, it was very difficult for the researchers to study the actual chemical reaction between the dye molecules and the fibres or determine the printing mechanism [4, 36]. Hence, the aim of this study was to determine the chemical structure of the functional groups available in three primary colours (Cyan, Magenta and Yellow) and Black colour [74] of the commercially available ink-jet printing inks used for ink-jet printing.

3.4.1 Instrumentation

IR was used to produce the IR transmittion spectra of the purified ink sample. The IR transmittion spectra were recorded on Perkin-Elmer System 2000 Fourier Transform Infrared (FT-IR) Spectrometer as shown in Figure 3-13 FT-IR machine offers the advantages of high sensitivity, resolution and speed of data acquisition that is crucial to the solid-state sample.

Figure 3-13 Perkin-Elmer System 2000 FT-IR Spectrometer

3.4.2 Experimental procedures

3.4.2.1 Separation and purification ink

Commercial ink containing reactive dye for ink-jet printing is a standardised product for specific end-use and is not a homogeneous chemical compound. Commercial ink often has impurities and may contain a large amount of shading components, most of which can interfere seriously the analysis of IR spectra. Therefore, separation and purification are necessary in order to obtain the pure state of dyes for accurate analysis.

Four commercially available ink-jet printing inks of Cyan, Yellow, Magenta and Black colours were adopted in this study. 50 ml of ink was first dehydrated in an oven at 40ºC for 120 hours. After dehydration, 50 ml of acetone was added to the ink sample and the impurities were filtered with the aid of filter paper and funnel.

Finally, the mixture of acetone and pure dye (filtrate) was put in an oven at 40ºC for 40 hours to completely evaporate all the organic solvent. All the ink samples were prepared in this way for analysis.

3.4.2.2 Sample preparation for IR analysis

The IR spectra were obtained by employing the potassium bromide (KBr) pellet preparation technique which is a simple and common method to prepare a sample ready for IR analysis. KBr was used and its powder was dried in an oven at 80ºC for 24 hours to completely remove the moisture before preparing the sample pellet. All the dried ink samples prepared from the purification process were immediately used to prepare the KBr sample pellet. The KBr sample pellet containing approximately 500μg to 1mg of the dry ink sample was mixed with the dry KBr powder (the ratio of the ink sample: KBr = 1:100).

The mixture was then milled with a small agate mortar until the dried ink powder was completely mixed with the KBr powder. After milling, the mixture was immediately compressed under hydraulic pressure for about 5 to 6 minutes, and the thickness of the KBr sample pellet was controlled to 1 to 2 mm. A KBr sample pellet was formed and ready for IR spectrum analysis

3.4.2.3 Obtaining the IR spectrum

A Perkin-Elmer System 2000 FT-IR Spectrometer was used to obtain the IR spectrum of the ink sample. Before measuring the sample, the background of the IR was scanned with the following scanning conditions: a resolution of 1 cm^{-1} and 15 scans. This process was crucial for eliminating the effect of background absorption. The KBr sample pellet was then scanned twice. After scanning, the spectra of the sample were generated and the major peaks were labelled with the help of computer software installed in the FT-IR spectrometer.

3.4.2.4 Interpretation of IR spectrum

An IR spectrum consists of two main regions , i.e. (i) above 1500cm^{-1} there are absorption bands that can be assigned to individual functional groups, and (ii) the region below 1500cm^{-1} (the fingerprint region) contains many bands. The bands within the fingerprint region, which arise from the functional groups, can be used for identification, but such assignments should be considered only as an aid to identification and not as conclusive proof [68].

Firstly, the interpretation of the IR spectra for the three primary colours and Black colour involved a manual search of the reference IR functional group tables. The preliminary analysis of the IR spectra was conducted with the help of a reference table shown in Table 3-4 to indicate the possible functional groups existing in the commercial ink-jet printing inks of three primary colours and Black colour. This preliminary analysis can help narrow the range of interpretation.

Table 3-4 Regions of the IR Spectrum for Preliminary Analysis [75]

Region (cm^{-1})	**Group**	**Possible Compounds Present**
3700-3100	-OH	Alcohol, aldehyde, carboxylic acids
	-NH	Amides, amines
	≡C-H	Alkynes
3100-3000	=C-H	Aromatic compounds
	$-CH_2$ or $-CH=CH-$	Alkenes or unsaturated rings
3000-2800	$-CH$, $-CH_2-$, $-CH_3$	Aliphatic groups
2800-2600	-CHO	Aldehydes (Fermi doublet)
2700-2400	-POH	Phosphorus compounds
	-SH	Mercaptans and thiols
	-PH	Phosphine
2400-2000	-C≡N	Nitriles
	$-N=N^+=N^-$	Azides
	-C≡C-	Alkynes
1870-1650	C=O	Acid halides, aldehydes, amides, amino acids, anhydrides, carboxylic acids, esters, ketones, lactams, lactones, quinines
1650-1550	C=C, C=N, NH	Unsaturated aliphatics, aromatics, unsaturated heterocycles, amides, amines, amino acids
1550-1300	NO_2	Nitro compound
	CH_3 and CH_2	Alkanes, alkenes, etc
1300-1000	C-O-C and C-OH	Ethers, alcohols, sugars
	S=O, P=O, C-F	Sulphur, phosphorus, and fluorine compounds
1100-800	Si-O and P-O	Organosilicon and phosphorus compounds
1000-650	=C-H	Alkenes and aromatic compounds
	-NH	Aliphatic amines
800-400	C-halogen	Halogen compounds
	Aromatic rings	Aromatic compounds

Secondly, the IR spectra were examined thoroughly by comparing them with some reference reactive dyes structures as shown in Figures 3-14 to 3-19 [76]. For a more detailed examination of the IR spectra, each of the following spectrum absorptions was checked aiming to determine the possible functional groups or chemical compounds present in the unknown structure of commercial ink-jet printing inks of three primary colours and Black colour:

- IR absorption of single bonds to hydrogen;
- IR absorption of double bonds C=O, C=N, C=C, N=N, N=O
- IR absorption of aromatic compounds
- IR absorption in the fingerprint region including sulphur compounds, phosphorus compounds, ethers, halogen compounds and inorganic ions.

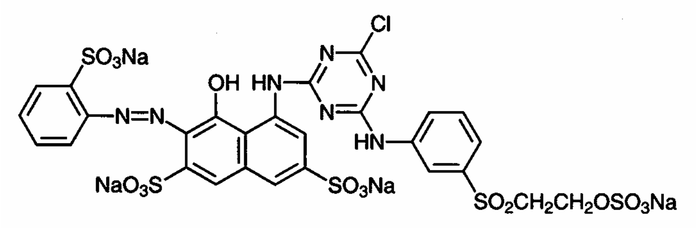


Figure 3-14 C.I. Reactive Red 194

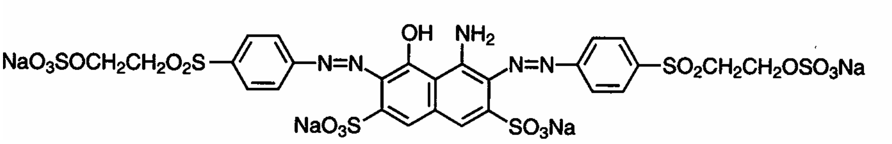


Figure 3-15 C.I. Reactive Black 5

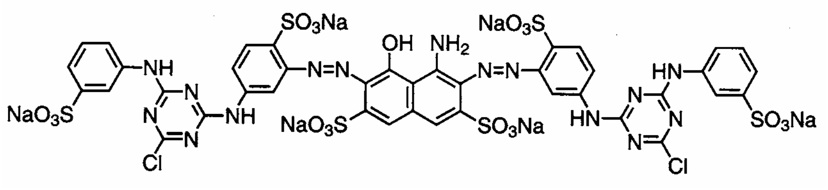


Figure 3-16 C.I. Reactive Blue 171

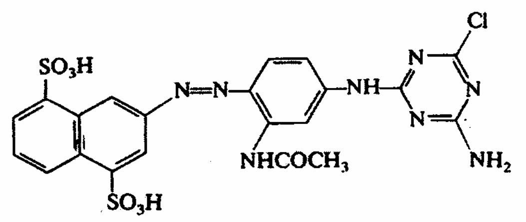


Figure 3-17 C.I. Reactive Yellow 3

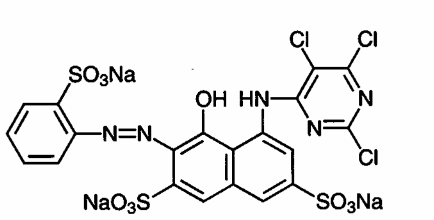


Figure 3-18 C.I. Reactive Red 17

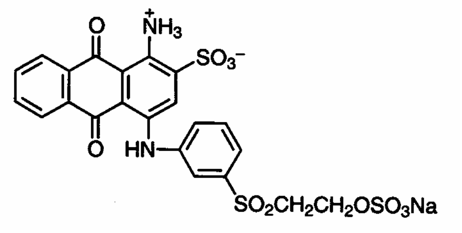


Figure 3-19 C.I. Reactive Blue 19

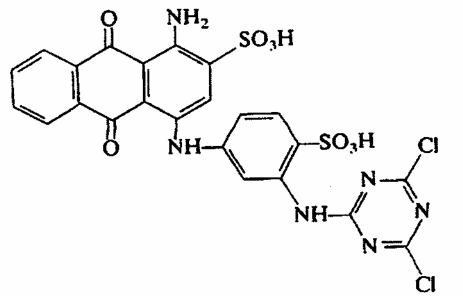


Figure 3-20 C.I. Reactive Blue 4

3.4.3 Result and discussion

3.4.3.1 IR spectrum of Cyan ink

The IR spectrum of Cyan ink is shown in Figure 3-21. Based on the IR analysis, the possible functional groups and chemical compounds present in Cyan ink are presented in Table 3-5.

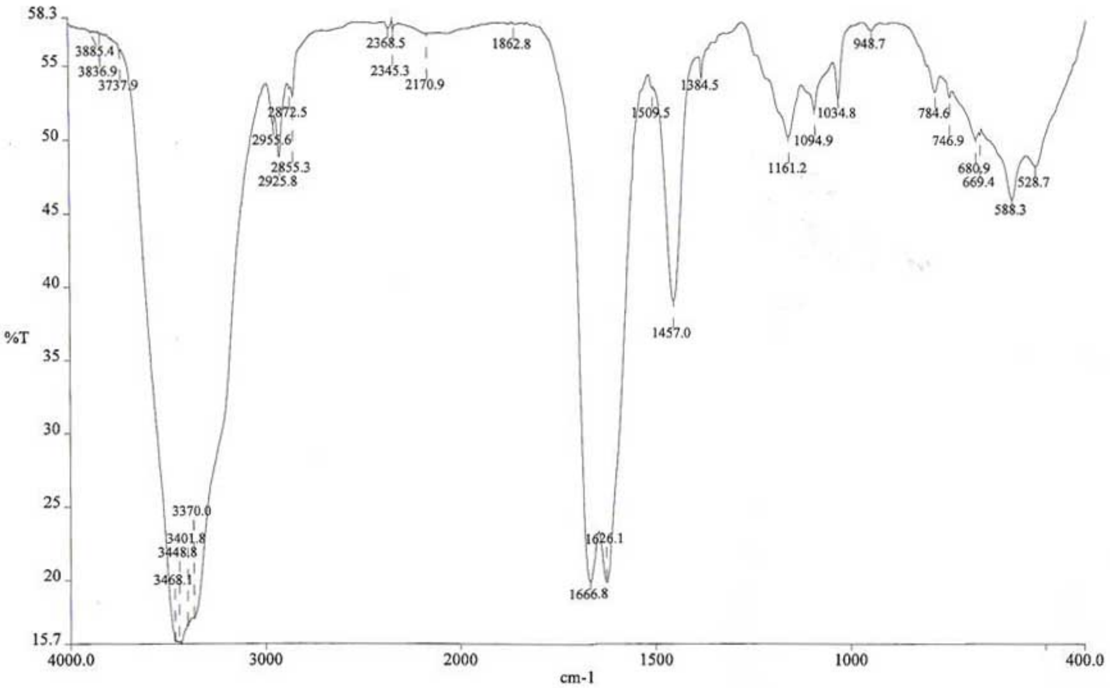


Figure 3-21 IR spectrum of Cyan ink

Table 3-5 Possible functional groups and compounds present in Cyan ink

Region (cm^{-1})	**Group**	**Possible compounds present**
3700-3100	-OH -NH C-H	Alcohols, aldehydes, carboxylic acids Amides, amines Alkynes
3000-2800	-CH, $-CH_2-$, $-CH_3$	Aliphatic groups
1870-1650	C=O	Acid halides, aldehydes, amides, amino acids, anhydrides, carboxylic acids, esters, ketones, lactams, lactones, quinines
1650-1550	C=C, C=N, NH	Unsaturated aliphatics, aromatics, unsaturated heterocycles, amides, amines, amino acids
1550-1300	NO_2 CH_3 and CH_2	Nitro compounds Alkanes, alkenes, etc.
1300-1000	C─O─C and C─OH S=O, P=O, C─F	Ethers, alcohols, sugars Sulphur, phosphorus, and fluorine compounds
1000-650	=C─H ─NH	Alkenes and aromatic compounds Aliphatic amines
800-400	C─halogen Aromatic rings	Halogen compounds Aromatic compounds

A further examination of the IR spectrum of Cyan colour was conducted by comparing its IR spectrum with that of the reference reactive dye structures. After analysis, the possible functional groups and chemical compounds present in Cyan ink were stated in the following.

Analysis of the IR spectrum of Cyan ink above 1500cm^{-1}

For IR absorption of single bonds to hydrogen, the bands show:

i H-bonded ─OH with ─O─H stretching at 3600-3200 cm^{-1};

ii =N─H and =N─H with N─H stretching at 3500-3300 cm^{-1};

iii =CH_2 with saturated C─H stretching at 2960-2850 cm^{-1};

iv ─O─CH_3 with miscellaneous C─H stretching at 2850-2810 cm^{-1};

v ─NH_2 with N─H bending at 1650-1560 cm^{-1};

vi =CH_2 with saturated C─H deformations at 1470-1430 cm^{-1}.

For IR absorption of double bonds C=O, C=N, C=C, N=N, N=O, the bands show:

i =C=O with C=O stretching at 1690-1660 cm^{-1};

ii Conjugated cyclic system of C=N with C=N stretching at 1660-1480cm^{-1};

iii C=C conjugated with aromatic ring with C=C stretching at ~1625cm^{-1}

iv N=N stretching at 1500-1400cm^{-1}.

For IR absorption of aromatic compounds that exhibit characteristic absorption in several regions, the bands show:

i Several weak bands from overtones and combination vibrations at 2000-1600cm^{-1};

ii C=C stretching at 1600-1500cm^{-1};

iii A fingerprint band with little diagnostic value at 1225-950cm^{-1};

Analysis of the IR spectrum of Cyan ink below 1500cm^{-1}

The fingerprint region ranging from 840-810cm^{-1} exhibits the substitution patterns of the benzene ring and the bands show:

i Monosubsituted benzene (five neighbouring H) at 770-685cm^{-1};

ii 1,2-disubsitution or 1,2-dimethylbenze (four neighbouring H) at 760-740cm^{-1};

iii 1,3-disubstitution, or 1,2,3-trisubstitution (three neighbouring H) at 800-770cm^{-1}.

For IR absorption in the fingerprint region, the bands show:

i Aryl-Cl with C-Cl stretching at 1100-1030cm^{-1};

ii R-SO_3- with =S=O stretching at 1250-1140cm^{-1} and 1070-1030cm^{-1};

iii R-SO_2-R with S=O stretching at 1370-1290 cm^{-1}and 1170-1110 cm^{-1};

iv C-S stretching at 720-600cm^{-1}.

3.4.3.2 IR spectrum of Magenta ink

The IR spectrum of Magenta ink is shown in Figure 3-22. Based on the analysis and further examination of the spectrum, the possible functional groups and compounds present in magenta ink were confirmed to be the same as that of Cyan ink except for the band at 3000-2800cm^{-1}.

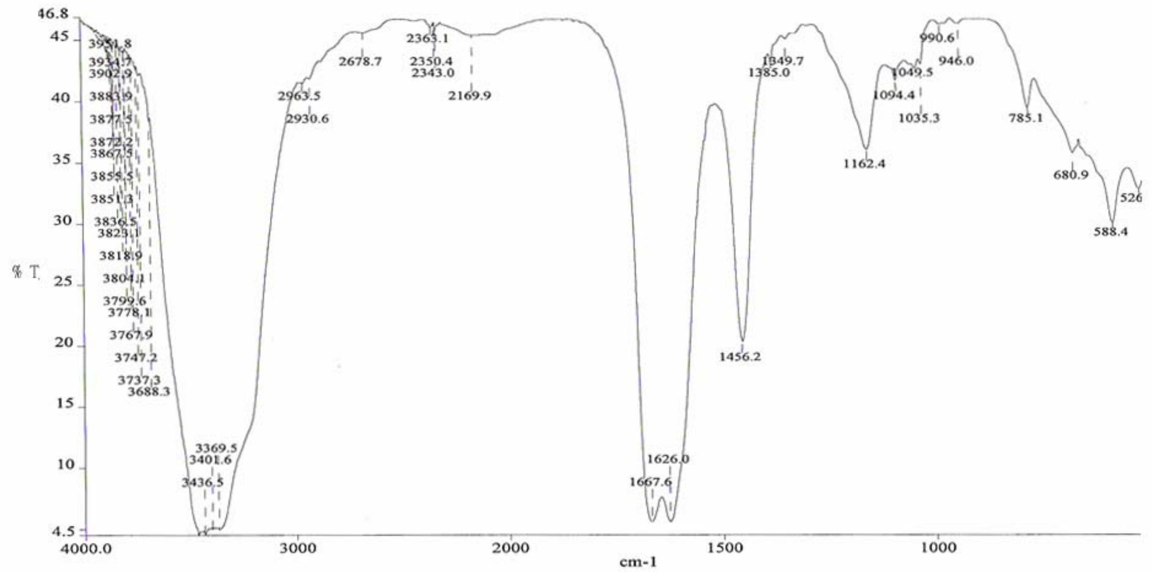


Figure 3-22 IR spectrum of Magenta ink

3.4.3.3 IR spectrum of Black ink

The IR spectrum of Black ink is shown in Figure 3-23. Based on the analysis and a further examination of the spectrum, the possible functional groups and compounds in Black ink were were confirmed to be the same as that of Cyan ink.

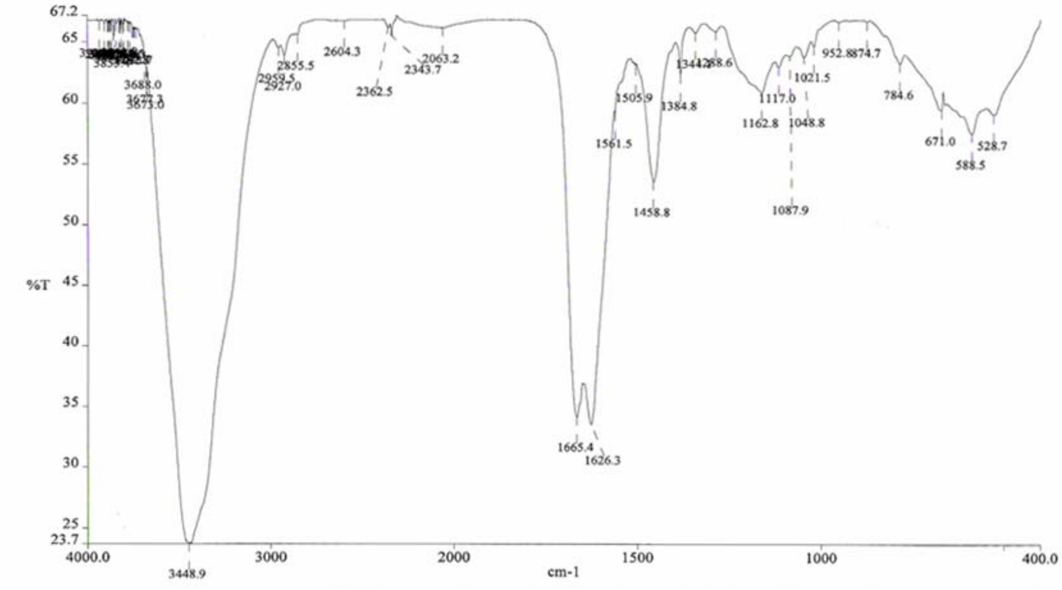


Figure 3-23 IR spectrum of Black ink

3.4.3.4 IR spectrum of Yellow ink

The IR spectrum of Yellow ink is shown in Figure 3-24. The analysis showed that the possible functional groups or compounds present in Yellow ink were the same as that of in Cyan ink. A further examination of the IR result did confirm that the IR spectrum of Yellow ink above 1500cm^{-1} was same as cyan colour of ink. The functional groups and chemical compound of this part could be regarded as similar to that of Cyan ink. However, the fingerprint region, i.e. below 1500 cm^{-1}, of the IR spectrum of Yellow ink was different from that of Cyan ink.

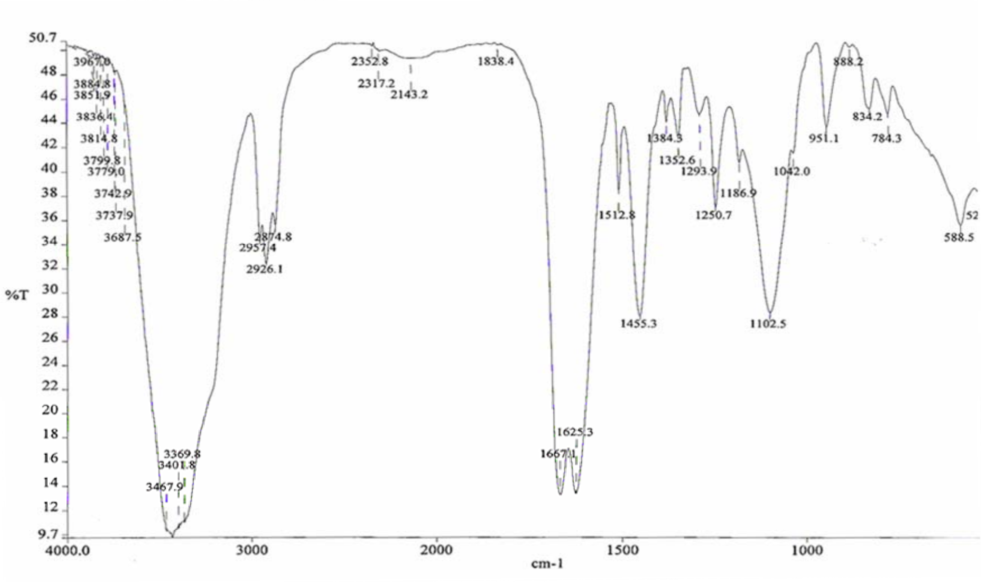


Figure 3-24 IR spectrum of Yellow ink

Analysis of the IR spectrum of Yellow ink below 1500cm^{-1}

The fingerprint region ranging from 840-810cm-1 demonstrates the substitution patterns of the benzene ring and the bands show:

i Monosubsituted benzene (five neighbouring H) at 770-685cm^{-1};

ii 1,2-disubsitution or 1,2-dimethylbenze (four neighbouring H) at 760-740cm^{-1};

iii 1,3-disubstitution, or 1,2,3-trisubstitution (three neighbouring H) at 800-770cm^{-1};

For the IR absorption in the fingerprint region, the bands show:

i Aryl-NO_2 with N-O stretching at 1540-1500cm^{-1};

ii Aryl-Cl with C-Cl stretching at 1100-1030cm^{-1};

iii R-SO_3- with S=O stretching at 1250-1140cm^{-1} and 1070-1030cm^{-1};

iv R-SO_2-R with S=O stretching at 1370-1290cm^{-1} and 1170-1110 cm^{-1};

v RO-SO_3- with S=O stretching at 1315-1220cm^{-1} and 1140-1050cm^{-1};

vi C-S stretching at 720-600cm^{-1}.

3.4.4 Functional groups and compounds present in the four ink

Since there were overlapping bands in the IR specrtra; thus the analysed functional groups and compounds only showed the possibility of the existence of such bands. In this study, the IR spectrum of Cyan ink could be used as a reference.

By comparing the IR spectra obtained from the four unknown commercial ink-jet printing inks, it was found that the IR spectrum absorption frequencies of Cyan, Magenta, and Black inks were very similar. This revealed that they might possess similar or the same functional groups and chemical compounds. However, this did not mean that they possessed the same structure. The number, arrangement and combination of the functional groups and compounds could vary so that different chromophoric groupings were present in their dye structures. When compared, the IR spectrum of Yellow ink above 1500cm^{-1} was the same as that of Cyan ink. However, the IR spectrum of Yellow ink below 1500cm^{-1} was different from that of Cyan ink.

The resultant bands obtained from the IR spectrum of Magenta ink were very similar to that of Cyan ink. Hence, further analysis of the functional groups and chemical compounds of Magenta ink could be referred to that of Cyan ink. A prominent difference between them was the absence of the bands of 3000-2800 cm^{-1} in Magenta ink. This revealed that the chemical structure of Magenta ink did not contain any aliphatic alkanes groups (-CH, $-CH_2-$, $-CH_3$). Moreover, the IR spectrum of Magenta showed a stronger band at 1456cm^{-1} of the azo group (-N=N-) that contributed to the chromophoric group.

The functional groups and compounds of Black inks were very nearly the same as that of the Cyan ink. However, the intensities of the bands around 3000-2800cm^{-1} of the alkane groups and 1458cm^{-1} of the azo groups (-N=N-) in the IR spectrum of Black ink were weaker than that of Cyan ink. Hence, further analysis of the functional groups or chemical compounds of Black ink could also be referred to that of Cyan ink.

The resultant bands above 1500cm^{-1} obtained from the IR spectrum of Yellow ink were very similar to that of Cyan ink. Therefore, some individual functional groups or chemical compounds of Yellow ink in this region could be referred to that of Cyan ink. However, the band of 3000-2800 cm^{-1} (-CH, -CH_2-, -CH_3) in the IR spectrum of Yellow ink was much stronger than that of Cyan ink. The fingerprint region of the IR spectrum of Yellow ink was different from that of the others.

Phenolic -OH, primary amines -NH and secondary amines -NH_2 often exist in dye structures. The absorption bands of the N-H stretching may sometimes be confused with those of hydrogen bonded -OH. The -NH absorption is usually sharper because of a much weaker tendency of the N-H group to form hydrogen bonds [68]. However, in the case of reactive dye, both -OH and NH group may exist in the dye structure or either. The O-H, N-H and -NH_2 groups were demonstrated by the reference reactive dyes shown in Figures 3-20 and 3-21.

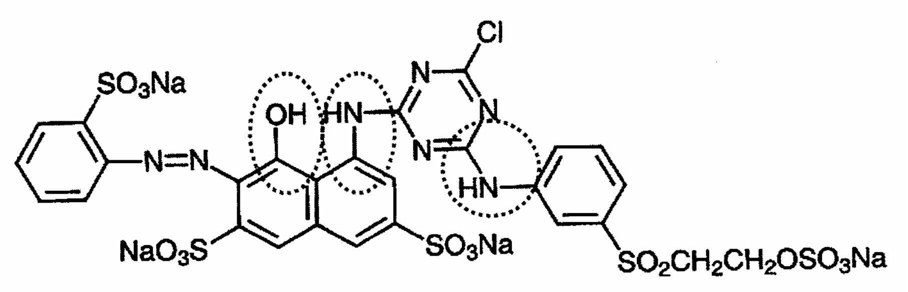


Figure 3-25 C.I. Reactive Red 194 dye containing O-H and =N-H groups

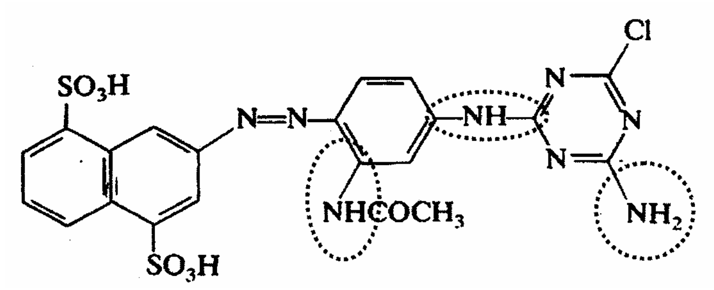


Figure 3-26 C.I. Reactive Yellow 3 dye containing O-H and =N-H groups

The alkane groups, -CH, $-CH_2$, $-CH_3$, often exist in dye structure. However, they were generally quite weak in IR spectra because of the low intrinsic intensity of the C-H stretch bands and the usually low concentration of aliphatic groups. Since scattering is usually a problem in this region of the spectrum, it is difficult to get much information from these bands even when using grating resolution [77, 78]. The IR spectra of Cyan ink and Black ink showed a weak peak in the region, while Yellow ink showed a much stronger peak. The alkane group was absent in the Magenta ink. The saturated $-CH_2$ group can be demonstrated by the reference reactive dye shown in Figure 3-27.

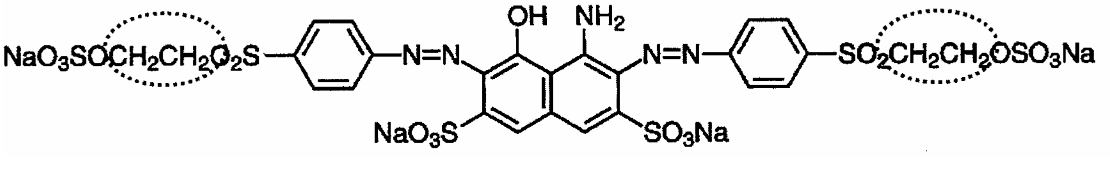


Figure 3-27 C.I. Reactive Black 5 dye containing CH, $-CH_2-$, $-CH_3$ groups

Special C-H absorption can also exist in the structure of reactive dyes. Ether, C-O-C, can be found in some reactive dyes. However, it is only a possible case as its absorption is overlapped with alkanes. The ether group was demonstrated by the reference reactive dye shown in Figure 3-28.

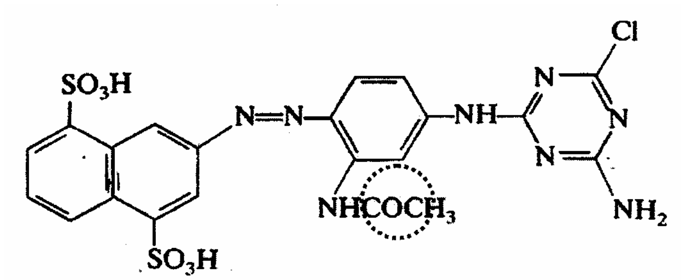


Figure 3-28 C.I. Reactive Yellow 3 dye containing the C-O-C group

Carbonyl groups in chromophores tend, in general, to be conjugated with double bonds or aromatic rings (often in both substituents on the carbonyl) [77]. The C=O group may be overlapped with the N-H bending and C=C conjugated with aromatic rings in the IR spectrum. Therefore, it cannot be used to identify whether or not the dye belongs to the anthraquinone type of reactive dye. Ketone, C=O, can be demonstrated showed by the reference reactive dye shown in Figure 3-29.

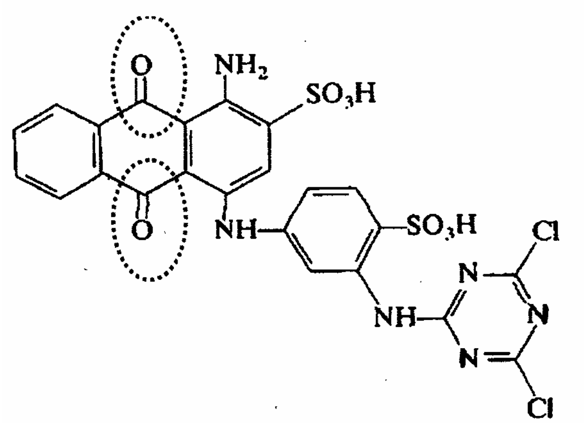


Figure 3-29 C.I. Reactive Blue 4 dye containing the =C=O group

The C=N group can be found in some reactive dyes. It may be overlapped with the carbonyl compound and N-H bending in the IR spectrum. With reference to reactive dye, C=N often exists in a conjugated cyclic system. The C=N conjugated cyclic system was demonstrated by the reference reactive dyes shown in Figures 3-30 and 3-31.

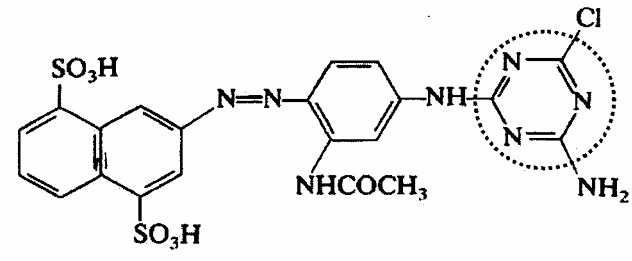


Figure 3-30 C.I. Reactive Yellow 3 dye containing the C=N group

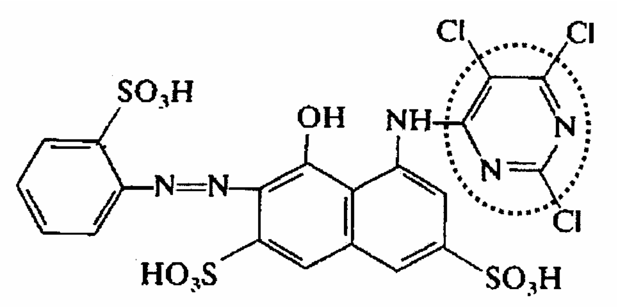


Figure 3-31 C.I. Reactive Red 17 dye containing the C=N group

Azo groups N=N, are most abundant in reactive dye. The N=N stretching may be overlapped with C-H deformation vibration. Therefore, this band cannot be used to identify whether or not the dye belongs to the azo type. This band is better identified in the Raman spectrum where it is much stronger. The N=N groups was demonstrated by the reference reactive dyes shown in Figure 3-32.

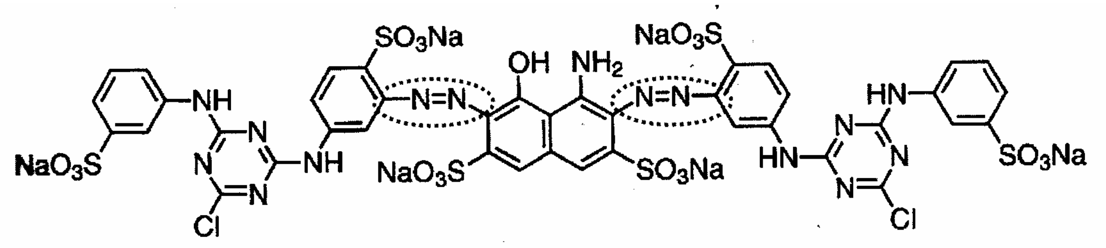


Figure 3-32 C.I. Reactive Blue 171 dye containing the N=N group

Aromatic compounds exists in all reactive dyes. The aromatic rings can be identified by several regions of bands in the IR spectra. Aromatic rings were demonstrated by the reference reactive dye shown in Figure 3-33.

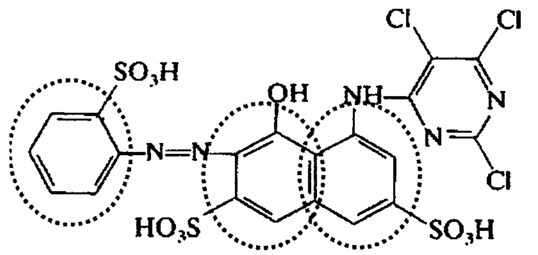


Figure 3-33 C.I. Reactive Red 17 dye containing an aromatic compound

Sulphonate salt with the R-SO_3- groups are essential components of the reactive dye. They are present in all the four unknown commercial ink-jet printing inks. The R-SO_2-R groups also may be present in these four unknown inks. The RO-SO_3- groups occasionally exist in the reactive dye structure. These groups may exist in yellow colorant but not in the other colorants. The R-SO_3-, R-SO_2-R, and RO-SO_3- groups were demonstrated by the reference reactive dyes shown in Figures 3-34 and 3-35.

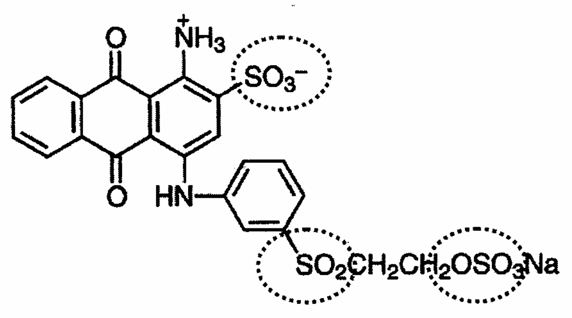


Figure 3-34 C.I. Reactive Blue 19 dye containing the R-SO_3-, R-SO_2-R and RO-SO_3 groups

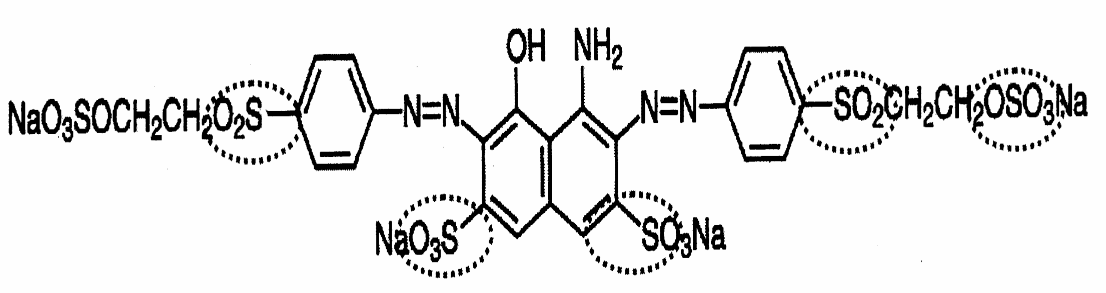


Figure 3-35 C.I. Reactive Black 5 dye containing the R-SO_3-, R-SO_2-R and RO-SO_3- groups

Chloroaromatic compounds often exist in the structure of reactive dye. The chloroaromatic groups were demonstrated by the following reference reactive dyes shown in Figures 3-36 and 3-37.

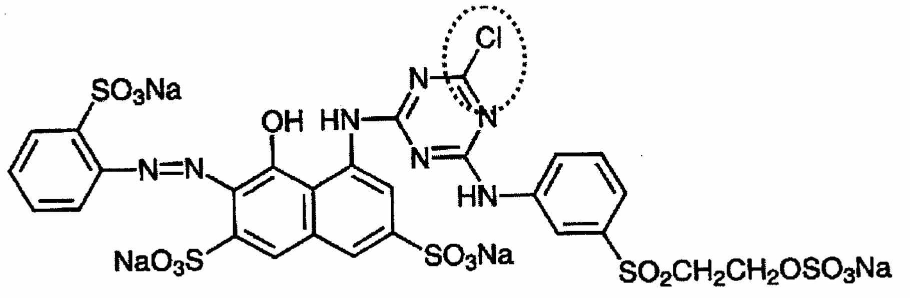


Figure 3-36 C.I. Reactive Red 194 dye containing chloroaromatic compounds

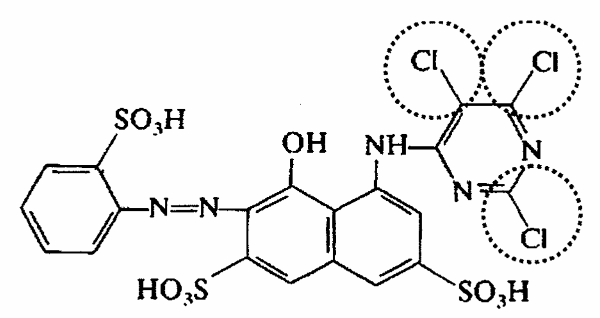


Figure 3-37 C.I. Reactive Red 17 dye containing chloroaromatic compounds

3.4.5 Conclusion

Since commercial ink may not be a homogenous product, thus the functional group frequencies can help determine the chemical constitution of reactive dyes present in the commercial ink. On the whole, the IR spectroscopy can be enormously useful in analysing the chemical constitutions of the commercial ink. After analysing the functional group absorbance frequencies of the IR spectrum for the four different commercial ink-jet printing inks, their chemical constitutions, i.e. the reacting system, are summarised in Table 3-6.

Table 3-6 Chemical constitution of the four different commercial ink-jet printing inks

Commerical Ink	**Reacting system**		
	Vinylsulphone ($1370-1290cm^{-1}$)	**Triazine ($1450-1350cm^{-1}$)**	**Pyrimidine ($1580-1520cm^{-1}$)**
Cyan	X	√	X
Magenta	√	X	X
Yellow	√	X	X
Black	√	X	X

CHAPTER 4.

OPTIMISATION OF INK-JET PRINTING SYSTEM FOR COTTON FABRIC

4.1 Introduction

Based on the study of previous literature review, the content of pre-treatment print paste, i.e. alginate, urea and alkali, together with the steaming time after ink-jet printing play the major role in affecting the final colour yield of the printed cotton fabric [4, 6, 45, 66, 79, 80]. In order to achieve the maximum colour yield, the combination of these factors must, therefore, be studied in depth. Hence, a detailed study of these factors that influence the colour yield of ink-jet printed cotton fabric should be conducted. In a number of research of references, the orthogonal table method was used because this could yield useful results with the minimum amount of experiments [81].

The final colour yield was not only influenced by an individual factor, i.e. amount of alginate used, amount of alkali used, amount of urea used and duration of steaming time, but also an interaction effect among these factors. Therefore, the aim of the present study was to analyse the interaction effect between each factor on the final colour yield of the ink-jet printed cotton fabric by means of fractional fractorial design technique.

The optimum conditions employed to achieve the maximum colour yield of the three primary colours (Cyan, Magenta and Yellow) and Black colour were obtained by the response surface experimental design technique. The findings obtained from this study could provide a better understanding of the optimised effect of these factors, i.e. the pre-treatment paste content and steaming time, on the colour yield of the ink-jet printed cotton fabric.

The individual influence and interaction effect of pre-treatment print paste content on the colour yield of the ink-jet printed cotton fabric were investigated using (1) orthogonal analysis and (2) fractional factorial design respectively, while the optimisation of ink-jet printing system for cotton fabric was investigated using response surface design.

4.2 Experimental procedures

4.2.1 Fabric

100% singed, desized, scoured and bleached cotton plain weave fabric of 136g/m^2 with 133 ends/inch (40s) and 72 picks/inch (40s) was used in the present study. The commercially pre-treated cotton fabric with the same fabric specification as the control fabric was adopted.

4.2.2 Preparation of pre-treatment print paste

Sodium alginate, sodium bicarbonate and urea were all incorporated in the pre-treatment paste. A stock alginate was prepared by dissolving 50g of sodium alginate in 950ml of deionised water. The amount of sodium alginate used in the pre-treatment print paste was measured directly from the stock alginate. Unless otherwise stated, all chemicals used were of Analytical Reagent grade. The pre-treatment paste was prepared with various amounts of sodium alginate, sodium bicarbonate, urea and water, and the final weight was made up to 200g according to the information mentioned in Tables 4.1, 4-3 and 4-9. The chemicals in the pre-treatment paste were well mixed together by a laboratory mixer.

4.2.3 Fabric pre-treatment

The pre-treatment print paste was padded onto the cotton fabric using a padding machine (Labortex Co. Ltd) with the pressure of 2.6 kg/m^2 and padding speed of 2.5 rpm until a pick-up of 80% was achieved. The pre-treated fabrics were dried in oven at 80°C and then conditioned before ink-jet printing.

4.2.4 Ink-jet printing and post-treatment

The model of ink-jet printer was Mimaki Tx2-1600 (Mimaki Engineering Co., Ltd.), a piezo electric drop-on-demand machine using eight refillable colour cartiridges. Four commercially available reactive inks with Cyan, Magenta, Yellow and Black colours were obtained from the TianLi Modern Office Articles (Shanghai) Co., Ltd, and used without further purification. A pattern of square with 8cm x 8cm size was generated using the DGS (Dua Graphic Systems) software and TexPrint software to commend operation with 360 dpi x 360 dpi for easy comparison.

After ink-jet printing, the printed fabrics were air-dried and then steamed with superheated steam at 110°C for fixing the colour. The steaming time was employed in accordance with the experimental arrangement. The steamed fabrics were finally washed in 10g/l nonionic detergent until all the unreacted dyes and chemicals were removed.

4.2.5 Colour yield measurement

The printed fabrics were conditioned before the measurement of colour yield using Macbeth Colour Eye 7000A spectrophotometer under illuminant D_{65}. In this study, the summation of K/S, i.e. K/S(sum), over wavelength interval within the visible spectrum was calculated. The K/S values obtained from the wavelength of 400nm to 700nm wavelength with 20nm interval were summed and calculated according to Equation (1). The higher the K/S(sum) value, the more the dye-uptake will be resulting in better colour yield.

$$K/S = (1-R)^2 / 2R \quad \text{------------ Equation (1)}$$

where K = absorption coefficient, depending on the concentration of colorant

S = scattering coefficient, caused by the dyed substrate

R = reflectance of the coloured sample

4.2.6 Measurement of viscosity

50g of alginate powder was dissolved in 950g of water. A Brookfield Digital Viscometer, model DV-E, with RV spindle (S06) was used at 20 rpm to determine the paste viscosity and the measurement range was in milliPascal seconds (mPa s).

4.2.7 Determination of colour fastness of printed fabric

The colour fastness of the printed fabrics was assessed by the AATCC Test Method 16-2001 (Colour fastness to Light), AATCC Test Method 61-2001 (Colour fastness to Laundering) and AATCC Test Method 8-2001 (Colour fastness to Crocking).

4.2.8 Microscopic examination of printed fabric

The cross-sectional view of the printed cotton fabrics was observed by a microscope (Nikon, Model OPTIPHPT-PO) with a magnification of 400.

4.3 Experimental design

4.3.1 Orthogonal analysis

In order to determine the optimum condition, a $L_9(3)^4$ orthogonal analysis was used with the details shown in Tables 4-1 and 4-2. The pre-treatment print pastes were prepared in accordance with the requirements stated in Table 4-2 and made up to the final weight of 200g with deionised water. The pH value of the pre-treatment print pastes was kept at 9-10.

Table 4-1 Factors and levels used in orthogonal analysis

Factor	**Pre-treatment print paste gradient**			**Post-treatment**
Level	**Sodium alginate**	**Urea**	**Sodium bicarbonte**	**Steaming time**
I	50g	5g	2g	3 min
II	100g	10g	4g	5 min
III	150g	20g	8g	10 min

Table 4-2 Experimental arrangements

Runs	**Pre-treatment print paste gradient**			**Post-treatment**
	Sodium alginate	**Urea**	**Sodium bicarbonte**	**Steaming time**
1	I	I	I	I
2	I	II	II	II
3	I	III	III	III
4	II	I	II	III
5	II	II	III	I
6	II	III	I	II
7	III	I	III	II
8	III	II	I	III
9	III	III	II	I

4.3.2 Fractional factorial design

Two-level fractional factorial design was used to explore the effect of different factors, i.e. (i) amount of alginate, (ii) amount of sodium bicarbonate and (iii) amount of urea present in the pre-treatment paste recipe together with (iv) duration of steaming time, on the ink-jet printed quality with reactive dyes. A 2^4 two-level full factorial design of 16 trials was run according to the design matrix as shown in Table 4-4. The experiments were performed in random order and the results were finally analysed with Minitab programme package software (Minitab Inc.). Details of the experimental design arrangement are shown in Tables 4-3 and 4-4.

Table 4-3 Factors and respective levels used in two-level fractional factorial design

Factor	**Name**	**Level**	
		(-)	**(+)**
A	Alginate	100g	150g
B	Urea	10g	20g
C	Sodium Bicarbonate	4g	8g
D	Steaming time	5min	10min

Table 4-4 A two-level design with four factors has sixteen matrix

Trials	**Factor**			
	Factor A	**Factor B**	**Factor C**	**Factor D**
1	+	-	-	-
2	+	-	+	+
3	+	+	-	-
4	-	+	-	-
5	-	-	-	-
6	+	+	+	+
7	-	+	-	+
8	-	+	+	-
9	+	-	+	-
10	+	+	+	-
11	-	-	+	-
12	-	-	-	+
13	+	+	-	+
14	+	-	-	+
15	-	+	+	+
16	-	-	+	+

4.3.3 Response surface design

The experimental levels of the two factors for each colour were calculated according to the Box-Hunter central rotatable experimental design as shown in Tables 5-2 to 5-5. The complete central composite rotatable design for the two factors at five experimental levels required thirteen experiments and included five repeated experiments to obtain an estimate for the within-treatments variation.

Table 4-5 Experimental values of factors for different coded levels of Cyan colour

Factor	**Coded Levels**				
	-1.414	-1	0	1	1.414
Urea (X_1), gram	7.93	10	15	20	22.07
Sodium Bicarbonate (X_2), gram	3.18	4	6	8	8.83

Remark: the amount of sodium alginate used = 150 gram and mixed-up with water to final weight = 200 gram; steaming time = 5 minutes [66]

Table 4-6 Experimental values of factors for different coded levels of Magenta colour

Factor	**Coded Levels**				
	-1.414	-1	0	1	1.414
Urea (X_1), gram	7.93	10	15	20	22.07
Sodium Alginate (X_2), gram	89.65	100	125	150	160.36

Remark: the amount of sodium bicarbonate used = 8 gram and mixed-up with water to final weight = 200 gram; steaming time = 5 minutes [66]

Table 4-7 Experimental values of factors for different coded levels of Yellow colour

Factor	**Coded Level**				
	-1.414	-1	0	1	1.414
Urea (X_1), gram	7.93	10	15	20	22.07
Steaming Time (X_2), minute	3.96	5	7.5	10	11.04

Remark: the amount of sodium alginate used = 150 gram; amount of sodium bicarbonate used = 8 gram and mixed-up with water to final weight = 200gram [66]

Table 4-8 Experimental values of factors for different coded levels of Black colour

Factor	**Coded Level**				
	-1.414	-1	0	1	1.414
Urea (X_1), gram	7.93	10	15	20	22.07
Steaming Time (X_2), minute	3.96	5	7.5	10	11.04

Remark: the amount of sodium alginate used = 150 gram; amount of sodium bicarbonate used = 8 gram and mixed-up with water to final weight = 200gram [66]

Information obtained from the fractional factorial design was used to run the central composite design with the two operational factors at five experimental levels of thirteen trials as stated in Table 4-9. All the experiments were performed in random order. Response surface design showing that Z factor is the function of colour yield, X factor is the X_1 (amount of urea used in the pre-treatment paste), and Y factor is the X_2 (other three operational factors namely (i) the amount of sodium alginate, (ii) the amount of sodium bicarbonate used (iii) the duration of steaming time after ink-jet printing) was calculated by the multiple regression analysis using the Minitab programme package software.

Table 4-9 Response surface domains and coding of the factors with four different colours

Trials	**Level of factor**	
	Coded	
	X_1	**X_2**
1	-1.414	0
2	-1	-1
3	1	-1
4	-1	1
5	0	0
6	0	0
7	0	1.414
8	0	0
9	0	0
10	0	-1.414
11	0	0
12	1	1
13	1.414	0

4.4 Results and discussion

4.4.1 Orthogonal analysis

The optimum condition of the pre-treatment print pastes and steaming time was achieved by means of the orthogonal analysis with the results summarised in Table 4-10.

Table 4-10 Orthogonal table for the optimisation of each colour

Trials	**Substrate**			**Post-treatment**	**Dye uptake (K/S)**			
	Sodium alginate	**Urea**	**Sodium bicarbonate**	**Steaming time**	**C**	**M**	**Y**	**K**
1	I	I	I	I	78.66	51.02	44.53	143.45
2	I	II	II	II	87.84	66.11	59.23	165.94
3	I	III	III	III	70.10	40.05	34.71	114.12
4	II	I	II	III	81.53	57.21	56.05	162.81
5	II	II	III	I	95.79	68.81	69.77	190.71
6	II	III	I	II	71.77	43.93	43.57	119.33
7	III	I	III	II	96.78	89.10	72.53	217.71
8	III	II	I	III	95.77	67.59	61.36	167.57
9	III	III	II	I	81.19	52.40	53.53	146.34
Cyan (C)								
ΣI	236.60	256.97	246.20	255.64				
ΣII	249.09	**279.40**	250.56	**256.39**				
ΣIII	**273.74**	223.06	**262.67**	247.40				
Difference	37.14	56.34	16.47	8.99				
Magenta (M)								
ΣI	157.18	197.33	162.54	172.23				
ΣII	169.95	**202.51**	175.72	**199.14**				
ΣIII	**209.09**	136.38	**197.96**	164.85				
Difference	51.91	66.13	35.42	34.29				
Yellow (Y)								
ΣI	138.47	173.11	149.46	167.83				
ΣII	169.39	**190.36**	168.81	**175.33**				
ΣIII	**187.42**	131.81	**177.01**	152.12				
Difference	48.95	59.15	27.55	23.21				
Black (K)								
ΣI	423.51	523.97	430.35	480.50				
ΣII	472.85	**524.22**	475.09	**502.98**				
ΣIII	**531.62**	379.79	**522.54**	444.50				
Difference	108.11	144.43	92.19	58.48				

Tables in bold form showed the greatest value among the values in the levels of different factors used

4.4.1.1 Effect of sodium alginate on the pre-treatment print paste

Sodium alginate is a very important print paste thickener in textile printing because of the ready solubility and excellent stability even after high-temperature fixation treatment. It is especially important for the preparation of print pastes for reactive dyes as the extent of its interaction with most reactive dyes is very small. This is mainly due to the absence of primary hydroxyl groups in sodium alginate and the repulsion of dye anions by the ionised carboxyl groups of the polymer under alkaline condition (pH ~ 9-10) [82]. Hence, sodium alginate was used in the present study and its effect on the colour yield of four different colours is shown in Figure 4-1.

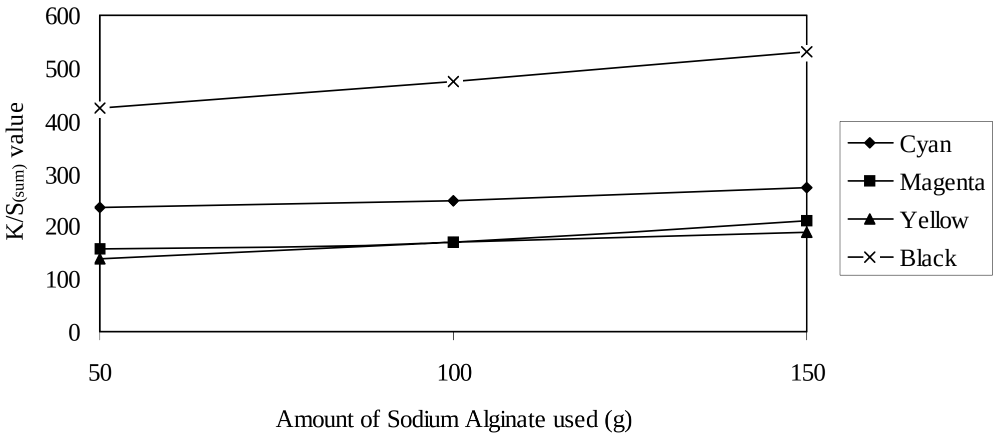


Figure 4-1 Effect of the amount of sodium alginate used on the colour yield of four different colours

Figure 4-1 clearly shows that the Black colour had the highest colour yield followed by Cyan, Magenta and Yellow colours. When the amount of sodium alginate used in the pre-treatment print paste was increased, the colour yields of the printed fabrics were enhanced correspondingly. This concluded that sodium alginate could serve the function of increasing the colour yield of ink-jet printing. In the pre-treatment print paste, sodium alginate served as a migration inhibitor in the printing paste to control the sharpness of borders of the final ink-jet printed pattern [38, 83].

During the steaming process, steam condensed onto the film of sodium alginate which would swell and contain a miniature dyebath on the fibre surface. The dye then dissolved and diffused through the swollen alginate film to the fibre surface. Although the condensed steam might cause a bleeding of the outlines due to the presence of urea in the pre-treatment print paste, yet the sodium alginate could reduce the effect of bleeding. On the other hand, the sodium alginate could control the penetration of the dye into the fabric [3, 38].

When the concentration of sodium alginate was too high, the fixation yield would be reduced. One reason was that a thick film of alginate might act as a diffusion barrier for the dye and so less dye was fixed on the fibre itself [3]. Furthermore, when the amount of sodium alginate was increased to 200g, the viscosity became too great thereby imposing the difficulty of padding the pre-treatment print paste on the fabric. As penetration was viscosity-dependent, it was necessary to find a carefully balanced compromise between penetration and diffusion [38, 82].

4.4.1.2 Effect of sodium bicarbonate on the pre-treatment print paste

Similar to that in the dyeing process, alkali is used in the printing process for the colour development of all shades [82, 83]. The presence of alkali is essential to produce ionisation of accessible cellulose hydroxyl groups which can then react with the reactive dyes in the fixation stage. Sodium bicarbonate has been the preferred alkali because it is cheap and can give sufficient stability to the pre-treatment print paste mixed with most of the reactive dyes available in the markets [82]. During steaming, sodium bicarbonate loses carbon dioxide and increases the ionisation of cellulose which thus promotes the dye-fibre interaction in the fixation stage.

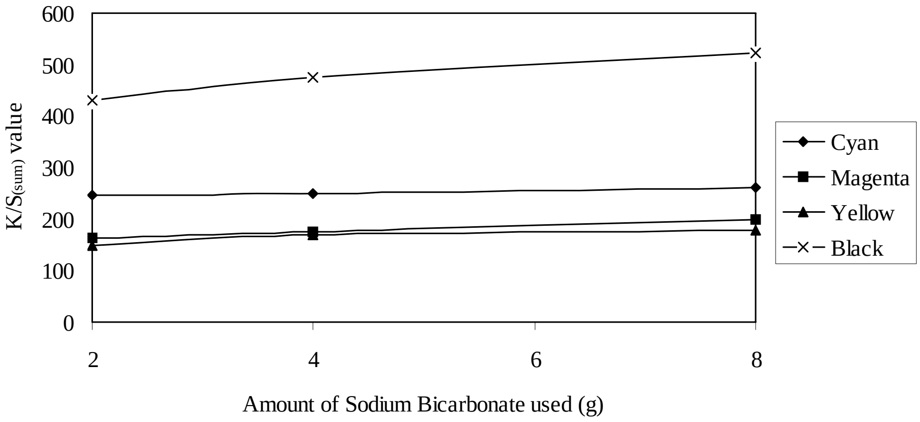


Figure 4-2 Effect of the amount of sodium bicarbonate used on the colour yield of four different colours

Figure 4-2, shows that the Black colour had the highest colour yield followed by Cyan, Magenta and Yellow colours. However, the effects of Cyan, Magenta and Yellow colours were not significant when compared with the Black colour. Generally speaking, when the amount of the sodium bicarbonate used in the pre-treatment print paste was increased, the colour yields of the printed fabrics were increased.

4.4.1.3 Effect of urea on the pre-treatment print paste

Urea is essential in the pre-treatment print paste because during the steaming process, particularly in the superheated steam right after ink-jet printing, it is mainly used for swelling the cotton fibres so that the dye can penetrate the fibres rapidly [83, 84]. The urea acts as a solvent for the reactive dye as it performs as a moisture-absorbing agent in the pre-treatment print paste to increase the moisture regain during the steaming process. Hence, it accelerates the migration of dye from the thickener film, i.e. sodium alginate, into the cotton fibre. The urea also reduces the yellowing of cotton under hot, dry, alkaline conditions [82, 84].

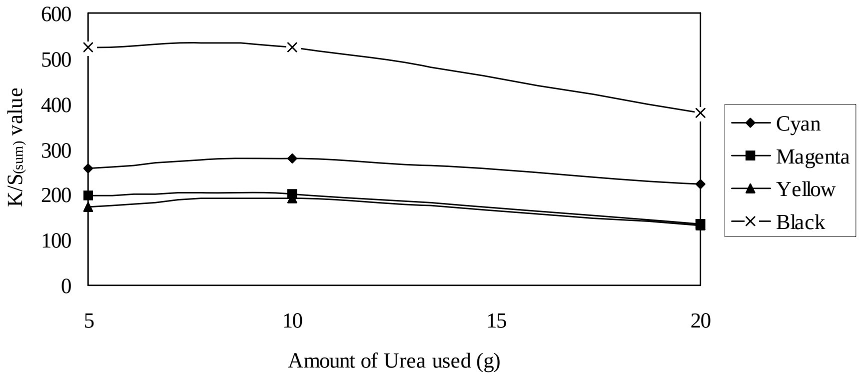


Figure 4-3 Effect of the amount of urea used on the colour yield of four different colours

Figure 4-3 shows the colour yield of four different colours under the influence of various amounts of urea used in the pre-treatment print paste. The results showed that the urea could apparently deepen the colour of the ink-jet printed cotton fabric to achieve the maximum colour yield when 10g of urea was used in the pre-treatment print paste. When compared, the Black colour obviously showed the highest colour yield followed by the Cyan, Magenta and finally Yellow colours. The order of effect was similar to that of the results reported previously in Section 4.4.1.2.

However, an interesting thing observed in Figure 4-3 was that when the amount of urea used in the pre-treatment print paste was more than 10g, the colour yield of the ink-jet printed fabrics would decrease. When the amount of urea used was further increased to 20g, the colour yield of the ink-jet printed fabric dropped significantly which was even paler than that of 5g of urea used. Such drop of colour yield with respect to the increasing amount of urea used in the pre-treatment print paste might be due to the increase of moisture regain of fibres during the steaming process. Owing to the hygroscopic nature, urea was used as a moisture-absorbing agent in the steaming process. A large amount of urea used in the pre-treatment print paste could enhance the moisture absorption and cause the hydrolysis of reactive dye during the steaming process.

4.4.1.4 Effect of steaming time on the post-treatment

Steam serves as a convenient source of both water and heat which can be transferred rapidly and uniformly over the surface areas of the ink-jet printed cotton fabrics. Superheated steam is used because it shows the advantages of faster heating, shorter fixation time and less colours spread [85].

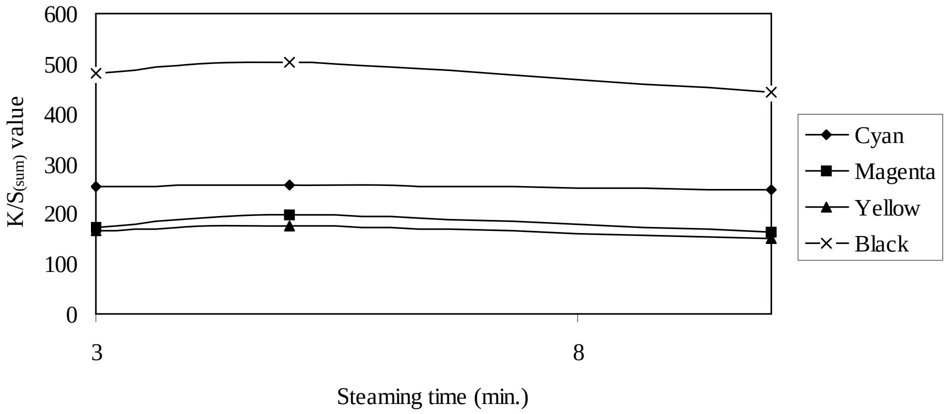


Figure 4-4 Effect of steaming time on the colour yield of four different colours

Figure 4-4 demonstrates the effect of steaming time on the colour yield of four different ink-jet printed colours on the cotton fabric. The black colour showed the highest colour yield followed by Cyan, Magenta and Yellow with the same sequence shown in the previous Sections 4.4.1.3. It was noted that the optimum K/S values of all different colours were obtained at the steaming time of 5 minutes. However, when the steaming time was prolonged to more than 5 minutes, the colour yield of the ink-jet printed fabrics would be reduced to different extents. The reduction of colour yield at the prolonged steaming time might be a combined effect of both chemicals and steaming time used.

With regard to the prolonged steaming time at higher temperature, i.e. 110°C, decomposition of urea would occur producing ammonia and biuret-type products inside the steaming chamber [85]. Owing to the reaction of reactive dyes with ammonia and the loss of alkali, lower colour yield would be obtained under these conditions. Furthermore, prolonged steaming time would also provide sufficient moisture for the moisture-absorbing agent, i.e. urea, to absorb. As a result of the combination effect, hydrolysis might occur and reduce colour yield.

4.4.1.5 Importance of each factors

Orthogonal analysis is a useful and simple technique for analysing the process variables or factors involved in a production process. Previous researchers [86-88] showed that it could provide a simple and convenient way for finding out the optimum condition and the level of importance of different factors in a production process.

After considering the results obtained from the orthogonal analysis as shown in Tables 4-1 and 4-2, it was concluded that all the four factors used namely sodium alginate, urea, sodium bicarbonate and steaming time could affect the K/S value by contributing different effects on the final colour yield. However, the level of importance based on the orthogonal analysis was in the order of urea > sodium alginate > sodium bicarbonate > steaming time.

4.4.2 Fractional factorial design

After processing the experimental trials, the K/S curves of different trials were plotted and the sum of K/S values of each trial was subsequently calculated. By computing the sum of K/S values of each trial with the help of Minitab programme package software (Minitab Inc.), the dominant factors of the printed results were then assessed by the Pareto chart, main effect interaction plot and interaction effect between the four different factors.

4.4.2.1 Pareto chart

Factor that causes the most effect on the final colour yield can be determined by examining the quality data with the graphical capabilities of a bar chart which is called the Pareto chart. In the Pareto chart, the dominant factor is placed in the upper position [79]. The Pareto charts of the four different colours are shown in Figures 4-5 to 4-8.

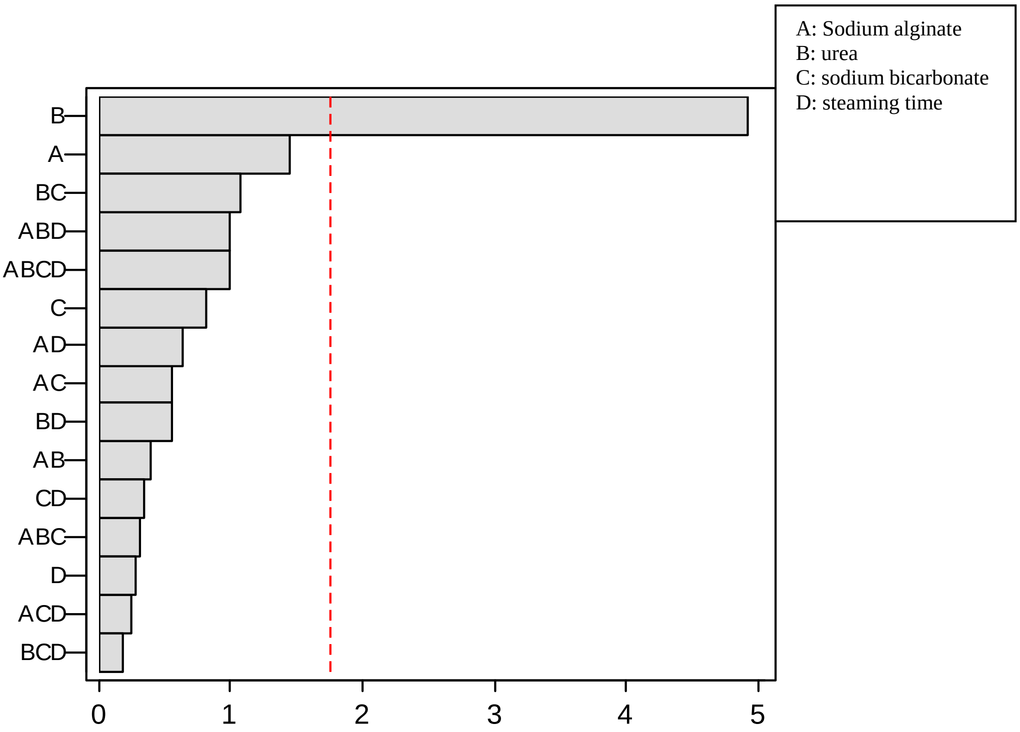


Figure 4-5 Pareto chart of Cyan colour

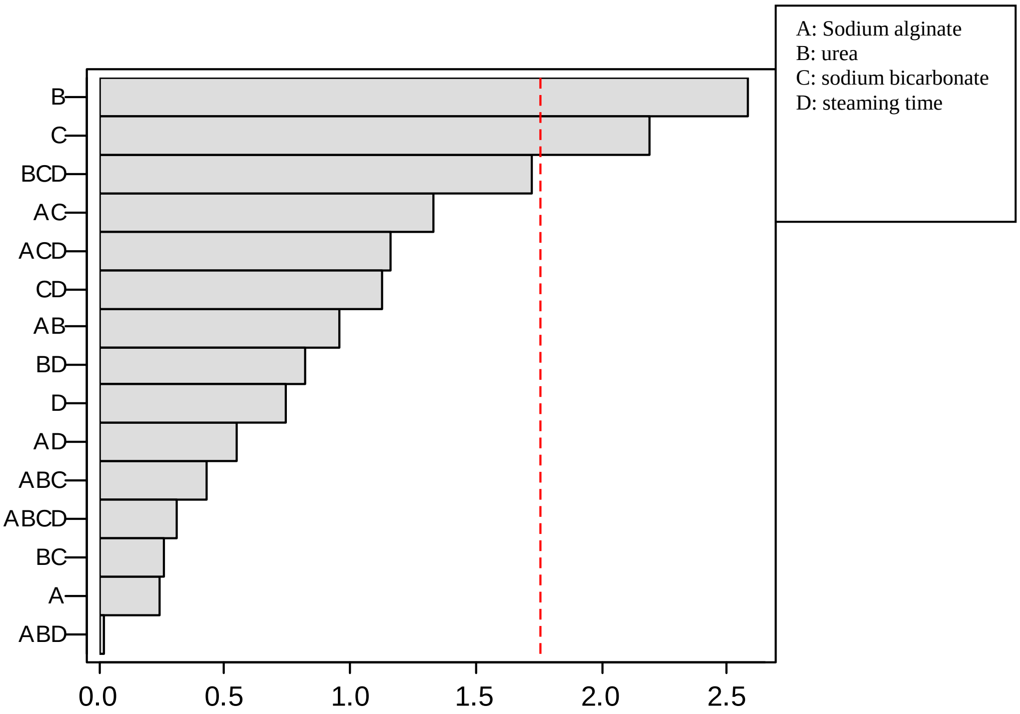


Figure 4-6 Pareto chart of Magenta Colour

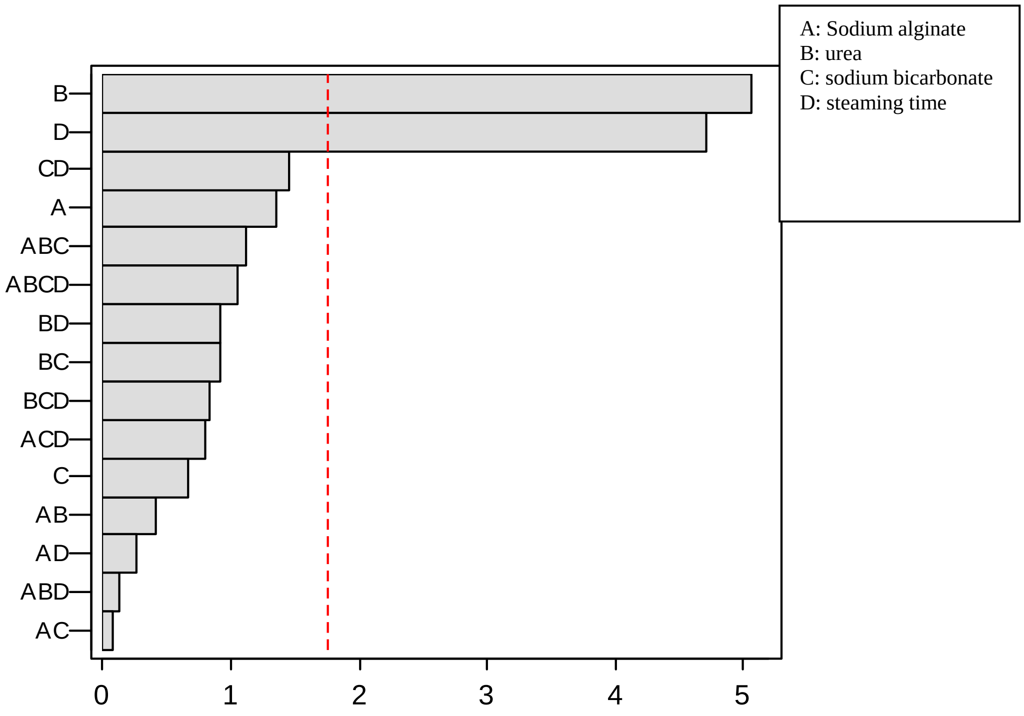


Figure 4-7 Pareto chart of Yellow Colour

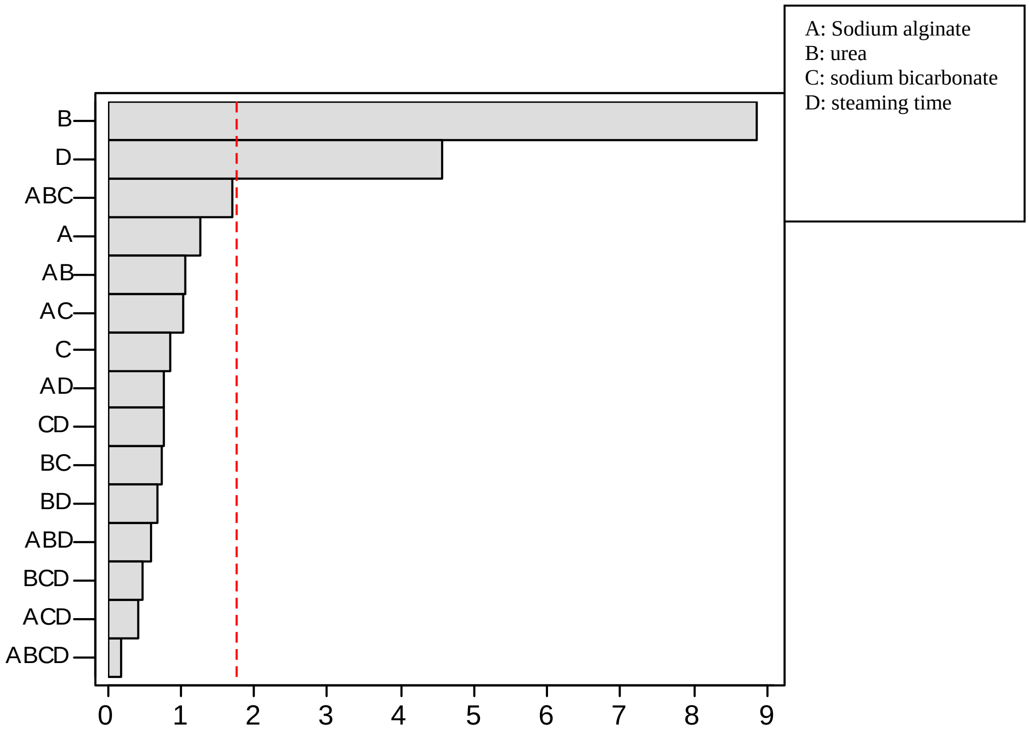


Figure 4-8 Pareto chart of Black Colour

The significance of the effect of the four different factors on the final colour yield of the four different colours are shown in Table 4-11.

Table 4-11 Significance of the effect of the four different factors on the final colour yield of the four different colours

Colour	**Significance of factors**			
	Most significant factor	——→		**Least significant factor**
Cyan	Urea	Alginate	Sodium bicarbonate	Steaming time
Magenta	Urea	Sodium bicarbonate	Steaming time	Sodium alginate
Yellow	Urea	Steaming time	Sodium alginate	Sodium bicarbonate
Black	Urea	Steaming time	Sodium alginate	Sodium bicarbonate

4.4.2.2 Main factors interaction plot

Table 4-11, showed that “the amount of urea” used in the pre-treatment paste was confirmed as the major and significant factor in affecting the final colour yield of the ink-jet printed fabric when compared with the other three factors. The interaction of this factor with the other factors with respect to the colour yield was demonstrated in the main factor interaction plot [79].

Based on the results of the main factor interaction plot, it was further confirmed that increasing or decreasing the amount of urea used in the pre-treatment paste could enhance the increment of colour yield. Furthermore, the amount of urea used also interacted with one of the other factors to affect the final colour yield of ink-jet printed fabric, i.e. dominantly two factors interacted with each other would result in affecting the final colour yield. Table 4-12 summarises these two dominant factors for each colour.

Table 4-12 The two dominant factors affecting the final colour yield of each colour

Color	**Two dominant factors**
Cyan	Amount of urea used and amount of sodium alginate used
Magenta	Amount of urea used and amount of sodium bicarbonate used
Yellow	Amount of urea used and duration of steaming time
Black	Amount of urea used and duration of steaming time

4.4.2.3 Interaction plot

Similar to the main factor interaction plot, the interaction effect can be calculated and displayed graphically to show the joint effect of the two factors mentioned in Table 4-8 for each colour. The interaction plot displays the average at each of the combinations of the two factors A and B [(-,-); (+,-); (-,+); (+,+)] using the B factor level as the horizontal axis and the average as the vertical axis, the averages having the same level of A, i.e., [(-,-); (-,+) and (+,-); (+,+)] are joined by a line [79]. The interaction plots of four different colours are shown in Figures 4-9 to 4-12. The interaction effects between the factors that affected the final colour yield of printed fabrics were demonstrated in the interaction plots. The interaction plot showed that different factors interacted with each other.

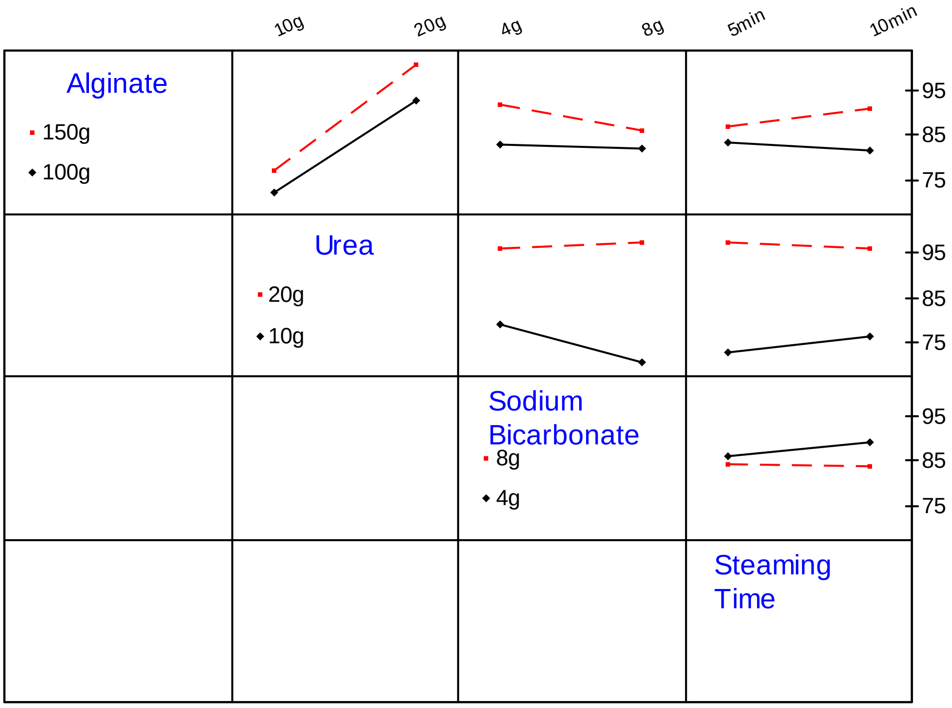


Figure 4-9 Interaction plot of ink-jet printed cotton fabric with Cyan ink

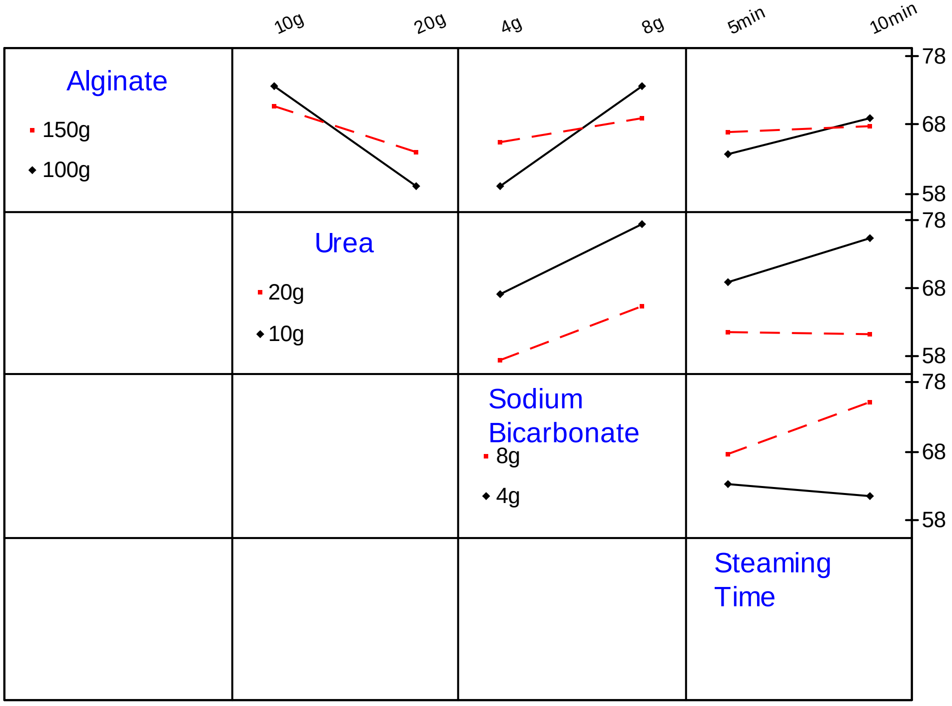


Figure 4-10 Interaction plot of ink-jet printed cotton fabric with Magenta ink

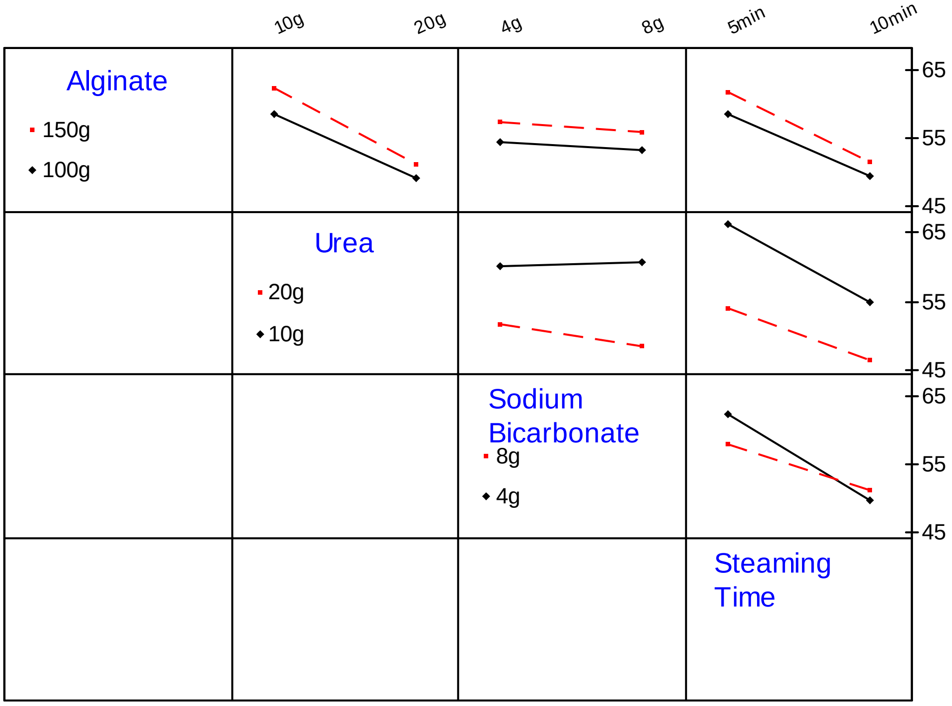


Figure 4-11 Interaction plot of ink-jet printed cotton fabric with Yellow ink

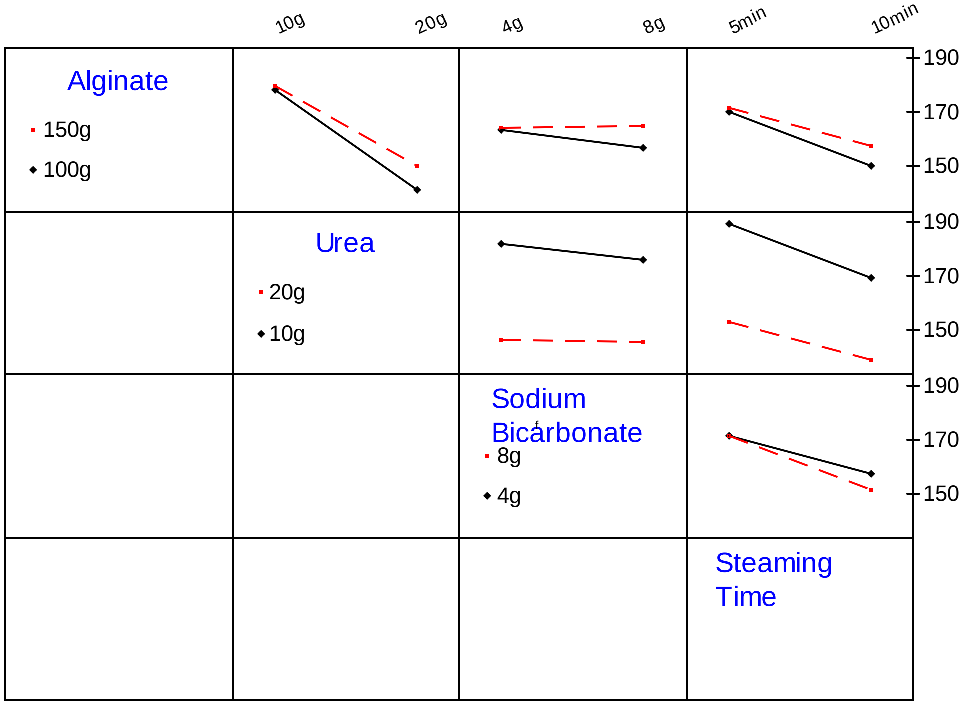


Figure 4-12 Interaction plot of ink-jet printed cotton fabric with Black ink

4.4.2.4 Assessment of the significance of each factor in ink-jet printing

4.4.2.4.1 Influence of urea on printing quality

From the analysis of Pareto charts, the amount of urea used in the pre-treatment paste was located at the highest position when compared with all the other factors in each colour. This implied that it was a dominant factor with respect to the colour yield of the four different colours.

The interaction plot of Cyan colour showed that the final colour yield of the ink-jet printed cotton fabric attained the maximum colour yield when 20g of urea was used in the pre-treatment paste.

However, for the Magenta, Yellow and Black colours, when the amount of urea used in the pre-treatment paste was more than 10g, the colour yield of the respective ink-jet printed fabric would decrease. When the amount of urea used was further increased to 20g, the colour yield of the respective ink-jet printed fabric dropped significantly, which was even paler than that of 5g of urea used. The drop of colour yield with respect to the increasing amount of urea used in the pre-treatment paste might be due to the increase of moisture regain of the fibres during the steaming process. Such a large amount of urea used in the pre-treatment paste could enhance the moisture absorption and also cause the hydrolysis of reactive dye during the steaming process.

In addition, the Magenta, Yellow and Black inks had vinylsulphone type of dye structure. This type of dye had a tendency to become deactivated in the presence of urea. It was believed to be probably due to the thermal decomposition of urea to biuret and ammonia followed by the conversion of the vinylsulphone dye to the inactive aminoethylsulphone rather than a direct reaction between the dye and urea [76].

4.4.2.4.2 Influence of sodium alginate on printing quality

From the Pareto charts analysis, the amount of sodium alginate used in the pre-treatment paste was located at the second position when compared with all the other factors in Cyan colour. This implied that it was belonged to another dominant factor with respect to the colour yield of Cyan colour.

The interaction plots of Cyan colour showed that when the amount of sodium alginate used in the pre-treatment paste was increased, the colour yield of the ink-jet printed fabrics was enhanced correspondingly. This concluded that sodium alginate could serve the function of increasing the colour yield of ink-jet printing.

Although the condensed steam might cause a bleeding of the outlines due to the presence of urea in the pre-treatment paste, yet the alginate could reduce the effect of bleeding. On the other hand, sodium alginate could control the penetration of the dye into the fabric [3, 38].

When the concentration of sodium alginate was too high, the fixation yield could be reduced correspondingly. One reason was that a thick sodium alginate film might act as a diffusion barrier for the dye and so less dye was fixed onto the fiber itself [3]. Furthermore, when the amount of sodium alginate was increased to 200g, the viscosity became too great thereby imposing the difficulty of padding the pre-treatment print paste onto the fabric. As penetration was viscosity-dependent, it was necessary to find a carefully balanced compromise between penetration and diffusion [38, 82].

Table 4-13 shows the viscosity of sodium alginate at different concentrations. The result indicated that when the concentration of sodium alginate in the pre-treatment paste was increased from 100g to 150g, the viscosity increased significantly imposing the difficulty for padding. However, using 150g of sodium alginate in the experiment had less significant effect on the colour yield of Magenta, Yellow and Black colours. Furthermore, the colour yield of these colours became worse when the steaming time was prolonged to 10 minutes.

Table 4-13 Viscosity of sodium alginate at different concentrations

Viscosity (mPa s)	**150g (total volume 200g)**	**100g (total volume 200g)**
Sodium Alginate	34400	4200

4.4.2.4.3 Influence of sodium bicarbonate on printed quality

From the analysis of Pareto charts, the amount of sodium bicarbonate used was located at the second position when compared with all the other factors in Magenta colour. This implied that it was belonged to another dominant factor with respect to the colour yield of Magenta colour.

With regard to the interaction plot between the sodium bicarbonate and steaming time in Magenta colour, when 8g sodium bicarbonate used in the pre-treatment paste was increased, the colour yield of the printed fabrics was enhanced correspondingly. The result obtained was similar to those results reported previously in Section 4.4.1.2 [82]. However, 8g sodium bicarbonate was less significant to the other three colours, i.e. Cyan, Yellow and Black.

4.4.2.4.4 Influence of steaming time on printed quality

From the analysis Pareto charts, the duration of steaming time used was located at the second position when compared with all the other factors in Yellow and Black colours. This implied that it was belonged to another dominant factor with respect to the colour yield.

The interaction plot showed that both Yellow and Black colours exhibited the highest colour yield when the steaming time used was 5 minutes. When the steaming time was extended to more than 5 minutes, the colour yield at prolonged steaming time might be a combined effect of both chemicals and steaming time used.

As a result of the combination effect, hydrolysis might occur and reduce color yield. However, the interaction between sodium bicarbonate and steaming time for Cyan and Black colours was less significant.

In addition, both fixation and hydrolysis were two different competition processes in textile printing which were occurring simultaneously. Too long the fixation time could affect the stability of dye-fibre bond under hot alkaline condition causing a significant decrease in colour yield.

4.4.2.5 Colour fastness of the printed fabric

Obviously, the colour fastness of ink-jet printed cotton fabric with the experimental arrangements shown in Table 4-10 achieved better results (about 1/2 Grade better) than the commercially available pre-treated cotton fabric. In addition, when the cross-sectional view of the printed cotton fabric was examined as shown in Figure 4-13, the penetration of inks into the cotton fabric with the experimental arrangement listed in Table 4-14 and 4-15 were better than the commercially available pre-treated cotton fabric, i.e. more dyes could penetrate into the fibres. This further explained why better colour fastness properties of ink-jet printed cotton fabric could be achieved.

Table 4-14 Colour fastness results of printed cotton fabrics to light and crocking

Trials	**Light (C/M/Y/K)**	**Crocking**	
		Wet (C/M/Y/K)	**Dry (C/M/Y/K)**
Control	4/3/4/3	3/3/3/3	4/4/4/4
1-16	4-5/4/4-5/4	4/4/4/4	4-5/4-5/4-5/4-5

(Control = commercially pre-treated cotton fabric, C = Cyan, M = Magenta, Y = Yellow, K = Black)

Table 4-15 Colour fastness results of printed cotton fabrics to laundering

Washing							
Trials	**Staining (C/M/Y/K)**						**Colour Change (C/M/Y/K)**
	Acetate	**Cotton**	**Nylon**	**Polyester**	**Acrylic**	**Wool**	
Control	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4
1 – 16 trails	4-5/4-5/ 4-5/4-5	4-5/4-5 /4-5/4-5	4-5/4-5/4-5/4-5	4-5/4-5/ 4-5/4-5	4-5/4-5/ 4-5/4-5	4-5/4-5/4-5/4-5	4-5/4-5/ 4-5/4-5

(Control = commercially pre-treated cotton fabric, C = Cyan, M = Magenta, Y = Yellow, K = Black)

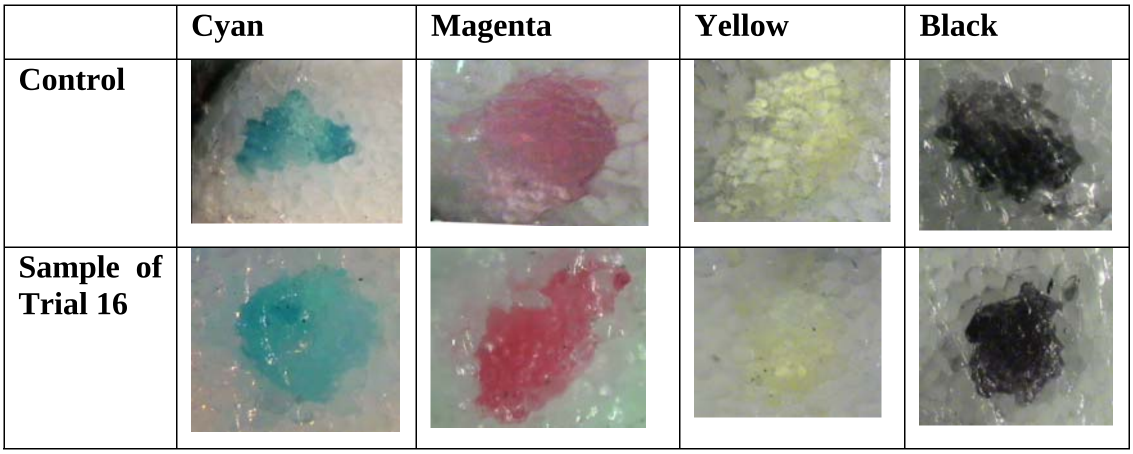
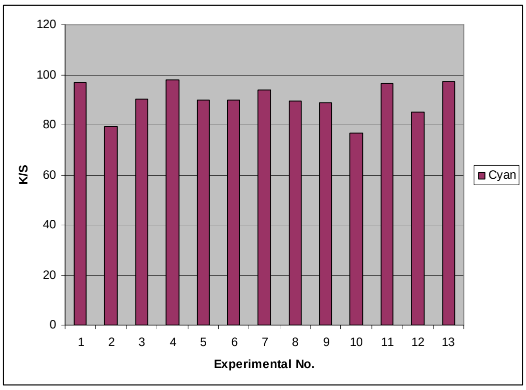


Figure 4-13 The cross-sectional view of the printed cotton fabrics

4.4.3 Response surface design

Although the ink-jet inks used for the three primary colours and Black colour were belonged to the same reactive dye class, they had different dyeing characteristics and nature during ink-jet printing [66]. The technique of the response surface methodology was employed to help determine the optimisation of these four different colours for ink-jet printing of cotton fabric.

The K/S values of four colours were calculated and presented in the K/S histograms as shown in Figures 4-14 to 4-17.



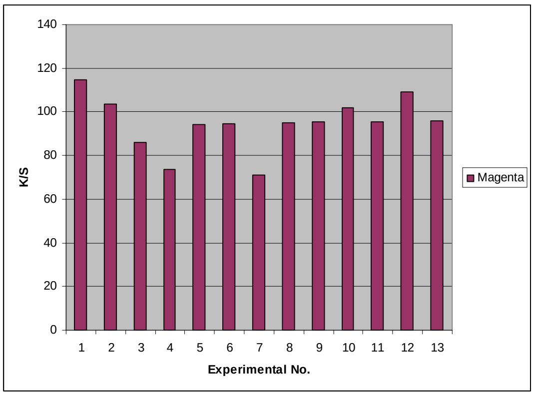
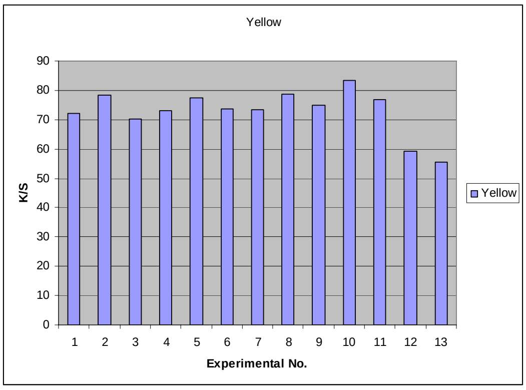


Figure 4-14 Experimental results obtained for the cyan colour

Figure 4-15 Experimental results obtained for the magenta colour



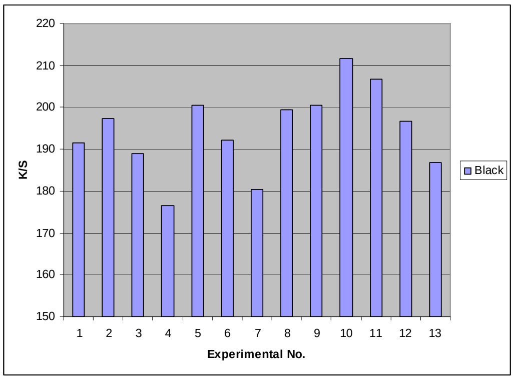


Figure 4-16 Experimental results obtained for the yellow colour

Figure 4-17 Experimental results obtained for the black colour

Based on the data obtained from the regression coefficient and adjusted polynomial equations, the optimum printing system of each colour yield was generated by means of the surface plots as shown in Figures 4-18 to 4-21. The adjusted polynomial equations obtained for the final colour yield (sum of K/S) of the four different colours are given in Table 4-16.

Table 4-16 The adjusted polynomial equations for the factors of each colour

Colour	**Response surface equation**
Black	$Y = 185 - 12.04X_2 - 14.15X1_2$ $R_2=0.76$
Yellow	$Y = 81.73 + 8.40X_1 - 3.56X_2 - 1.04X1_2$ $R_2=0.97$
Cyan	$Y = 89.35 + 8.59X_2 + 6.27X1_2$ $R_2=0.86$
Magenta	$Y = 76.36 - 8.03X_1 - 1.53X_2 -12.97X1_2$ $R_2=0.77$
R_2 = Coefficient of determination	

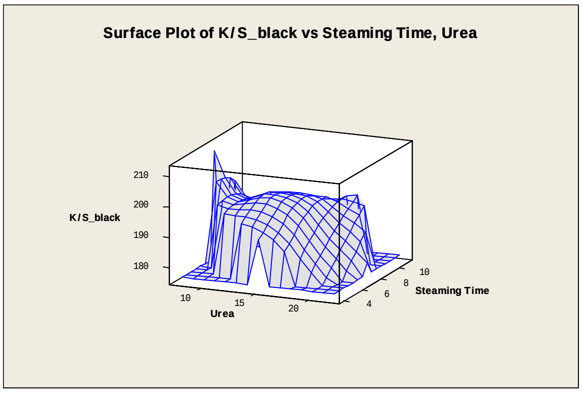


Figure 4-18 Surface plot of the effect between urea and steaming time on the colour yield of Black colour

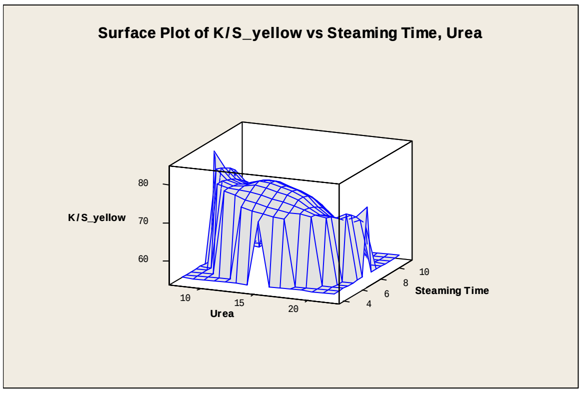


Figure 4-19 Surface plot of the effect between urea and steaming time on the colour yield of Yellow colour

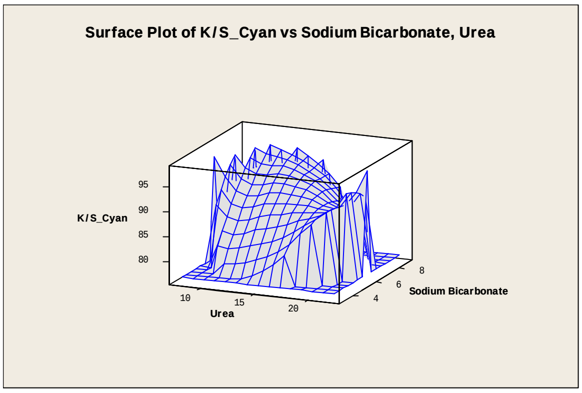


Figure 4-20 Surface plot of the effect between urea and sodium bicarbonate on the colour yield of Cyan colour

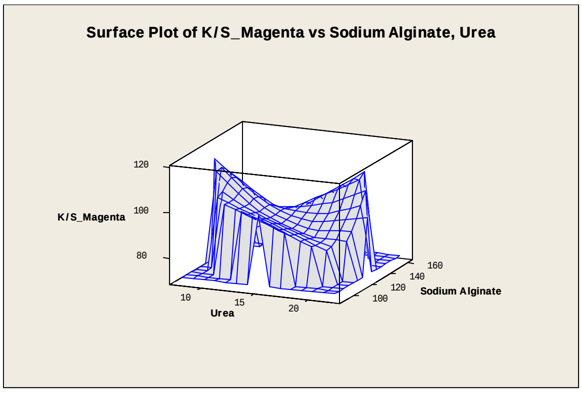


Figure 4-21 Surface plot of the effect between urea and sodium alginate on the colour yield of Magenta colour

Higher value of R_2 indicates better correlation between the factors and colour yield. The spatial diagrams of the response surface for Black and Yellow colours are given in Figures 4-18 and 4-21 respectively. The figures clearly show that the factor of urea with maximum colour yield on both the Black and Yellow colours is followed by the steaming time.

It is apparent that the Black colour shown in Figure 4-18 has the optimum colour yield when the amount of urea used is between 12 gram to 15 gram and the steaming time used is between 6 minutes to 8 minutes. It is also evident that the Yellow colour yield shown in Figure 4-19 increases when the amount of urea used is between 10 gram to 17 gram and the steaming time used is between 5 minutes to 9 minutes.

The spatial diagram of the response surface for Cyan colour is given in Figure 4-20 which shows that the amount of urea used has dominant influence on the Cyan colour followed by the amount of sodium bicarbonate used. Furthermore, the colour yield increases when the amount of urea used is between 10 gram to 15 gram and the amount of sodium bicarbonate used is between 6 gram to 9 gram.

The spatial diagram of the response surface for Magenta colour is given in Figure 4-21 which shows that the amount of urea used has dominant influence on Magenta colour followed by the sodium alginate factor. It is evident that the colour yield increases when the amount of urea used is between 8 gram to 10 gram and the amount of sodium alginate used is 90 gram to 110 gram.

4.4.3.1 Influence of urea on printed quality

Previous research confirmed that the amount of urea used in the pre-treatment paste played the most dominant effect among other factors when determining the final colour yield of ink-jet printing. Urea is essential in the pre-treatment print paste because in the steaming process, especially in superheated steaming, it is mainly used for the swelling of the cotton fibres so that the dye can penetrate rapidly into the cotton fibres [83, 84]. Since urea holds the water very strongly, thus the mixture of both urea and water can provide the solvent medium required for the reaction to occur inside the fibre.

Figures 4-20 shows that when the amount of urea used in the pre-treatment print paste was increased, the colour yield of the ink-jet printed colours of Cyan would increase correspondingly.

However, Figures 4-21 show that when the amount of urea used in the pre-treatment print paste was gradually increased, the colour yield of the ink-jet printed colours of

Magenta would increase initially and then decrease gradually. Such drop of colour yield with respect to the increasing amount of urea used in the pre-treatment print paste might be due to the increase of moisture regain of the fibres during the steaming process.

4.4.3.2 Influence of steaming time on printed quality

The spatial diagram of Black and Yellow colours shown in Figures 4-18 and 4-19 respectively demonstrated that these two colours exhibited the best colour yield which could be achieved when the steaming time was prolonged from 5 minutes to 9 minutes. This concluded that steaming time could serve the function of increasing the colour yield. However, when the steaming time was further increased, the colour yield of Black and Yellow colours would decrease as a result of the enhancement of the hydrolysis of reactive dye on the printed pattern.

4.4.3.3 Influence of sodium bicarbonate on printed quality

The spatial diagram of Cyan colour shown in Figure 4-20 demonstrated that when the amount of sodium bicarbonate used in the pre-treatment print paste was within the range of 6 gram to 9 gram, the colour yield of the printed fabrics was enhanced correspondingly. This concluded that sodium bicarbonate at higher concentration could serve the function of increasing the colour yield of Cyan.

4.4.3.4 Influence of sodium alginate on printing quality

The spatial diagram of Magenta colour shown in Figure 4-21 indicated that when the amount of sodium alginate used in the pre-treatment print paste was increased from 90 gram to 110 gram, the colour yield of the printed fabrics was enhanced correspondingly. This concluded that the sodium alginate could serve the function of increasing the colour yield of Magenta.

In textile printing, the sodium alginate could control the penetration of reactive dye into the fabric [6, 39]. When the concentration of sodium alginate was too high, the fixation yield could be reduced. This was due to the fact that a thick film of sodium alginate could act as a diffusion barrier for the dye penetration and so less dye was fixed onto the fibre itself [6]. Furthermore, a high amount of sodium alginate used in the pre-treatment print paste could impose the difficulty of padding this past on the fabric. As penetration was viscosity-dependent, it was necessary to find a carefully balanced compromise between penetration and diffusion [39].

4.4.3.5 Optimum condition of the operational factor

The results obtained from the experimental design could help interpret the optimum printing system for four different colours, and the overall results are summarised in Table 4-17.

Table 4-17 Optimum printing system for four different colours

Colour	**Sodium Alginate used (gram)**	**Urea used (gram)**	**Sodium Bicarbonate used (gram)**	**Steaming Time Minute)**
Cyan	150	10-15	6-9	5
Magenta	90-110	8-10	8	5
Yellow	150	10-17	8	5-9
Black	150	12-15	8	6-8

In order to verify the accuracy of the operational factors used in the optimum printing system, further experiments were conducted using the commercially available pre-treated fabric as the control fabric for comparing the colour yields, and the results are shown in Table 5-9.

Table 4-18 Comparison of colour yield (K/S value) of fabric treated under the optimum printing system with the commercially available pre-treated fabric for four different colours

Colour	**Cyan**	**Magenta**	**Yellow**	**Black**
Control fabric	105.25	100.28	77.16	226.25
Treated fabric	115.75	110.66	90.30	213.88

The results shown in Table 4-18 demonstrated clearly that the cotton fabric printed with each colour and treated under the optimum printing system had the highest colour yield when compared with those shown in Figures 4-14 to 4-17. Furthermore, the treated cotton fabric had a better colour yield for Cyan, Magenta and Yellow when compared with the control cotton fabric. Although the control fabric had a better colour yield for Black than the pre-treated fabric, yet their difference was not so significant. On the whole, the optimum condition described in Table 4-18 could enhance the pre-treated cotton fabric to acquire a higher colour yield similar to that of the commercially pre-treated cotton fabric.

4.5 Conclusion

Optimum condition concerning the contents of pre-treatment print paste and steaming time was newly developed and verified in order to obtain the maximum colour yield by using orthogonal analysis and response surface design. It was confirmed that the final colour yield of the cotton fabric treated under the newly developed optimum condition could compete with the commercially pre-treated cotton fabric available in the market. As a matter of fact, the newly developed optimum condition could provide helpful information for the industries to develop their own pre-treatment print paste recipe for ink-jet printing and so the main aim of this study was achieved.

However, based on the newly developed pre-treatment paste formulation, it was recommended that further investigation should be conducted to study the effect of pre-treatment print paste and steaming time on the individual reactive ink. In addition, the sharpness of the printing image and the durability of the pre-treated cotton fabric should be studied.

The results obtained from the fractional factorial design further confirmed that each factor had interaction effect with each other such that the maximum colour yield obtained was the compromised effect of these factors. Based on the results of the highest colour yield generated on the cotton fabric, it was found that the amount of urea was the first dominant factor when compared with the other factors in each colour.

Optimum printing system for ink-jet printing, i.e. the amount of sodium alginate, urea and sodium bicarbonate used in the pre-treatment paste, together with the duration of steaming time after printing was successfully developed and verified with the experimental design methodology.

CHAPTER 5.

APPLICATION CHITOSAN TO MODIFY COTTON FABRIC SURFACE FOR BETTER PRINTING QUALITY

5.1 Introduction

In this chapter, chiosan was used to modify cotton fabric surface aiming to obtain better printing quality. The investigation of chitosan was divided into two parts, (1) the effectiveness of chitsoan and its feasibility to replace sodium alginate as a thickener in the pre-treatment process were studied with the aid of orthogonal analysis, and (2) two-bath method was proposed to separate the chitosan paste from sodium bicarbonate and urea before being padded onto the fabric surface.

Currently, sodium alginate is an important thickener commonly used to prepare the pre-treatment print paste for ink-jet printing due to its ready solubility and excellent stability even after high-temperature fixation treatments [66]. Similar to sodium alginate, chitosan is also widely used as novel biomaterial. As a natural polymer, sodium alginate and chitosan are biocompatible, biodegradable and non-toxic [67]. Previous research reported that chitosan could be applied to different textile areas [53], e.g. chitosan was used in conventional textile printing for improving the dye uptake and colour fastness.

The use of chitosan as thickener to replace alginate in the pre-treatment print paste for ink-jet printing has been tried and evaluated in the previous studies [89]. Pre-treatment print pastes prepared from the mixture of chitosan and acetic acid with the appropriate viscosity gave satisfactory prints on the woven cotton fabric. Due to the presence of acetic acid at pH 5 and the sodium bicarbonate at pH 9-10 in the chitosan paste, neutralisation would occur. Although neutralisation was not so significant in the pre-treatment print paste, it may affect the final colour yield. In order to eliminate the neutralisation matter, two-bath method was proposed in the present study.

5.2 Experimenal procedures

5.2.1 Fabric

100% singed, desized, scoured and bleached cotton plain weave fabric of 136g/m^2 with 133 ends/inch (40s) and 72 picks/inch (40s) was used in this study.

5.2.2 Preparation of pre-treatment print paste

A stock sodium alginate was prepared by dissolving 50g of sodium alginate in 950ml of deionised water. Chitosan ($R-NH_2$) in solid form was supplied by Sigma Co. (USA). All chitosan solution prepared were then kept overnight at ambient temperature.

A solution of chitosan was prepared with various amount of 10% acetic acid according to the information mentioned in Tables 5.1. The chitosan solution was stirred and filtered to remove the suspended impurities.

A stock solution of chitosan was prepared by dissolving 5g of chitosan completely into 500ml of 10% acetic acid according to the information in Tables 5.3.

The pre-treatment print paste was prepared with various amounts of chemicals and water, and the final weight was made up to 200g according to the information mentioned in Tables 5-1 and Tables 5-3. All the chemicals used in the pre-treatment print paste were well mixed together by a laboratory mixer.

5.2.3 Fabric pre-treatment

The pre-treatment print paste was padded onto the cotton fabric using a padding machine supplied by Labortex Co. Ltd with the pressure of 2.6 kg/m_2 and padding speed of 2.5 rpm to give pick-up of 80% was achieved. The chitosan-treated cotton fabrics were dried in an oven at 80°C and cured at 170°C for 1.5 min while the control fabric was dried in the oven at 80°C. All the pre-treated fabrics were conditioned before ink-jet printing.

5.2.4 Ink-jet printing and post-treatment

The model of ink-jet printer used was Mimaki Tx2-1600 (Mimaki Engineering Co., Ltd.) which was a piezo electric drop-on-demand machine using eight refillable colour cartridges. Four commercially available ink-jet inks were obtained from the TianLi Modern Office Articles (Shanghai) Co., Ltd with Cyan (C), Magenta (M), Yellow (Y) and Black (K) colours were used without further purification.

A pattern of 80mm x 80mm square was printed for each single colour with 360 dpi x 360 dpi for easy comparison. After ink-jet printing, the printed fabrics were air-dried and then steamed at 110°C for colour fixation. The steamed fabrics were finally washed in 10g/l nonionic detergent until all the unreacted dyes and chemicals were removed.

5.2.5 Colour yield measurement

The printed fabrics were set conditioned before the measurement of colour yield with a Macbeth Colour Eye 7000A Spectrophotometer. The condition of measurement was set under specular excluded with large aperture. The fabric was folded two times to ensure opacity and the measured twice, i.e. measurement conducted in both warp and weft directions. The measured results were finally averaged.

The colour yield expressed in K/S value ranging from the wavelength of 400nm to 700nm with 20nm interval within the visible spectrum was calculated. The K/S values were summed according to Equation (1). The higher the K/S (sum) value, the more the dye-uptake will be resulting in better colour yield.

$K/S = (1-R)^2 / 2R$ ------ Equation (1)

Where,

K = absorption coefficient, depending on the concentration of colorant

S = scattering coefficient, caused by the dyed substrate

R = reflectance of the coloured sample

5.2.6 Two-bath method

5.2.6.1 Acidic bath

Firstly, the cotton fabrics were soaked for 2-3 minutes in the stock chitosan solution prepared in Section 5.2.2, and then padded uniformly through a padding mangle with a pick-up of 80%. Secondly, the padded fabrics were cured 170˚C for 1.5 minute. All the chitosan-treated fabrics were washed with deionised water after curing.

5.2.6.2 Alkaline bath

For bath two, the sodium bicarbonate and urea were all incorporated in the pre-treatment paste. It was padded onto the cotton fabric using a padding machine supplied by Labortex Co. Ltd with the pressure of 2.6 kg/m^2 and padding speed of 2.5 rpm until a pick-up of 80% was achieved. All the pre-treated fabrics were conditioned before ink-jet printing.

5.2.7 Surface appearance of the fabric

The surface appearance of the cotton fabric was observed using a Joel's equipment JSM-6335F Field Emission Scanning Electron Microscope (SEM).

5.2.8 Outline sharpness measurement

In order to compare the outline sharpness of the prints, the width of the printed pattern in both warp and weft directions was measured using an optical light microscope (Nikon Optiplot-pol) with a magnification of 400.

5.2.9 Determination of tensile strength of printed fabric

The tensile properties of the printed fabrics were measured according to the ASTM D5034, 1995 using an Instron 4411 Tensile Tester.

5.2.10 Test of anti-bacterial effect

Anti-bacterial tests were conducted on the chitosan-treated cotton fabric, alginate-treated cotton fabric and control fabric by means of the quantitative anti-bacterial test method (AATCC 100 - 1993 Test Method). The quantitative anti-bacterial evaluation is given by Equation (2):

$$R(\%) = (B - AB)/B \times 100 \text{ ---------- Equation (2)}$$

R = the percentage reduction ratio,

A = the number of bacteria recovered from the inoculated treated test specimen swatches in a jar incubated over the desired contact period, and

B = the number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation.

5.3 Experimental design - orthogonal analysis

In order to study the individual factor for each colour, a $L_9(3)^4$ orthogonal analysis was used with the details shown in Tables 5-1 and 5-2. The pre-treatment print paste was prepared in accordance with the requirements stated in Table 6-2 and made up to the final weight of 150g with deionised water. In addition, a control pre-treatment print paste was prepared containing 150g of sodium alginate, 10g of urea and 8g of sodium bicarbonate and making up to the final weight of 200g by deionised water [66].

Table 5-1 Factors and levels used in orthogonal analysis

Factor	**Pre-treatment print paste gradient**			**Post-treatment**
Level	**Chitosan**	**Urea**	**Sodium bicarbonate**	**Steaming time**
I	15 ml	5g	2g	3 min
II	25 ml	10g	4g	5 min
III	40 ml	20g	8g	10 min

Table 5-2 Experimental arrangement

Trails	**Pre-treatment print paste gradient**			**Post-treatment**
	Chitosan	**Urea**	**Sodium bicarbonate**	**Steaming time**
1	I	I	I	I
2	I	II	II	II
3	I	III	III	III
4	II	I	II	III
5	II	II	III	I
6	II	III	I	II
7	III	I	III	II
8	III	II	I	III
9	III	III	II	I

5.4 Experimental design - two bath method

Table 5-3 Experimental design of pre-treatment print paste

Sample	**Factor**				
	Chitosan	**Sodium alginate**	**Urea**	**Sodium bicarbonate**	**Steaming time**
Chitsan-treated	Padded	--	10g	8g	5 min
Alginate-treated	--	150g	10g	8g	5 min
Control	Fabric supplied by the commercial supplier				

5.5 Result and discussion

5.5.1 Orthogonal analysis

The optimum condition of the pre-treatment print pastes containing chitosan together with steaming time was determined by means of the orthogonal analysis with the results summarised in Table 5-4.

Table 5-4 Orthogonal table for the optimisation of each colour

Trails	**Substrate**			**Post-treatment**	**Colour yield (K/S)**			
	Chitosan	**Urea**	**NaHCO3**	**Steaming time**	**C**	**M**	**Y**	**K**
1	I	I	I	I	62.93	40.82	35.62	114.76
2	I	II	II	II	70.27	52.89	47.38	132.75
3	I	III	III	III	56.08	32.04	27.77	91.3
4	II	I	II	III	65.22	45.77	44.84	130.25
5	II	II	III	I	76.93	55.05	55.82	152.57
6	II	III	I	II	57.42	35.14	35.86	95.46
7	III	I	III	II	77.42	71.28	58.02	174.17
8	III	II	I	III	76.62	54.07	49.09	134.06
9	III	III	II	I	64.95	41.92	42.82	117.04
Cyan (C)								
ΣI	189.28	205.57	196.97	204.81				
ΣII	199.57	**223.82**	200.44	**205.11**				
ΣIII	**218.99**	178.45	**210.43**	197.92				
Difference	29.71	45.37	13.46	7.19				
Magenta (M)								
ΣI	125.75	157.87	130.03	137.79				
ΣII	135.96	**162.01**	140.58	**159.31**				
ΣIII	**167.27**	109.10	**158.37**	131.88				
Difference	41.52	52.91	28.34	27.43				
Yellow (Y)								
ΣI	110.77	138.48	120.57	134.26				
ΣII	136.52	**152.29**	135.04	**141.26**				
ΣIII	**149.93**	106.45	**141.61**	121.70				
Difference	39.16	45.84	21.04	19.56				
Black (K)								
ΣI	338.81	419.18	344.28	384.37				
ΣII	378.28	**419.38**	380.04	**402.38**				
ΣIII	**425.27**	303.80	**418.04**	355.61				
Difference	86.46	115.58	73.76	46.77				

Tables in bold form showed the greatest value in the levels of different factors used

5.5.1.1 Effect of chitosan and acetic acid on the pre-treatment print paste

Figure 5-1 clearly shows that the Black colour had the highest colour yield followed by Cyan, Magenta and Yellow colours. When the amount of chitosan used in the pre-treatment print paste was increased, the colour yields of the printed fabrics were enhanced correspondingly. This confirmed that chitosan could serve the function of increasing the colour yield of ink-jet printing. This behaviour could be probably due to the fact that the amino groups present in the chitosan took up proton from the slightly acidic dyebath to form the $-NH_3^+$ groups. These $-NH_3^+$ groups being electropositive in nature could facilitate the transfer of the negatively charge dye anions from the bath onto the fabric, thereby improving colour fixation [90, 91].

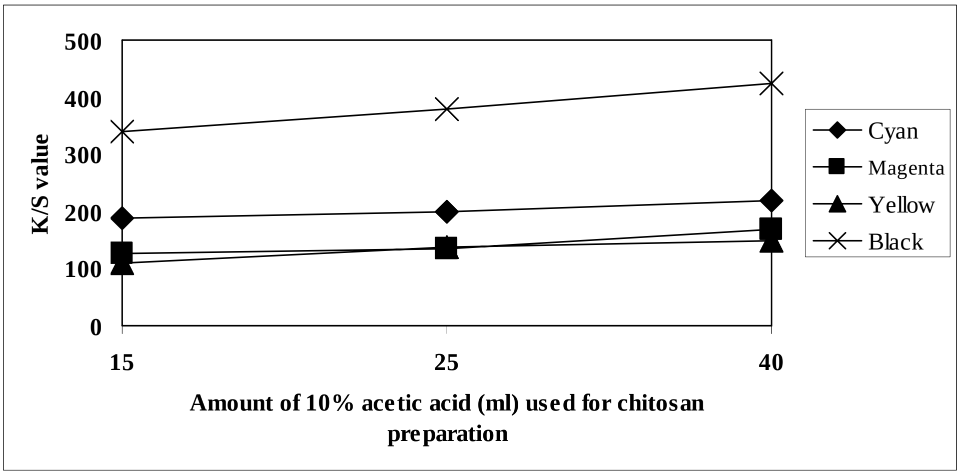


Figure 5-1 Effect of the amount of chitosan used on the colour yield of different colours

Furthermore, Figure 5-1 also shows the colour yield of these four different colours under the influence of various amounts of acetic acid used in the pre-treatment print paste. It was apparent that the amount of chitosan used was proportional to the amount of acetic acid used in the pre-treatment print paste. For example, when the amount of acetic acid used in the pre-treatment print paste was increased, the colour of the ink-jet printed cotton fabric could be deepened. The maximum colour yield could be achieved when 5g chitosan was used 40 ml of 10% acetic acid in the pre-treatment print paste.

5.5.1.2 Effect of sodium bicarbonate on the pre-treatment print paste

Figure 5-2 shows that Black colour had the highest colour yield followed by Cyan, Magenta and Yellow colour. However, the effects of sodium bicarbonate on the pre-treatment print paste in Cyan, Magenta and Yellow colours were not significant when compared with the Black colour. Generally speaking, when the amount of the sodium bicarbonate used in the pre-treatment print paste was increased, the colour yields of the printed fabrics were increased.

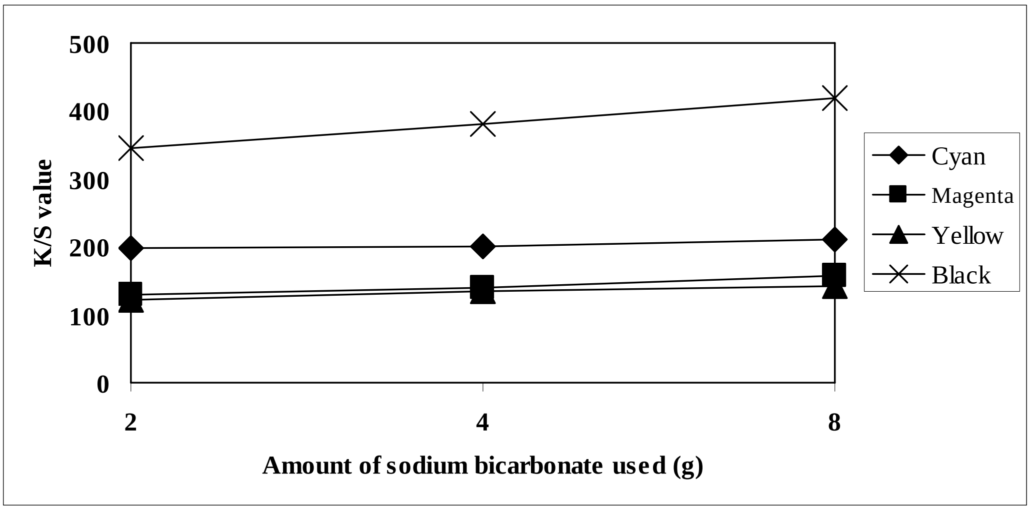


Figure 5-2 Effect of the amount of sodium bicarbonate used on the colour yield of different colours

Furthermore, it was noted that the neutralisation effect was not significant in the pre-treatment print paste because when the amount of both acetic acid and sodium bicarbonate was increased, no significant reduction of the final colour yield was observed.

5.5.1.3 Effect of urea on the pre-treatment print paste

Figure 5-3 shows the colour yield of different colours under the influence of various amounts of urea used in the pre-treatment print paste. The results showed that the urea could deepen the colour of the ink-jet printed cotton fabric to achieve the highest colour yield when 10g of urea was used in the pre-treatment print paste. When compared, the Black colour obviously showed the highest colour yield followed by the Cyan, Magenta and finally Yellow colours. The order of effect was similar to that of the results reported previously in Section 4.4.1.3 and 4.4.2.2.1 [66, 92].

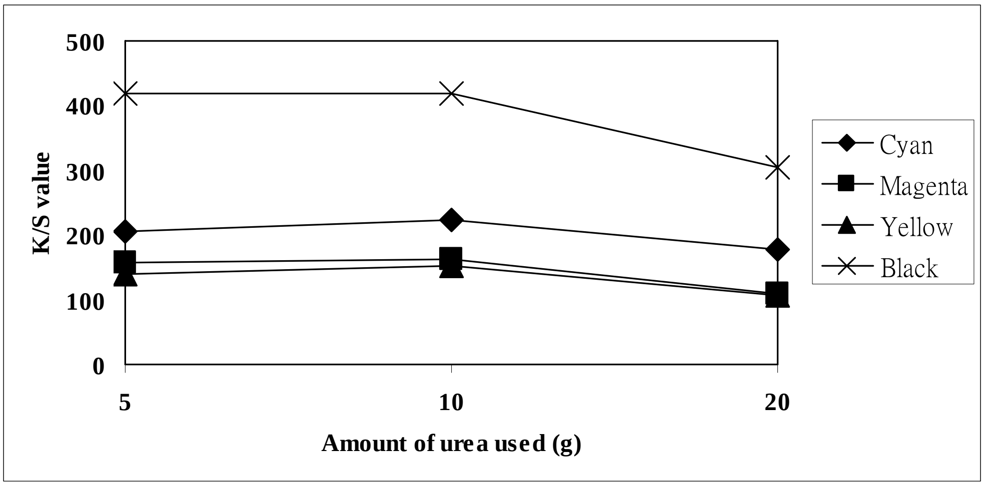


Figure 5-3 Effect of the amount of urea used on the colour yield of four different colours

However, an interesting observation shown in Figure 5-3 was that when the amount of urea used in the pre-treatment print paste was more than 10g, the colour yield of the ink-jet printed fabrics would decrease. When the amount of urea used was further increased to 20g, the colour yield of the ink-jet printed fabric dropped significantly which was paler than that of 5g of urea used. Such drop of colour yield with respect to the increasing amount of urea used in the pre-treatment print paste might be due to the increase of moisture regained by the fibres during the steaming process.

5.5.1.4 Effect of steaming time on the pre-treatment print paste

Figure 5-4 demonstrates the effect of steaming time on the colour yield of different ink-jet printed colours of the cotton fabric. The Black colour showed the highest colour yield followed by Cyan, Magenta and Yellow colours with the same sequence shown in Sections 4.4.1.4. It was noted that the optimum K/S values of all four different colours were obtained at the steaming time of 5 minutes.

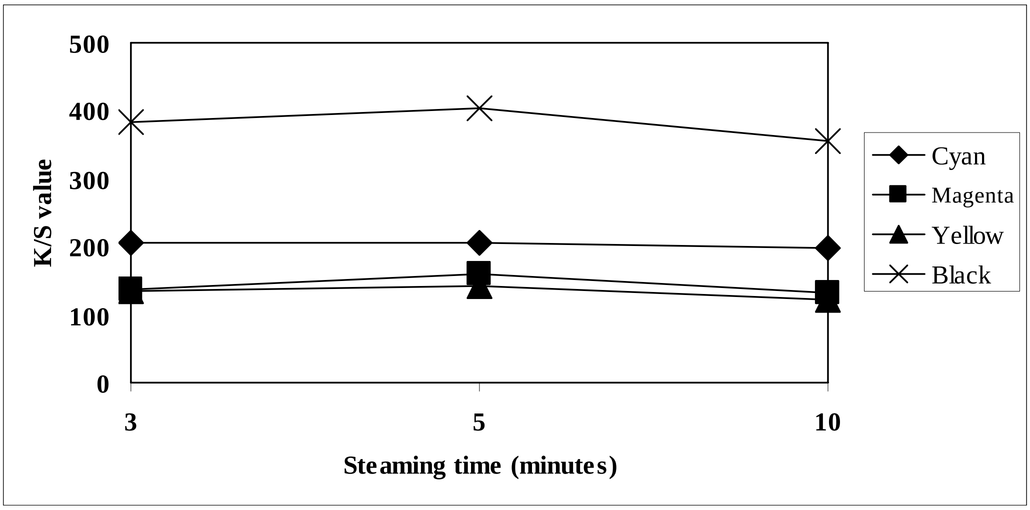


Figure 5-4 Effect of steaming time on the colour yield of four different colours

5.5.1.5 Importance and effect of chitosan on the colour yield of ink-jet printed cotton fabric

Orthogonal analysis is a useful and simple technique for analysing the process variables or factors involved in a production process. Previous researchers [80, 86-88] showed that orthogonal analysis could provide a simple and convenient way for finding out the optimum condition and the level of importance of different factors in a production process.

After considering the results obtained from the orthogonal analysis as shown in Table 5-4, it was concluded that all the four factors being studied namely chitosan, urea, sodium bicarbonate and steaming time could affect the K/S value by contributing different effects on the final colour yield. However, the level of importance based on the orthogonal analysis [66, 80, 87] was in the order of urea > chitosan > sodium bicarbonate > steaming time.

In order to verify the printed quality by means of colour yield, further experiments were conducted with the use of control fabric and the results are shown in Table 5-5.

Table 5-5 Colour yield of chitosan-treated cotton fabric

Colour	**Cyan**	**Magenta**	**Yellow**	**Black**
Control fabric	110.75	95.66	90.30	260.88
Chitosan-treated cotton fabric	88.60	76.53	72.24	208.70

Control fabric = commercial pre-treated cotton fabric

The results shown in Table 5-5 demonstrated clearly that the cotton fabric treated with chitosan under the optimum condition could achieve a better colour yield when compared with those shown in Table 5-4. As estimated, about 80% of the final colour yield was obtained for all four different colours of the chitosan-treated cotton fabric when compared with the control fabric. On the whole, the four different inks could not achieve the same level of colour yield after chitosan treatment.

5.5.1.6 Colour fastness of the ink-jet printed cotton fabric

The chitosan-treated cotton fabric had a better colour fastness property than the control fabric, i.e. improvement of at least 1/2 Grade. The ratings of different colour fastness of the fabrics are shown in Table 5-6 and 5-7.

Table 5-6 Colour fastness results ink-jet of printed cotton fabrics to light and crocking

Sample	**Light (C/M/Y/K)**	**Crocking**	
		Wet (C/M/Y/K)	**Dry (C/M/Y/K)**
Control cotton fabric	4/3/4/3	3/3/3/3	4/4/4/4
Chitosan-treated cotton (1-9)	4-5/4/4-5/4	4/4/4/4	4-5/4-5/4-5/4-5

(Control = commercially pre-treated cotton fabric, C = Cyan, M = Magenta, Y = Yellow, K = Black)

Table 5-7 Colour fastness results of ink-jet printed cotton fabrics to laundering

Washing							
Sample	**Staining (C/M/Y/K)**						**Colour Change (C/M/Y/K)**
	Acetate	**Cotton**	**Nylon**	**Polyester**	**Acrylic**	**Wool**	
Control cotton fabric	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	4/4/4/4	3/4/4/4
Chitosan-treated (1-9 trails)	4-5/4-5/4-5/4-5	4/4-5/4-5/4-5	4-5/45/4-5/4-5	4-5/4-5/4-5/4-5	4-5/4-5/4-5/4-5	4-5/4-5/4-5/4-5	4/4-5/4-5/4-5

(Control = commercially pre-treated cotton fabric, C = Cyan, M = Magenta, Y = Yellow, K = Black)

The improvement in the colour fastness of the chitosan-treated fabric might be associated with the introduction of primary amino groups into the cellulosic fibre structure. Most probably after these groups were deposited in the crevices between the fibres, they might impart a cationic surface which attracted the oppositely charged reactive dye anions [93]. As a result, the ink-jet printability of the chitosan-treated cotton fabric was improved.

5.5.1.7 Surface appearance of ink-jet printed cotton fabric

The surface appearance of the control and chitosan-treated cotton fabrics was morphologically observed by the SEM as shown in Figure 5-5 to 5-8.

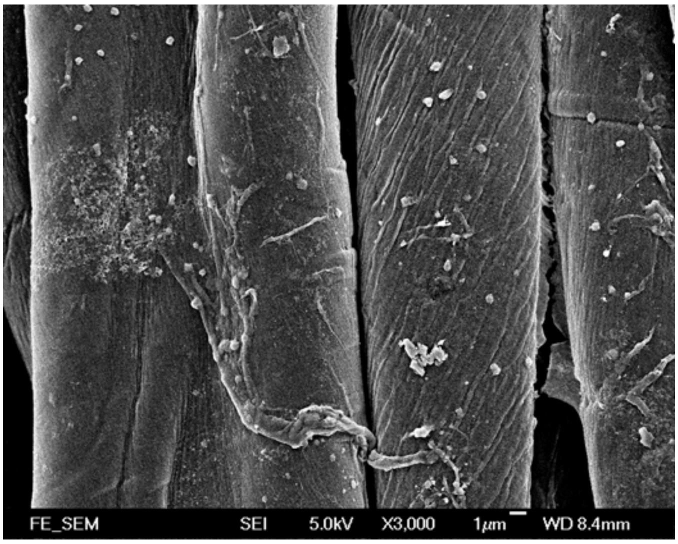


Figure 5-5 Surface appearance of the control cotton fabric in the pre-treatment stage

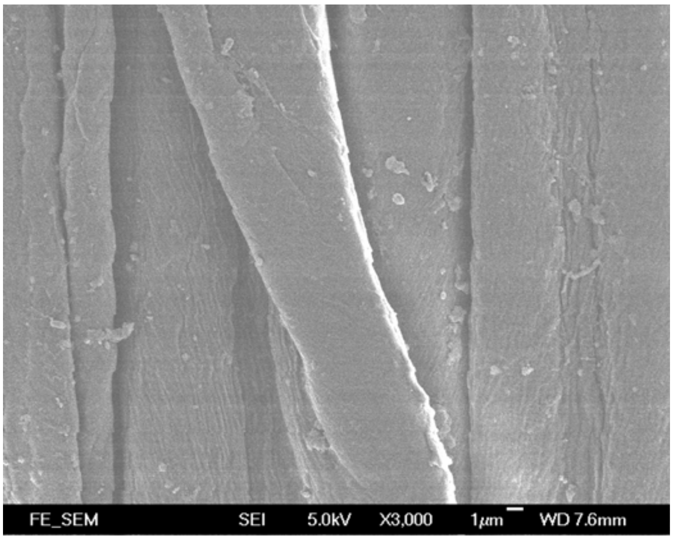


Figure 5-6 Surface appearance of the control cotton fabric after washing

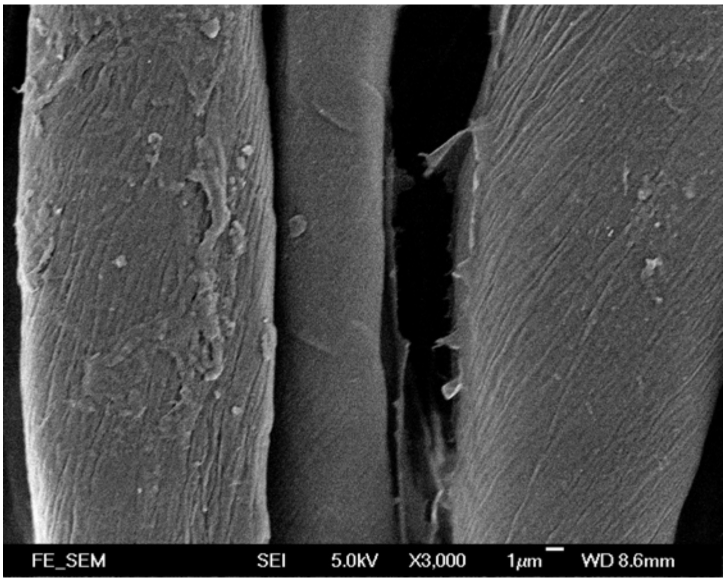


Figure 5-7 Surface appearance of the chitosan-treated cotton fabric in the pre-treatment Stage

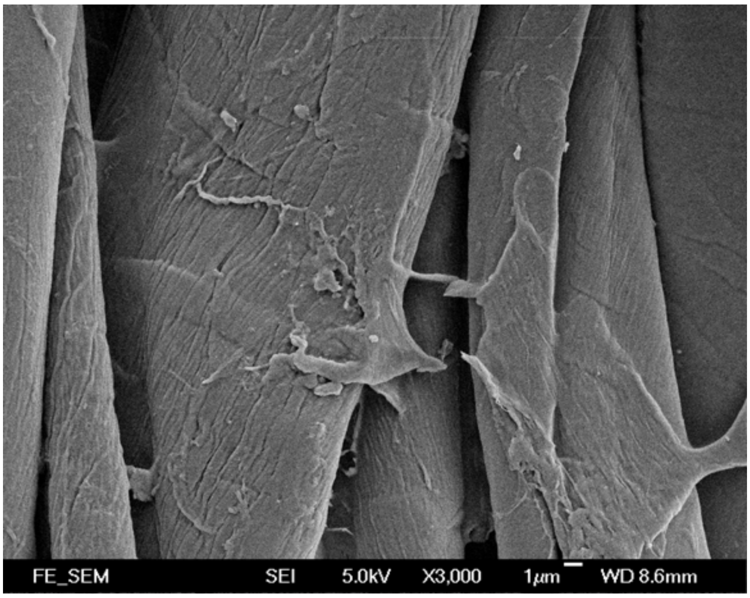


Figure 5-8 Surface appearance of the chitosan-treated cotton fabric after washing

Figures 5-5 and 5-6 show the surface appearance of the control fabric in the pre-treatment stage and after-washing stage respectively. It was obvious to see that sodium alginate adhered initially on the cotton fibre surface in the pre-treatment stage. However, the sodium alginate was completely removed from the fibre surface in the after-washing stage.

On the other hand, Figures 5-7 and 5-8 show that, chitosan also adhered initially on the surface of cotton fibre surface in the pre-treatment stage. On the contrary, chitosan still remained on the fibre surface in the after-washing stage. Furthermore, it was noted that the chitosan deposited on the crevices formed a crosslinking between cotton fibres.

When comparing the SEM images between the control and chitosan-treated cotton fibers, the surface of the chitosan-treated fibre had many long narrow lines. Based on the SEM analysis, it was clear that the treatment of the cotton fibres with chitosan would result in a unique morphological form having a more textured surface than the control fabric. This was suggested to be caused by polymer precipitation [93].

5.5.1.8 Outline sharpness of the ink-jet printed fabric

The outline sharpness of the ink-jet printed pattern was measured by the optical analysis method and the results are shown in Table 5-8.

Table 5-8 Outline sharpness of ink-jet printed cotton fabric

	Colour							
	Cyan		**Magenta**		**Yellow**		**Black**	
	Warp (mm)	**Weft (mm)**	**Warp (mm)**	**Weft (mm)**	**Warp (mm)**	**Weft (mm)**	**Warp (mm)**	**Weft (mm)**
Control fabric	82	81	82	81	82	81	82	81
Chitosan-treated fabric	81	80	81	80	81	80	81	80

For both the control and chitosan-treated fabrics, the ink-jet printed patterns of four different colours in the warp direction were thicker than those in the weft direction. This might be due to the differential wicking effect caused by the warp and weft yarns. When considering the width of the printed pattern, the patterns printed on the chitosan-treated cotton fabrics were narrower than the control fabric in both warp and weft directions. The result confirmed that chitosan treatment could enhance the outline sharpness of the prints as a result of strong ionic attraction between cationic cotton and anionic reactive inks.

5.5.2 Two-bath method

5.5.2.1 Colour yield measurement

Figure 5-9 show that the colour yields of four different colours of chitosan-treated cotton fabrics were better than those of the alginate-treated fabrics. This confirmed that the chitosan could be feasible to replace sodium alginate as thickener in the print paste of ink-jet printing. In addition, the Black colour yield of chitosan-treated fabric was increased over 20% when compared with the control fabric.

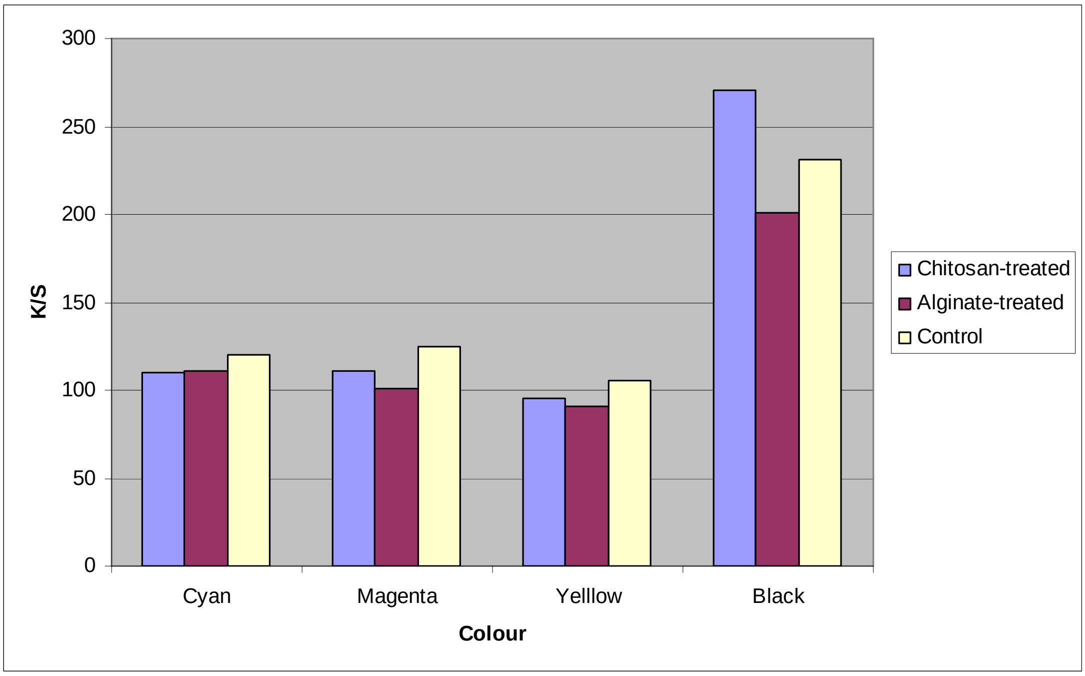


Figure 5-9 The effect of pre-treatment on four different colours of ink-jet printed fabric
*Control fabric supplied by supplier

The chitosan-treated cotton fabric of Magenta, Yellow and Black colours had higher colour yield than the alginate-treated fabric treated. With reference to previous studies, the reactive system of these three colours was belonged into vinylsuphone reactive dye class [94] which had higher extent of dye fixation on the chitosan-treated cotton when compared with the homobifuctional monochloratriazine dyes such as Cyan colour [95]. It was believed the amino group present in chitosan could take up a proton from the slightly acidic bath and so $-NH_3^+$ groups are formed. These groups being electropositive in nature could facilitate the transfer of the negatively charge dye anion from the bath onto the fabric, thereby improving exhaustion [91].

5.5.2.2 Determination of tensile strength of printed fabric

The result of breaking load is shown in Table 5-9. The chitosan-treated cotton fabric experienced a slight decrease in breaking load, i.e. a drop of 0.7% in warp direction when compared with both the alginate-treated and control cotton fabrics, and a drop of 0.8% in weft direction when compared with the alginate-treated fabric. The decrease in break load might be due to the acid damage of the force occurred inside the chitosan-treated cotton fabric fabricated at pH5 in acid medium.

Table 5-9 Breaking load of ink-jet printed fabric

	Warp Direction	**Weft Direction**
	Load at Max.Load (N)	**Load at Max.Load (N)**
Chitosan-treated	407.550	247.000
Alginate-treated	410.450	269.250
Control fabric	410.600	244.200

5.5.2.3 Anti-bacterial evaluation of the treated fabric

AATCC Test Method 100 was used to determine the anti-bacterial activity of the pre-treated cotton. Table 5-10 shows the bacterial concentration of Staphylococcus aureus bacteria with respect to the control and pre-treated fabrics during 0 hours and 48 hours.

Table 5-10 Anti-bacterial evaluation of the chitosan treated fabric by AATCC 100 test method

Sample	**Bacterial concentration**		
	0 hours	**48 hours**	**% of bacterial removal (-ve)/increase (+ve)**
Chitosan-treated	8.1 x107	0	-100%
Alginate-treated	2.41x108	7.1x107	- 70.54%
Control	1.28x108	2.22 x108	+172.44%

The results indicated that the chitosan-treated fabric showed positive result of anti-bacterial effect, meaning that the bacteria could be completely killed by the chitosan present in the chitosan-treated cotton fabric. Therefore, the chitosan-treated cotton fabric was very effective to resist bacteria when compared with both the alginate-treated fabric and the control fabric. Although the alginate-treated fabric had the function of anti-bacterial effect, its performance was worse than the chitosan-treated fabric. The control fabric did not exhibit any anti-bacterial effect as reflected by a large number of bacteria growth.

5.6 Conclusion

The experiments conducted involved the evaluation of chitosan as a thickener in the pre-treatment print paste for ink-jet printing. Based on the results of different colour fastness tests, chitosan in principle could work as a pre-treatment print paste thickener. However, the colour yield obtained for the chitosan-treated fabrics could not achieve the same results as the alginate-treated fabrics previously developed for ink-jet printing. Nevertheless, the colour fastness properties and the outline sharpness of the prints of cotton fabric were greatly improved by the chitosan treatment.

Two-bath method was tentatively developed to separate the chitosan paste from sodium bicarbonate and urea before being padded onto the fabric surface. Based on the results of the highest colour yield obtained on the cotton fabric, it was confirmed that the two-bath method was successfully developed. In particular, the yield of Black colour had been significantly improved as reflected by an increase of over 20% colour yield when compared with the control fabric. In addition, it was found that chitosan could also impart higher anti-bacterial property onto the cotton fabric.

CHAPTER 6.

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This thesis aims to provide an optimum printing systems for ink-jet printing of cotton fabric.

6.1.1 Characterisation of ink-jet printing ink

The techniques used in the study included Ultraviolet-Visible Spectroscopy, Thin-Layer Chromatography and Fourier Transform Infrared Spectroscopy.

(1) Ultraviolet-Visible Spectroscopy (UV/VIS)

The results of UV/VIS revealed the maximum absorbance of the four different colours of reactive ink-jet inks and hence their respective colours were known.

It was found that maximum absorption peak of (1) Cyan (C) colour was 662.45nm which was within the absorption region of orange-red light (610-700nm), (2) Magenta (M) colour was 510.41nm which was within the absorption region of green light (500-540nm) and Yellow (Y) colour was 418.42nm which was within the absorption region of violet-blue light (400-430nm). In addition, Black (K) colour should have a broad band of absorption within the 400nm-650nm region and a relatively sharper absorption peak located at 604.27nm.

(2) Thin-Layer Chromatography (TLC)

TLC had been used to separate various dye components present in the reactive ink for dye analysis and confirmation. It was found that the solvents of 100% methanol, acetonitrile/water mixture, and methanol/acetonitrile:water mixture were suitable for separating the Cyan, Magenta, Yellow and Black printing inks by using the Aluminum Silical gel 60 TLC plates. Based on the results of observation, it was confirmed that each printing inks was composed of only one particular dye component.

(3) Infrared Spectroscopy (IR)

The functional groups and chemical composition of the ink-jet printing inks had been deduced by using the IR analytical technique and compared with the chemical structures of known reactive dyes. It was found that the Magenta, Yellow and Black printing inks possessed vinylsulphone reacting system, while the Cyan printing ink possessed triazine reacting system.

6.1.2 Optimisation of ink-jet printing system for cotton fabric

Orthogonal design has been used to determine the effect of pre-treatment print paste and post-treatment process on the colour yield of ink-jet printed cotton fabric with respect to the three primary colours (Cyan, Magenta and Yellow) and Black colour of reactive ink-jet ink. Based on the experimental results, it was confirmed that (1) the contents of pre-treatment print paste, i.e. sodium alginate, urea and alkali, and (2) the steaming time of post-treatment process after ink-jet printing did play the major role in affecting the final colour yield of the printed cotton fabric with the importance of factors: urea > sodium alginate > sodium bicarbonate > steaming time.

Fractional factorial experimental design has also been used to further study the factors of pre-treatment print paste, i.e. the amount of sodium alginate, urea and sodium bicarbonate used, and steaming time. Based on the results of the highest colour yield generated on the cotton fabric, it was found that the amount of urea used was the dominant factor when compared with the other factors used in each ink. In addition, the final colour yield was not only influenced by an individual factor, but also due to an interaction effect among these factors.

The optimum content of pre-treatment print paste and the proper condition of post-treatment after ink-jet printing were successfully developed to obtain the highest colour yield of Cyan, Magenta, Yellow and Black colours with the aid of the response surface experimental design technique. The highest colour yield achieved is shown in Table 6-1.

Table 6-1 Optimisation of ink-jet printing system to achieve the highest colour yield of each colour

Colour	Amount of Sodium Alginate used (gram)	Amount of Urea used (gram)	Amount of Sodium Bicarbonate used (gram)	Steaming Time (Minute)
Cyan	150	10-15	6-9	5
Magenta	90-110	8-10	8	5
Yellow	150	10-17	8	5-9
Black	150	12-15	8	6-8

Furthermore, the newly developed pre-treated cotton fabric had a better final colour yield of Cyan, Magenta and Yellow colours when compared with the commercially pre-treated cotton fabric, except Black colour.

6.1.3 Application of chitosan to modify cotton fabric surface for better printing quality

The feasibility of using chitosan to replace sodium alginate as a thickener in the pre-treatment print paste was studied with the aid of orthogonal design. Two-bath method was successfully developed to separate the chitosan paste from sodium bicarbonate and urea before being padded onto the fabric surface. The experimental results also confirmed that chitosan could contribute higher colour yield to the ink-jet printed on the cotton fabric.

Based on the results of scanning electron microscope (SEM) observation and different colour fastness assessments, chitosan was confirmed to be a good pre-treatment print paste thickener. When compared, the outline sharpness of the printed pattern on the chitosan-treated cotton fabric was observed to be narrower than that of the alginate-treated cotton fabric in both warp and weft directions. This implied that the chitosan-treated fabric could be printed with the sharpest pattern. The chitosan-treated fabrics of Magenta, Yellow and Black colours had higher colour yield than the alginate-treated cotton fabrics. The result indicated that the vinylsulphone reactive dyes had higher extent of fixation on the chitosan-treated cotton fabric. In particular, the Black colour had been significantly improved as reflected by an increase of over 30% colour depth. In addition, it was found that chitosan could also impart higher anti-bacterial property onto the cotton fabric.

6.2 Recommendation for future works

The major objectives of the research project have been achieved and some future works are recommended in order to further improve and maximise the effectiveness techniques of the newly developed optimum printing system.

1. To formulate different dye classes of ink-jet inks for various fabric types so that a series of inks with wide colour ranges can be produced to meet the demand of printing industry at lower cost.
2. To develop the specific pre-treatment print paste recipes for different types of fabric such as silk, nylon, polyester and cotton/polyester blend etc.
3. To study the feasibility of applying chitosan to other types of fabric substrate such as silk, nylon and polyester etc.
4. To develop the optimum printing systems for other types of fabric using the statistical modelling.
5. To apply the Low Temperature Plasma (LTP) physical treatment technique for fabric surface modification aiming to improve ink-uptake.

CHAPTER 7.

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