การเตรียมหมึกพิมพ์อิงก์เจ็ตประเภทสารสีสำหรับการพิมพ์หกสีบนผ้าไหม

นายพิเชษฐ์ ธนพงศ์จงรวย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเทคโนโลยีทางภาพ ภาควิชาวิทยาศาสตร์ทางภาพถ่ายและเทคโนโลยีทางการพิมพ์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

PREPARATION OF PIGMENTED INKJET INK FOR SIX-COLOR PRINTING ON SILK FABRIC

Mr. Pichet Thanapongjongruay

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Imaging Technology
Department of Photographic Science and Printing Technology
Faculty of Science
Chulalongkorn University
Academic Year 2009

Thesis Title	PREPARATION OF PIGMENTED INKJET INK FOR SIX-COLOR PRINTING ON SILK FABRIC
By	Mr. Pichet Thanapongjongruay
Field of Study	Imaging Technology
Advisor	Professor Suda Kiatkamjornwong, Ph.D.
Co-Advisor	Hiromichi Noguchi, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

…………………………………………Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

…………………………………………Chairman
(Associate Professor Aran Hansuebsai, Ph.D.)

…………………………………………Advisor
(Professor Suda Kiatkamjornwong, Ph.D.)

…………………………………………Co-Advisor
(Hiromichi Noguchi, Ph.D.)

…………………………………………Examiner
(Siriwan Phattanarudee, Ph.D.)

…………………………………………External Examiner
(Wiyong Kangwansupamonkon, Ph.D.)

พิเชษฐ์ ธนพงศ์จงรวย : การเตรียมหมึกพิมพ์อิงก์เจ็ตประเภทสารสีสำหรับการพิมพ์หกสีบนผ้าไหม. (PREPARATION OF PIGMENTED INKJET INK FOR SIX-COLOR PRINTING ON SILK FABRIC) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. สุดา เกียรติกำจรวงศ์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. ฮิโระมิจิ โนะกุจิ, 142 หน้า.

งานวิจัยนี้ได้เตรียมหมึกพิมพ์อิงก์เจ็ตประเภทสารสีห้าชุด และปรับสภาพผิวผ้าไหมด้วยไคโทซาน ไกลซีน และเอ็น-[(2-ไฮดรอกซิล-3-ไทรเมทิลแอมโมเนียม)โพรพิล]ไคโทซานคลอไรด์ (เอชทีเอซีซี) เพื่อเพิ่มคุณภาพงานพิมพ์ผ้าไหม หมึกพิมพ์อิงก์เจ็ตหกสีของแต่ละชุดประกอบด้วยหมึกพิมพ์สีดำ น้ำเงินเขียว ม่วงแดง เหลือง น้ำเงินเขียวอ่อน และม่วงแดงอ่อน ซึ่งเตรียมจากสารสีที่กระจายตัวด้วยวิธีการปรับสภาพผิวสารสี อัตราส่วนของสารสีต่อสารยึดเป็น 1:2 สารยึดเป็นพอลิเมอร์ร่วมของอิมัลชันสไตรีน-อะคริเลต เตรียมหมึกพิมพ์ด้วยสัดส่วนระหว่างไดเอทิลีนไกลคอลกับกลีเซอรอลต่างกันเพื่อกำหนดความหนืด แรงตึงผิว สภาพพ่นหมึกได้ และสภาพพิมพ์ได้ หมึกพิมพ์ที่เตรียมขึ้นมีค่าความเป็นกรด-เบสในช่วง 6.7 – 8.8 ประจุบนผิวของอนุภาคหมึกพิมพ์อยู่ในช่วง (-35) ถึง (-50) มิลลิโวลต์ ขนาดอนุภาคในช่วง 100-300 นาโนเมตร ค่าแรงตึงผิวในช่วง 39 ถึง 46 มิลลินิวตันต่อเมตร หมึกพิมพ์สีดำที่เตรียมด้วยสัดส่วนของสารสีต่อสารยึด 1:0 1:0.5 1:1 1:1.5 และ 1:2 แสดงทั้งลักษณะการไหลแบบนิวโทเนียนที่อัตราเฉือนต่ำ (21-142 ต่อวินาที) และการไหลแบบนอน-นิวโทเนียนที่อัตราเฉือนสูง (180-741 ต่อวินาที) หมึกพิมพ์หกสีชุดห้าที่ใช้สารสีต่อสารยึด 1:2 ซึ่งอยู่ในเกณฑ์ช่วงพ่นหมึกได้ของแผนที่ของความหนืด-แรงตึงผิว มีความหนืดในช่วง 2.78-3.44 มิลลิพาสคัล วินาที มีสภาพพ่นหมึกได้ครบทุกสี หมึกพิมพ์ชุดห้าซึ่งผ่านเกณฑ์ประเมิน จึงมีสมบัติเหมาะกับเครื่องพิมพ์อิงก์เจ็ตเอปซันซึ่งเป็นแบบไพโซอิเล็กทริก พิมพ์ผ้าไหมที่ปรับสภาพผิวก่อนพิมพ์ด้วยสารละลายไคโทซาน สารละลายไคโทซานผสมไกลซีน และสารละลายเอชทีเอซีซี ด้วยหมึกพิมพ์หกสีชุดห้า วิเคราะห์คุณภาพของผ้าไหมพิมพ์ซึ่งประกอบด้วยขอบเขตสีและความอิ่มตัวสี ความแข็งกระด้าง ความทนแสง และความทนการซัก พบว่า การปรับสภาพผิวผ้าก่อนพิมพ์สามารถเพิ่มขอบเขตสีและความอิ่มตัวสีของผ้าไหมพิมพ์ได้ การปรับสภาพผิวผ้าด้วยสารละลายไคโทซานผสมไกลซีน และสารละลายเอชทีเอซีซีเพิ่มขอบเขตสีและความอิ่มตัวสีมาก ซึ่งการปรับสภาพผิวด้วยเอชทีเอซีซีให้ความอิ่มตัวสีมากที่สุด การปรับสภาพผิวด้วยสารละลายเอชทีเอซีซีและสารละลายไคโทซานไม่เปลี่ยนแปลงความแข็งกระด้างของผ้า การปรับสภาพผิวผ้าไม่เปลี่ยนแปลงสมบัติด้านความคงทนของสีต่อแสง แต่สมบัติความคงทนของสีต่อการซักเพิ่มจากระดับ 4 เป็น 4-5 ตรวจสอบประสิทธิภาพการจับตัวเป็นก้อนของสารปรับสภาพผิวผ้ากับหมึกพิมพ์ด้วยเทคนิคยูวี-วิสิเบิลสเปกโทรสโกปี พบว่า สารละลายเอชทีเอซีซีมีปฏิสัมพันธ์กับสารสีในหมึกพิมพ์ได้ดีที่สุด

ภาควิชา วิทยาศาสตร์ทางภาพถ่ายและเทคโนโลยีทางการพิมพ์ ลายมือชื่อนิสิต..
สาขาวิชา เทคโนโลยีทางภาพ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก......................
ปีการศึกษา 2552 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม......................

4972411023: MAJOR IMAGING TECHNOLOGY
KEYWORDS: PIGMENTED INKJET INK / SURFACE MODIFIED PIGMENT / CHITOSAN / GLYCINE / HTACC / SILK FABRIC

PICHET THANAPONGJONGRUAY: PREPARATION OF PIGMENTED INKJET INK FOR SIX-COLOR PRINTING ON SILK FABRIC. THESIS ADVISOR: PROF. SUDA KIATKAMJORNWONG, Ph.D., THESIS CO-ADVISOR: HIROMICHI NOGUCHI, Ph.D., 142 pp.

This research prepared five sets of pigmented inkjet inks and pretreated the silk fabric with chitosan, glycine and *N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan chloride (HTACC) to enhance print quality. The six pigmented inkjet inks comprising black (Bk), cyan (C), magenta (M), yellow (Y), light cyan (LtC) and light magenta (LtM) colors were prepared with surface-modified pigments and a pigment-to-binder ratio of 1:2. The binder was the copolymer of styrene-acrylic acid emulsion. Different ratios of diethylene glycol and glycerol for verifying the ink viscosity, surface tension with jettability were investigated. The prepared inks had pH in the range of 6.7-8.8, zeta-potential in the range from (-35) to (-50) mV, the pigment particle sizes in the range of 100-300 nm, surface tension in the range of 39 – 46 mN m^{-1}. The black inks prepared by the pigment-to-binder ratios of 1:0, 1:0.5, 1:1, 1:1.5 and 1:2 exhibited both the Newtonian flow at low shear rates (21-142 s^{-1}) and non-Newtonian flow at high shear rates (180-741 s^{-1}). The ink formulation 5 with a pigment-to-binder ratio of 1:2 which was in the jettable range on a viscosity-surface tension criteria map had the viscosity in a range of 2.78 – 3.44 mPa s which jetted the printing pattern completely. The ink formulation 5 was thus best suited for printing with an Epson piezoelectric type inkjet printer. The silk fabric pretreated with chitosan, HTACC, and mixed chitosan and glycine was then each printed with the ink formulation 5. The printed silk fabrics were analyzed for color gamut and color saturation, stiffness, light and wash fastnesses. The printed silk fabrics exhibited that the color gamut and color saturation of the pretreated fabrics provided a wider color gamut than the printed colors on the untreated fabrics. The mixed chitosan and glycine, and HTACC pretreatments enhanced markedly the chroma while the color strength of the fabrics with HTACC pretreatments increased most. The pretreated silk fabrics by chitosan or HTACC did not increase the fabrics stiffness. The light fastness of the pretreated fabrics did not change from the untreated ones, although the wash fastness increased from 4 to 4-5. The extent of coagulation efficiency between the pretreatment reagents and inks was investigated by UV-visible spectroscopy from which HTACC can exhibit strong interaction with the pigments in the inks.

Department: Photographic Science and Printing Technology	Student's Signature
Field of Study: Imaging Technology	Advisor's Signature
Academic Year: 2009	Co-Advisor's Signature

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude and gratefulness to my thesis advisor, Professor Suda Kiatkamjornwong, Ph.D. for teaching and guiding research critical thinking, valuable suggestion, reviewing, corrections, rewriting this thesis. I would like to express my deep gratefulness to my co-advisor, Hiromichi Noguchi, Ph.D. for his advice, research instruction, and thesis writing. Moreover, I would like thank Associate Professor Aran Hansuebsai, Ph.D., Siriwan Phattanarudee, Ph.D., and Wiyong Kangwansupamonkon, Ph.D., the external examiner, for suggestion, comments and serving on the thesis committee.

I would like to sincerely thank to The East Asiatic (Thailand) Public Co., Ltd. for supporting the surface-modified pigments (CAB-O-JET®); to South City Petrochem Co., Ltd. for supporting the nonionic surfactant (Surfynol 104) and to Clariant Chemical Ltd. for supporting the Printofix binder 710. I am indebted to Associate Professor Supanee Chayabutra, Ph.D., Department of Chemistry of the Faculty of Science, Silipakorn University for providing some financial support, research facilities and testing equipment during the experimental work; to the Department of Photographic Science and Printing Technology of the Faculty of Science for research facilities, supporting equipment, chemicals, and working desk throughout the study. Many thanks go to the Graduate School, Chulalongkorn University for partial financial support for research materials and characterization. I am very thankful to Assistant Professor Supaporn Noppakundilograt, Ph.D., Mr. Atthaphong Thongduang and Miss Punthorn Buranagul for kind assistance throughout the study and also to any persons whose names are not mentioned here for their assistance; to my colleague at Material Research Centre for Art and Design, Silpakorn University for understanding and work helping; to my dear friend at Kasetsart University Laboratory School and Silpakorn University for their love, warm friendship and moral support.

In addition, Last but not least, I am very grateful to my family for their love, moral support and understanding throughout the entire study.

CONTENTS

PAGE

PAGE

PAGE

PAGE

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

ABBREVIATIONS

°C	: degrees Celsius
min	: minute
rpm	: revolutions per minute
M	: molar
% w v^{-1}	: percent weight by volume
MW	: molecular weight
D	: density
g	: gram
mg	: milligram
μm	: micrometer
nm	: nanometer
hr	: hour
ν	: wave number
FTIR	: Fourier Transform Infrared Spectroscopy
DSC	: Differential Scanning Calorimetry
t	: time
r	: pore radius
T_g	: Glass Transition Temperature
T_m	: Melting Temperature
γ	: surface tension
η	: viscosity
mPa s	: millipascal second
mN m^{-1}	: millinewton per meter

g cm^{-3}	: gram per cubic centimeter
s^{-1}	: per second
N m^{-2}	: Newton per square meter
cm^{-1}	: per centimeter

CHAPTER 1

INTRODUCTION

1.1 Scientific rationale

Textile inkjet printing has demonstrated high advantages over the screen printing method such as excellent quality, environment friendly, especially rapid response to the frequent shift of fabric fashion and can potentially enable cost-effective short-run for production. Inkjet printing furthermore allows visual effect such as tonal gradients and infinite pattern to repeat sizes that cannot be practically achieved with a screen printing process. Inks for textile printing are usually classified into two categories as dye and pigment inks. Pigmented-based inks show more environmental benefits and have shorter processes than dye-based inks because the final products printed can be achieved by simple heat curing without steaming and washing. More important issue is that pigment inks are suitable for inkjet printing on all kinds of fiber fabrics. Thus the pigment printing promises lower cost of both materials and processes compared to dyes. In addition, for textile printing applications that require permanence properties, such as water fastness, light fastness, and rub resistance, pigmented colorants are preferred. The inks made from the surface-modified pigment had a low viscosity and high surface tension because of a low dispersant content; moreover, this technique yielded high optical density, good tone reproduction, better color gamut, and gamut volume. The surface modified dispersion connects or makes to chemical bonding and the number of functional groups of the pigmented surface. These technique leads to well characterized pure pigments, enable us to decrease free polymers and impurities. However, pigments must form firm bonding with fibrous substrates with the aid of water-dispersed binder. In the case of textile printing, the binder is a necessary ingredient to maintain the performance of the image with respect to achieve acceptable fastness (washing and rubbing) and handle although, the concentration of binder for ink formulation is limited with viscosity profiles of the print head technology. One of the great challenge of pigmented textile inkjet ink formulation is the rheological property (viscosity), surface tension and mass density of the ink that was defined by the inkjet print head technology (Fang *et al.*, 2007; Hees *et* al., 2002; Zhang and Fang, 2009). The commercial inks for inkjet printing are now available with up to 6 to 12 colorants to achieve the required color gamut. The six colors ink set such as CMYKLtCLtM or CMYKOG which has been used by many textile printer manufacturers, for example Mimaki and Roland, from where C for cyan, M for magenta, Y for yellow, K for black, LtC for light cyan, LtM for light magenta, O for orange and G for green colors have produced remarkable printing quality.

Throughout the history, silk has maintained a position of great prestige and is considered a luxury fiber. It is called the “queen of fabric”. Silk is one of the oldest textile fibers known to man. Silk is yet another word for elegance, and silk garments are prized for their versatility, wear ability and comfort. Silk is the strongest natural fiber. Silk is a fine continuous monofilament fiber of high luster and strength and highly valued as a prestige fiber. A steel filament of the same diameter as silk will break before a filament of silk. Silk absorbs moisture, which makes it cool in the summer and warm in the winter. Because of its high absorbency, it is easily dyed in many deep colors. Silk retains its shape, drapes well, caresses the figure, and shimmers with a luster at its own. Silk may yellow and fade with the use of a high iron setting. Press cloths and a steam iron are recommended. Silk is also weakened by sunlight and perspiration.

The pretreatment process is necessary for the inkjet textile printing because the fabric is porous, soft and pliable; thus, the fabric needs to be pretreated. The pretreatment limits the excess spreading of inks. The chemical on the fabric helps smoothness on the fabric surface. The ink absorption is more uniform. Moreover, the functional groups of the pretreated compounds are expected to adsorb additional ink, resulting in a better fixation of ink on the fabric. The pre-treating solutions contain many functional groups to fix the ink molecules on the surface of fabric; thus, the ink penetration speed becomes slow and gives the higher color strength. Amino compound are used to pre-treat the silk fabric because this chemical is compatible with silk fibers in which amino acid was observed. Print quality in inkjet printing is strongly dependent on the interactions between the ink and the media. Print quality of the fibrous structure of textiles requires further research; a thorough understanding of ink-fabric interactions and their effects on print quality remains a widely open field for both academic and industrial research. Hydrophilic coated and laminated fabrics transmit water vapor selectively by a molecular process, i.e., by absorption, diffusion, and desorption through the solid polymer layer. Such a polymer film or coating shows no evidence of voids or microporous structure, and thus is not susceptible to surface contamination by dirt, dust, etc. The pretreatment reagents comprising serine, glycine, aspartic acid, sericin, chitosan, and a commercial pretreatment reagent call Sanfix 555 (Leelajariyakul *et al*., 2008; Phattanarudee *et al*., 2009) have been experimented. The pretreatments containing the amino compounds improved hydrophilicity of the silk fabric with the exception of chitosan. The color gamut of the printed silk with surface-modified pigmented ink from sericin, chitosan, and sanfix 555 pretreatments was wider than that from amino acid pretreatments. The amino compound can improve the color strength of the printed fabric from the in the molecular or chemical bonding interaction between anionic pigment surface (the sulphonate group) and the cationic components (the protonated amino group to become ($-NH_3^+$) to give ionic bond. However, the bending stiffness of the silk fabrics after chitosan pretreatment is significantly higher than those with other pretreatments.

Chitosan is the second most abundant polysaccharide in nature and it is environmentally friendly, i.e., biocompatibility, biodegradability and non-toxicity. It has been shown to be useful in many different applications; one of them is as a natural antimicrobial agent. Chitosan has advantages over other type of disinfectants because of its higher antibacterial activity, a broader spectrum of activity, a high killing rate and a lower toxicity towards mammalian cells (Shahidi *et al*., 1999). Chitosan is produced commercially by deacetylation of chitin (can be produced from chitin also), The amino group in chitosan has a pKa value of ~6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependence on pH and the %degree of deacetylation (%DA)-value. The carboxyl and amino groups of amino acids are ionized in solution at neutral physiological pH, with the carboxyl group bearing a negative charge ($-COO^-$) and the amino group a positive charge ($-NH_3^+$). A cationic of amino acid improves the ink adsorption containing the negative charge.

Over the past 20 years, chitosan has found applications, as antimicrobial agent, in many fields like pharmaceutical, food, agriculture and textiles. Chitosan has also been evaluated for numerous textile applications. The application of chitosan in textiles includes production of man-made fibres, cotton dyeing, silk dyeing, wool dyeing, polypropylene dyeing, durable press finishing, wool finishing, antimicrobial finishing, antistatic finishing, de-odorising finishing, sizing, textile printing and recently, textile inkjet printing. Despite all these advantages, chitosan lacks good solubility at pH above 6.5; its applications in a commercial application are not as wide as it should be. In comparison with three types of chitosan at the same deacetylation degree and different molecular weights used by Phattanarudee *et al.* (2009), the difficulties encountered were the solubility of chitosan which also depends greatly on molecular and its loading. Therefore, it is very necessary to prepare functional chitosan derivative in an attempt to increase its solubility in water and thereby to broaden its applications.

Due to the loss of its cationic nature at pH above 6.5, chitosan exhibits poor solubility. Hence, its applicability of a cationic of amino acid is limited to acidic conditions. By utilizing the reactivity of the primary amino group and the primary and secondary hydroxyl groups of chitosan, various derivatives of chitosan were prepared with goals to dissolve it in water over the entire pH range and to broaden its applicability. *N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan chloride (HTACC) can be conveniently prepared by chemical reaction of chitosan and glycidy-trimethyl-ammonium chloride (Li *et al*., 2004) and is a water soluble chitosan derivative in all pH ranges and shows the excellent antimicrobial activity. HTACC is expected to increase the color yield of cotton dyed with direct and reactive dyes without the addition salt.

1.2 Objectives of research work

The main objectives of the research are to:

1.2.1 To prepare and investigation of the six colored inkjet ink properties and the relation of the ink rheological profiles and printability.

1.2.2 To evaluate the effect of pretreatment reagents, chitosan, glycin, and HTACC on the quality of silk fabrics printed by inkjet printing.

1.2.3 To study the effect of pretreatment reagents on physical and chemical properties of printed silk fabrics.

1.2.4 To investigate the effect of pretreated reagents on color appearance, the fabric performance and usage of the printed silk fabric.

1.2.5 To elucidate the interaction between the pretreatment reagents and the inks.

1.3 Expected Benefit Obtainable from the Development of This Research

1.3.1 A set of the pigmented inkjet inks developed for silk printing.

1.3.2 Enhancement of the understanding of the ink interaction and the pretreatment reagents.

1.4 Scope of the research

This research involves the six color inks preparation and characterization of ink rheology profile to printability based on the various concentrations of viscosity modifier (diethylene glycol and glycerol) in the ink formulations. The prepared inks were examined for viscosity, surface tension, pH, particle size and its distribution, zeta-potential. The print qualities of the pretreated silk by the pretreated solutions of chitosan, chitosan/glycine mixture, and HTACC were investigated. The pretreated fabrics were also studied for stiffness. After printing, the untreated and the treated fabrics were studied for color gamut and gamut volume, color saturation, light fastness and wash fastness. Furthermore, the interaction between the diluted ink and pretreatment reagents was elucidated by UV-vis spectrophotometry.

1.5 Content of the research work

This thesis consists of 5 chapters including introduction, theoretical background and literature review, experimental, results and discussions, and conclusions and suggestions. Chapter 1 describes the introduction of the thesis, scientist rationale, scope of the work and expected benefits obtained from the thesis. Chapter 2 displays a brief description of inkjet textile printing, the ink system, the dispersion technologies in pigmented inkjet inks, and the pigmented ink formulation. A brief explanation of pretreatment, chitosan and HTACC and a brief discussion of textile printing, silk fiber and properties, textile testing are included. Literature review of some of the related research work is described. In Chapter 3, the details about the materials, apparatus and procedure of this research are explained. Chapter 4 presents the results and discussion of the ink properties, rheological property of the inks, jettability and printability, the effect of pretreatments on color properties, physical properties and fastness properties of the printed fabrics, the interactions between the pretreatment solution and pigment by spectroscopic methods. Chapter 5 concludes the outcome of the research and some suggestions for further work.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical background

The concept of printing textiles by inkjet technology is fairly new. Inkjet printing processes have been used in textile industry for some years and have started to claim growing share in textile print production worldwide bringing considerable savings. The textile printing by inkjet printing has been predicted to become popular in the near future because it offers a simple process and inevitable benefits. If, comparing with conventional printing processes, inkjet printing has significant advantages. Such advantages include the following (Daplyn and Lin, 2003; Kiatkamjornwong *et al*., 2005)

- Inkjet printing process does not require the use of printing plates and therefore, no lead time for plate making/plate mounting operation is needed.
- As no printing plate making is required, there is no need for usually time-consuming color separation process.
- As inkjet printing technology allows direct printing from graphic design software (via microcomputer) to printer, there is no need for the “traditional proofing”. Moreover, any modification made to the image can be incorporated into the final print conveniently.
- Inkjet printers are usually much less costly compared to the conventional printing presses.

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

- Inkjet printing allows very high degree of reproducibility. There is usually very little variation in image quality of prints from one batch to another.
- Inkjet printing also allows very high degree of printing stability. In other word, there is virtually no variation of image quality of prints from the beginning to the end of a print run. As such, the cost caused by starting, stopping and re-starting print runs can be eliminated.
- As ink-droplets are created only when required (in drop-on-demand inkjet printing), there is very low ink wastage associated with inkjet printing. Even continuous inkjet printing allows low ink wastage as ink droplets not reaching the substrate are collected, replenished and reused.
- As the whole printing operation is relatively simple, inkjet printers do not usually required any monitoring, provided that adequate fault correction mechanism is incorporated, which is the case for most wide format inkjet printers.

2.1.1 Issues in textile inkjet printing

Traditionally, textile printing inks are prepared in form of paste that is suitable to use with rotary or silk screens and can be formulated over broad range of viscosities according to the type of screen, image quality and printing speed. Since it is a contact printing method, print paste is forced through to screen meshes to the substrate giving direct control over the ink penetration on the substrate and through-prints can be achieved for fabrics with low densities. It is also a general practice to prepare required quantities of fresh inks just before the production runs or sample strike off so storage stability of a week would be sufficient in most cases. If the colorant or additives are sensitive then it can be prepare and applied immediately. In Contrast, physical and chemical properties of inks for inkjet should be optimized for specified inkjet technology and printheads. The rheology of ink is an extremely important parameter in the design of ink because this aids droplet formation through the nozzle in a controlled manner for any given inkjet technology.

There are two main technologies available

- Continues inkjet (CIJ)
- Drop on demand (DOD)

For both technologies there are different requirements for ink formulations. Continuous inkjet method is more suitable when a low resolution image satisfies the quality requirements. Whereas, DOD is the only inkjet method that is currently able to produce very high resolution images. Valve jet is another non impact method that produces very large drop size and suitable to print substrate where deep ink impregnation is more desirable then print quality. Zimmer has been offering printers based on valve jet technology for printing high pile substrate such as carpets and door mats. Required physical characteristics for continuous, DOD and valve jet are given in Table 2.1. Industrial DOD heads generally require higher viscosity inks, for example 8 to 20 cps. Xaar and spectra printhead are typical example of industrial print heads. Whereas, light duty print heads require low viscosity, for example 3-8 cps. Epson print heads are typical example for such printhead (Ali, 2008). For the commercial inkjet textile printer, DOD printhead show the potential over CIJ printhead.

Table 2.1: Working window for deferent Inkjet technologies

Ink Properties	CIJ	DOD		Valve Jet
		Piezoelectric	Thermal	
Viscosity (cP)	~1.5	5-20	~1.5	<2
Surface Tension (dynes/cm)	25-40	>32	>35	>24
Max particle size (microns)	1	1	0.2	5
Conductivity	Yes	No	No	No

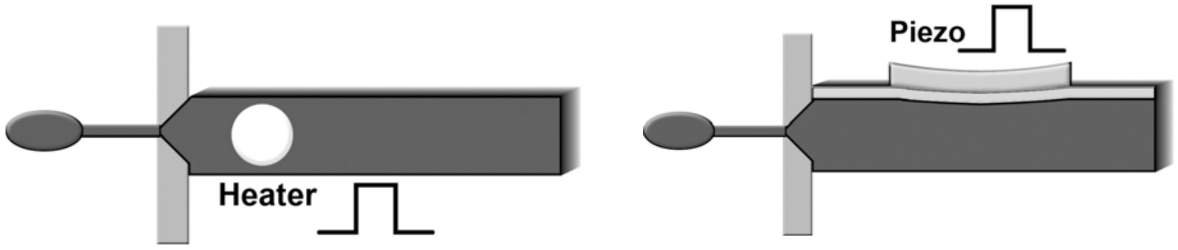
Drop-on-Demand inkjet (DOD) is a broad classification of inkjet technology where drops are ejected only when required. In general, the drops are formed by the creation of a pressure pulse. The particular method used to generate this pressure pulse is what defines the primary subcategories within DOD. The primary subcategories are thermal, piezoelectric, and electrostatic. Sometimes, an additional category is discussed (MEMS), but MEMS drop-on-demand print heads are invariably still based on either piezoelectric or thermal inkjet technology.

Thermal inkjet is the technology most used in consumer desktop printers and is making inroads in industry. In this technology, drops are formed by rapidly heating a resistive element in a small chamber containing the ink (Figure 2.1(a)). The temperature of the resistive element rises to 350–400 °C, causing a thin film of ink above the heater to vaporize. This vaporization rapidly creates a bubble, causing a pressure pulse that forces a drop of ink through the nozzle. Ejection of the drop then leaves a void in the chamber that is subsequently filled by replacement fluid in preparation for creation of the next drop.

The advantages of thermal inkjet include the potential for very small drop sizes and high nozzle density, which leads to compact devices and lower print head and product costs. Disadvantages are primarily related to limitations of the fluids that can be used. Not only does the fluid have to be something that can be vaporized (implying most generally an aqueous solution), but it must withstand the effects of ultra high local temperatures. With a poorly designed fluid, these high temperatures can cause a hard coating to form on the resistive element, which then reduces its efficiency and, ultimately, the life of the print head. The high temperature can also cause problems if, for example, the functionality of the fluid is damaged due to the high temperature (as is the case with certain delicate fluids and polymers).

Piezoelectric inkjet is currently the technology of choice for most emerging industrial applications. In this technology, a piezoelectric crystal (commonly lead zirconium titanate) undergoes distortion when an electric field is applied, and this distortion is used to mechanically create a pressure pulse that causes a drop to be ejected from the nozzle (Figure 2.1(b)). There are many variations of piezoelectric inkjet architectures including tube, edge, face, moving wall, and piston.

The advantages of piezo inkjet technology include the highest level of ink development freedom of any inkjet technology, and long head life. Disadvantages include higher cost for print heads and associated hardware, limiting cost effective integration in low-end products (Hudd, 2009).



(a) (b)

Figure 2.1: Drop-on-Demand inkjet technologies (a) Thermal printhead, (b) Piezoelectric printhead

Of all the types of inkjet printheads, thermal jets are undoubtedly the most successful. Besides their ubiquity in office and wide-format markets, they have been used to produce fabric proofs and limited production runs. The application of thermal ink jets to digital textile printing benefits from the economy of scale and design simplicity. However, a major failure mode for thermal jets is kogation where reactive ingredients or impurities in the ink cook onto the heat resistor. These deposits build up over time causing jet failure. The piezoelectric provide an advantage that relative to thermal inkjet ink latitude. Because the vapor pressure of water at the nucleation temperature is abnormally high, water is a very good “propellant”. Though examples of drop ejection of non-aqueous fluids from thermal inkjet devices have been disclosed, all commercially available thermal print heads fire aqueous inks. Piezoelectric heads, on the other hand, can easily fire any fluid, within a given range of operating viscosity and surface tension. For this reason, most industrial non-conventional applications of inkjet use piezoelectric technology (Freire, 2006).

2.2 Inks and processes for digital printing of textile

Inkjet printers used for printing on paper have been successfully adopted for printing onto textiles. This is not the case with the inks. Textile printing is different from paper printing. A conventional textile printer requires 8-12 basic colorants and up to 25 supplementary colorants to meet the wider color space and fastness requirements. For decades, paper printing has been based on four process colors (C; cyan, M; magenta, Y; yellow and K; black). Commercial inks for fabric inkjet printing are now available with up to 8 to 12 colorants to achieve the required color gamut. Printed textiles require aesthetic properties such as handle and feel. This is not the case with paper printing. In addition, an important difference is the high fastness to wash, rubbing and light required by the textile substrates. The number of inks available commercially, which can be used for digital textile printing is limited. There is a lack of suitable processes for the fixation of pigmented inks onto textile substrates. Hence, improved ink formulations with required rheology and fixation properties and processes for their fixation are needed to be developed for textile applications.

Significant research activities have been seen over past decade in the development of inks for textile inkjet printing. The inks must meet stringent physical and chemical requirements and must therefore be carefully formulated. Depending upon the type of colorants used, inks for digital printing of textiles can be broadly classified as dye based inks and pigment based inks. For textile inkjet printing, the first developments took place with water soluble dyes such as reactive and acid dyes. This was due to the relative ease in their development and availability of dye purification and filtration equipments with colorant manufacturers. However, reactive and acid dyes usually require post printing process steps to fix the dye on to the textile and to remove the unbound color. Inks based on dispersion technologies such as pigment and disperse dye inks are recent developments (Hauser and Buehler, 1998).

2.2.1 Dye-based inks

Dye based inks using reactive, disperse and acid dyes have been developed and are now available commercially. Despite high color quality, dye based inks suffer from some serious disadvantages. They are substrate dependent, requiring different sets of inks for different textile fibers. This substrate dependence requires frequent changes in color-ways and/or fabrics leading to costly machine downtime. Inkjet printing of blends (19% of total fabric market) is not yet possible with dye based inks.

Dye based inks require costly pre-treatments and post-treatments such as steaming and washing for their fixation. This may also add to the effluent waste and may require further expensive effluent treatment.

Reactive dyes are applied to cellulosic fibers from aqueous medium in the presence of an alkali to promote the fixation reaction of dye to fiber through covalent bond formation. The reactive dyes employed for inkjet inks must be of high purity grade. The chosen dyes should have high color strength, possess large extinction coefficients and show adequate solubility to enable water based inks of high concentration to be prepared. It is possible that the ink will fail to deliver good visual strength if it is washed away during post processing. Prints with a low degree of fixation will also result in poor crock fastness and ultimately will be rejected. Alkali may also be applied after printing but this will require a controlled process to avoid any bleeding and loss of image definition (Ali, 2008).

Acid dyes inkjet inks have strong affinity toward protein fibers and are especially useful in printing synthetic polyamide, silk and wool. Inkjet ink formulations with acid dyes are somewhat more straightforward then any other class of colorant. Acid dyes are substantially water soluble and can be formulated to concentration up to 10% w w^{-1} with ease; however, this will depend on the selection of dye that has good solubility product. Typically, humectants, co-solvents and other additive are added to the formulation to improve jetting performance. After printing fabric is steamed and subsequently washed to wash-off any unfixed or loosely fixed dye, rendering fabric excellent fastness to wash and rub (Ali, 2008).

Disperse dyes inkjet inks have an affinity for hydrophobic fibers; these are usually applied from fine aqueous dispersions, principally to polyester, but also to cellulose acetate and polyamides. Currently, disperse dyes are marketed in two typical type of inkjet process have been offered, both are suitable for printing on polyester; transfer printing and direct printing onto fabric. Disperse dyes are widely employed for transfer printing due to their ability to sublime and transfer to the surface that has more affinity for it. In this method of printing an image is printed onto an intermediate transfer sheet, and then image is transferred to another surface by applying heat to the intermediate sheet. An ink that uses such dyes is characterized as heat sensitive, dye diffusion or sublime inks. Direct printing on substrate is more desirable method for creating image on textile by inkjet. It eliminates the use of intermediate substrate that can be very costly for long production run. For both type of formulation it is important to select the dyes that are suitable for long term storage and resist the agglomeration (Ali, 2008).

2.2.2 Pigment-based inks

Different textile substrates have different colorant requirements due to the difference in the mode of color-substrate interaction. This is shown in Table 2.2. A single set of inks which can be used to print most of the textile substrates, especially blend fabrics, will have benefits such as lower production costs, better productivity, improved color prediction and reproducibility and low effluent. One approach that has been undertaken by researchers was to develop a universal set of dye based inks which can enable inkjet printing on chemically diverse textile materials. Another approach has been to develop pigment based inks as pigments are substrate independent and can be applied on most textile materials. Pigments appear to be the most suitable candidates to achieve the above mentioned benefits. With increasing environmental pressure on dye based colorant systems and with improvements in pigment applications, it is expected that there will be a rapid growth in pigment based colorant systems.

Table 2.2: Selection of colorant for textile substrates and their mode of interaction with fibers

Colorant	Fiber	Pre-treatment	Post-treatment	Color
Pigment	All fibers	Binder/Not required	Dry heat	No interaction – complex surface polymer bonding mechanism
Reactive dye	Cotton, Silk and Wool	Alkali	Steam and wash	Covalent fiber bonding
Disperse dye	Polyester	Thickener	High-temperature steam and Wash	Hydrophobic- Solid State Mechanism
Acid dye	Silk, Wool and Nylon	Acid donor	Steam and wash	Electrostatic and Hydrogen bonding with fiber

2.3 Pigmented inkjet ink formulation

Pigment inkjet ink composition for textiles is one of the most challenging areas for an inkjet ink formulator. Pigments do not have any affinity towards substrate and require a binding mechanism to bind the pigment to the substrate in order to achieve required technical properties such as wash fastness and crock fastness. Conventionally, no fabric pretreatment is necessary for patterns with full ground coverage and no further post washing is required, generally after printing subsequent heat treatment is critical for drying and to achieve a high degree of fixation. Pigments can be applied on any fabric and therefore, is suitable for printing fabric blends. However, in addition to meet required fastness properties, there are two major issues that are crucial for success of inkjet ink formulation that is suitable for application on textiles. A pigment based inkjet ink should have low viscosity stable pigment dispersion and a binder system that is stable and chemistry is suitable for given substrate (Ali, 2008).

2.3.1 Pigment dispersion

Particle sizes in the range of 20 to 200 nm are preferred for inkjet inks for reliable performance through nozzle. Pigment dispersion is probably the most important ingredient, and the rest of the ingredients in the inkjet textile ink formulation either serve to position the pigment particles to the right place on the substrate through a given print head in order to generate beautiful images, or to bind the pigment particles to the substrate so that the image can last a long time with respect to different types of resistance such wash and rub.

The pigment and the set of pigments selected determine the color gamut, the color density, the brightness and the UV resistance of the individual ink and the ink set. These properties are not unique to inkjet and are similar to conventional printing inks, so they will not be discussed further here.

The unique properties which are important in pigment dispersion selection for inkjet inks are stability in terms of the formulated inks, particle size and size distribution, viscosity, surface tension and pigment solids.

The stability of the pigment dispersion with respect to a variety of formulation ingredients, solvents, low surface tension surfactants and polymeric binders is very important because if the ink is not stable, the other properties become meaningless.

The particle size and size distribution, on the one hand, affects the image quality, especially color density, in terms of ink holdout and the effective use of each pigment particle for light absorption. Bigger particles are probably good for holdout, leading to higher color density, while smaller particles are probably better in terms of the effective use of each pigment particle for light absorption. When there are competing factors, optimum particle size exists for a given substrate. Although it is not relevant for textile printing, smaller particles tend to yield better gloss for glossy substrates. On the other hand, the particle size and size distribution have a lot to do with settling of the pigment in the ink, colloidal stability, and clogging of the nozzle and therefore the jetting reliability. If the particle size is too big or the distribution is too broad, it will have an adverse effect in start-up and reliable jetting due to settling and clogging. Too many small particles (below 0.05 microns) can also have adverse effects in terms of stability and jetting reliability, because smaller particles have higher surface area to volume ratio, and therefore higher dispersant demand, and at the same time the surface area per particle is smaller, therefore if the zeta potential or charge density is the same, smaller particles have less total charge per particle and the repulsive barrier is lower than that of big particles and in turn may be less stable. Small particles may also provide high probability for clogging due to particle congestion.

Typically pigment dispersions with low viscosity and high surface tension are more preferable. Low viscosity in pigment dispersion has more rooms for other ingredients, such as, polymeric binders and greater ease in maintaining overall viscosity of the final inks. If the surface tension of pigment dispersions is high, there are always ways to lower the surface tension of water-based systems by adding surfactants and organic solvents. On the other hand, if it is low, it will put a limit on the surface tension of the final ink.

Finally the solid level is a very important concern. Typically higher is better, because it leaves more room and flexibility for adding other ingredients to the ink formulation without compromising the pigment solids loading in the final ink: 10% is at the lower end of most pigment dispersion suppliers, 30 to 40% is at the high end and 20% is typical.

There are two major types of pigment dispersion, polymeric dispersant stabilized dispersions and self-dispersed dispersions. The type is not important as long as they provide the right properties outlined above. The self-dispersed type tends to be more stable with respect to solvent selection, while polymeric dispersant stabilized dispersions tend to have better permanence, such smear resistance benefited from the polymeric dispersant. Some of the key pigment dispersion suppliers are Rohm and Haas, Lanxess, Clariant, and Cabot. This is by no means a complete list (Fu, 2006).

Cabot Corporation has developed a proprietary technology to modify pigment surfaces by attaching various ionic functional groups such as sulphonate ($-SO_3^-$), carboxylate ($-COO^-$) or ($-R_4N^+$) to impart electrostatic stabilization and desired physicochemical properties to aqueous pigment dispersions. This technology eliminated the need for conventional dispersants. The technology was first utilized for surface modification of carbon black pigments which resulted in commercial products such as CAB-O-JET® 200 and CAB-O-JET® 300 black pigment dispersions. Surface treatment of pigment with its own derivatives has been very successful in ink applications.

2.3.2 Binder selection

While pigment is an important ingredient to provide the image, the binder is another key ingredient to maintain the permanence of the image with respect to washing and rubbing in the case of textile printing. Incorporating polymeric binders in inkjet inks is difficult in general. It is even more difficult for textiles because it requires not only high levels but also low T_g for good hand and feel. The following example will help to illuminate the difficulty. Most people have the experience of using Elmer's^{TM} glue, which is a soft and low T_g polymeric binder. How often we need to cut the tip in order to remedy the clogging to use it again and it has only one big nozzle. As stated in Section 13.2, the specific challenges are

- To keep the soft and low T_g binder from clogging the nozzles.
- To maintain the low viscosity and formulation space for jetting reliability and at the same time to load enough binder for wash and crock resistance, especially for low viscosity print heads.
- To achieve adequate (1 to 2 years) stability and shelf lifetime with regard to sedimentation, homo- and hetero-coagulation and phase separation.

To overcome these difficulties, leading companies in this field such as DuPont, Rohm and Haas, and BASF have developed proprietary polymer and formulation technology, which may include ink medium soluble, but water insoluble random or block copolymers with or without cross-linking functionality, dispersants, binders and other property combined cross-linkable multi-functional agents and protected cross-linkable latex polymers. For example, in the case of protected latex polymers, the soft and sticky binders are protected by a thin layer of shell, like an egg; it is not sticky in the ink before the protective shell is broken, and becomes sticky glue only when the protective shell is broken in the later curing stage (Fu, 2006).

2.3.3 Co-solvent and humectants

Pigment is the important ingredient to provide the image, and binder is the key ingredient to maintain the permanence of the image. But both need a carrier to deliver them to the substrate. In the case of water-based pigment textile inks, the carrier is mainly water (50 to 80%) mixed with water-soluble organic compounds, which are called co-solvents and humectants based on their functions. Co-solvents are organic compounds such as 2-pyrrolidone and propandiols, which help water to incorporate other ingredients into the system better. For example, 2-pyrrolidone may help water to dissolve some surfactants better and to make some polymer more soluble. Humectants are hydroscopic organic compounds such as polyethylene or propylene glycols with or without alkyd ether capping groups on one or both ends, glycerol, sorbitols, etc. Hydroscopic means capable of “pulling” water vapor form the air back to the liquid phase, which slows down or completely stops the drying of the ink when humectants reach a certain concentration under a given humidity and temperature condition. This is very important to prevent the ink from drying on the nozzle and from clogging the nozzle both during the printing and in the idling state. A single ingredient or compound, for example, 2-pyrrolidone, often serves as both co-solvent and humectants (Fu, 2006).

2.3.4 Surfactant selection

Surfactants are another key ingredient in terms of delivering the pigment and the binder from the ink to the substrate through the print head. High HLB (hydrophilic and lipophilic balance) surfactants are used typically for aiding the colloidal stability of the systems, and low HLB surfactants are used to lower the surface tension, so the ink can wet the nozzle capillary to establish and maintain the meniscus at the nozzle tip. The importance of maintaining the meniscus at the nozzle tip in the steady state and in the dynamic state during jetting cannot be overemphasized because it is so critical for start-up, reducing latency (defined as number of firings needed before the ink establishes the first stable drop of jetting), increasing the elapsed time between jetting without refreshing and ultimately long-term reliable continuous printing. For some print heads, reliable jetting or printing can be achieved even when the nozzle plate is wetted. This low HLB surfactant is also a major factor which determines the interaction between the ink and the substrate and therefore controls or affects wetting, bleeding, dot-gain, dot-quality and ultimately the image quality. Surfactants affect these properties through a physical parameter, namely surface tension (both static and dynamic). The most popular surfactants used for the purpose are relatively short-chain ethylene glycol nonionic surfactants such as the Air Products Surfynol^{TM} line of products like Surfynol^{TM} 465. Anionic surfactants such as Aerosol^{TM} OT are also used (Fu, 2006).

2.3.5 Rheology modifier selection

While a surfactant is the key ingredient used to control surface tension, a rheology modifier is the ingredient used to control the viscosity of the ink, or more precisely the rheology profile of the ink, which includes the yield stress and the viscosity at different shear modes and rates. The yield stress along with the meniscus has a major effect on the latency. The viscosity at low shear rate along with the surface tension determines the fill-up and the priming of the nozzles to establish the initial meniscus and the ready-to-jet condition. The viscosity at high shear rate, up to 1 million reciprocal seconds, is probably more relevant to fluid dynamics and the drop formation at the nozzle tip and thereafter. The viscosity and the mass density of the ink affect the oscillation and thee damping of the ink chamber and therefore the jetting. Water-soluble polymers such as polyethylene glycols (PEG) with molecular weight ranging from several hundreds up to hundreds of thousands could be rheology modifiers. The rheology modifiers along with the co-solvents, humectants ant the total solids in the case of pigmented inks with or without binders together determine the viscosity. Ideally the rheology modifier is selected with the following considerations in mind.

1. It should not strongly associate with multiple pigment and/or latex particles, causing coagulation and precipitation, unless the coagulation is well controlled.
2. Associative thickening should be avoided since even loose association through the rheology modifier molecule may increase yield stress and cause phase separation.
3. Depletion flocculation should also be avoided because it may cause phase separation and non-uniform color density in the print.

In case 2, the rheology modifier molecule will be more likely in the particle rich phase, while in case 3 the opposite applies in that the rheology modifier molecule will be more likely in the particle deficient phase.

In general, the viscosity of inkjet is low, below 20 cps. Even at this low viscosity, the rheology profile cannot be overlooked and it may be important that it is controlled intentionally with relatively high molecular weight water-soluble polymers.

2.4 Properties of inkjet inks

Inks for digital printing require a special control on parameters like viscosity, conductivity, surface tension, chemical stability, physical stability, pH and foam-free properties. Without the color chemistry base and in-formulation technology, the particle size distribution required for such inks is not possible. A further requirement is an ideal combination of ink and substrate (Diamond and Weiss, 2002).

2.4.1 Viscosity

The viscosity is an important property of the inkjet ink. The low viscosity is important not only for transport of the ink through the nozzle, but also for drop formation integrity. The viscosity range of inkjet inks is around 6–20 mPa s. A humectant such as glycol is the primary constituent that affects this parameter. In an inkjet system, the amount of humectant will affect the degree of crusting caused by dye precipitation. Too much humectant would greatly hinder the flow of ink through a 10 μm nozzle. The drop-on-demand printers require a more viscous ink. This is because, instead of high pressure, the drop-on-demand system uses an acoustic wave, usually produced by a piezoelectric transducer, to emit and propel an ink drop.

2.4.2 Specific gravity

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

2.4.3 Surface tension

Surface tension is one of the primary factors determining where the actual drop will form in continuous inkjet printers. In drop-on-demand printers, it helps to regulate control of the concave meniscus to hold ink in the system. Once the ink has been deposited onto the printing substrate, the interaction of the surface dynamics of both ink and paper plays a major role in how the final form of the dot will appear.

2.4.4 Optical density

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

2.4.5 Dielectric properties

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

2.4.6 pH

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

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

2.5 Influence of ink compositions and properties

Despite recent advances in ink chemistry and physics, one of the key challenges in ink formulation is to develop inks that are consistent. Ink formulations are maintained to keep key parameters within specifications, yet it is often noticed that there are marked differences in the jetting performance between batches or between colors of a CMYK set of apparently identical inks. As a consequence extensive and time consuming ink reformulation and validation (optimization and/or separate waveform development) needs to be carried out for each batch or between colors to achieve satisfactory jetting. This issue is further complicated when developing inks for niche applications which could contain special (i) pigments/particles with high loading concentration and density, (ii) polymers/binders of high molecular weight, (iii) carrier fluid with different physical and chemical properties. Any variations in the composition could change fluid physical properties (such as density, surface tension, viscoelasticity, speed of sound) beyond the existing printhead operating windows. The introduction of pigments to the carrier fluid produces considerable deviations from the Newtonian behavior. This is due to particle association (by chemical bonds and/or physical interaction) during flow. The size and concentration of the pigment particles affect viscosity and the likelihood of nozzle blockage. Dispersants are added to stabilize the pigments. Additives such as resins are often present to bind other components of the ink and contribute to the properties of the ink once on the substrate (e.g. gloss, resistance to heat, chemicals and water). All of these additives influence the viscosity of the fluid and also elasticity due to their polymeric nature. The fluid is subjected to high frequency pressure fluctuations in the channel during actuation and high shear at the nozzle wall. As the jet emerges from the nozzle, the viscosity and elastic stresses resist the necking motion of the liquid filament, whereas surface tension and inertia influence the resulting shape and form of the emerging drop. These opposing forces result in high extensional deformation of the jet and into a spherical drop. The optimum values of the surface tension and viscoelasticity becomes a compromise of what is required upstream (in the channel) and downstream (in-flight).

2.5.1 Surface tension

Surface tension is the driving force behind the jet pinch off and its role in inkjet ink is varied: (a) to enable proper jetting, (b) to form uniform droplets upon ejection and (c) to control spreading and contact angle of the drop on the substrate. It dictates the position of the ink meniscus within the nozzle along with drop quality in-flight. Inks with good wetting ability (low surface tension) are able to display a plug flow velocity profile through the channel and nozzle, where the velocity of the ink close to the wall of the channel is similar to that of the ink at the centre of the channel. Inks with poor wetting (high surface tension), display a more non-uniform velocity profile and the velocity of ink close to the wall are much lower than at the centre of the channel. Such non-uniformity in the velocity profile could lead to ink being left behind and influence drop and satellite formation. High surface tension requires an increase in drive voltage to jet and generate drops. In-flight, drops will be too small and may not spread enough on landing resulting in white space or under-banding and the image appearing too light. In contrast, too low surface tension may experience excessive nozzle plate wetting resulting in loss of jetting stability due to reduced ink ejection. In-flight drops may become too large, reducing resolution and on landing, droplets may spread too much causing excessive bleeding, wicking or over banding. The choice of surfactants and their concentration could have significant influence on the dynamic surface tension, jetting behavior and reliability of apparently identical inks that have similar static surface tension. If the bulk surfactant concentration is near the critical micelle concentration level, it could cause wide fluctuation in the fluid's properties and could have detrimental effect during ink jetting by either preventing or delaying the pinch off of the ligature from the nozzle and cause jet reliability issues. An ideal ink would possess a high dynamic surface tension to promote rapid meniscus recovery at high firing frequencies and a low static surface tension to achieve good substrate wetting. The static surface tension value of ink is usually dictated by the substrate wetting behavior and typically set between 20-40 mN m^{-1} for DOD fluids by adding surfactants and dispersants to some extent (Tuladhar *et al*., 2009).

2.5.2 Viscoelasticity

In the case of DOD, the acoustic waves which cause a droplet to be ejected are affected by ink viscosity. The acoustic waves will be dampened more with increased viscosity; therefore, the drive energy has to be increased in order to jet the fluid. In the channel, if the viscosity is too high, the ink may not flow through the printhead and too low viscosity may cause the ink to leak out of printhead. Once the jet detaches from the nozzle, high viscosity is preferable to reduce satellite formation in-flight and to avoid drop splattering or bouncing during landing. The ink viscosity is mainly dictated by the choice of carrier fluid and pigment loading. The operating temperature is varied to bring the fluid viscosity down to optimum operating window of 5-40 mPa s for most DOD printhead. It is well known that addition of a small amount of polymer significantly influences the jetting behavior due to subtle changes in their elasticity. High elasticity influences the jetting velocity, forms a thin ligature which breaks up at multiple points resulting in many satellites (or mist). In extreme cases, the jet does not detach from the nozzle and is either pulled back into the nozzle or floods the nozzle. Low or no elasticity results in satellite formation at high jetting speed. The presence of some optimum elasticity is required whereby the liquid filament connecting the main drop is instantly pulled into the main droplet after breaking from the nozzle giving a satellite free drop (Tuladhar *et al*., 2009).

2.6 Silk

Silk is a natural protein fiber excreted by the moth larva Bombyx mori, better known as the common silkworm. Silk is a fine continuous monofilament fiber of high luster and strength and is highly valued as a prestige fiber. Because of its high cost, it finds very 1imited use in textiles. A minor amount of wild tussah silk is produced for specialty items. Attempts have been made to commercialize silk from spiders over the years, but all ventures have met with failure. Domestic and wild silks are essentially uncrosslinked and relatively simple in amino acid composition compared to the keratin fibers. The properties for silk 1isted here are for silk formed by Bombyx mori moth larvae.

Liquid silk protein is extruded from two glands in the head of the silk worm. The fibers emerge from a common exit tube or spinneret and harden into a single strand by a protein gum called sericin. The completed silk cocoons are soaked in hot water to loosen the sericin, and the silk filaments are unwound. After unwinding, the silk filaments are washed in warm detergent solutions to remove the sericin. The fibroin silk fibers are simpler in structure than keratin and are composed predominantly of glycine, alanine, tyrosine, and serine. The silk is formed by the polymerization of amino acids with peptide link (-CO-NH-) to give long-chain molecules as shown in Figure 2.2. The average range of composition for silk is given in Table 2.3.

With no cystine present in the fibroin protein, little crosslinking is observed between protein chains. The degree of polymerization of silk fibroin is uncertain, with DPs of 300 to 3000+ having been measured in different solvents. In the absence of crosslinks and with limited bulky side chains present in the amino acids, fibroin molecules align themselves parallel to each other and hydrogen bond to form a highly crystal 1ine and oriented "pleated-sheet" or "beta" structure. Silk fibers are smoothing surfaced and translucent with some irregularity in diameter along the fiber. The fibers are basically triangular in cross section with rounded corners (Needles, 1986).

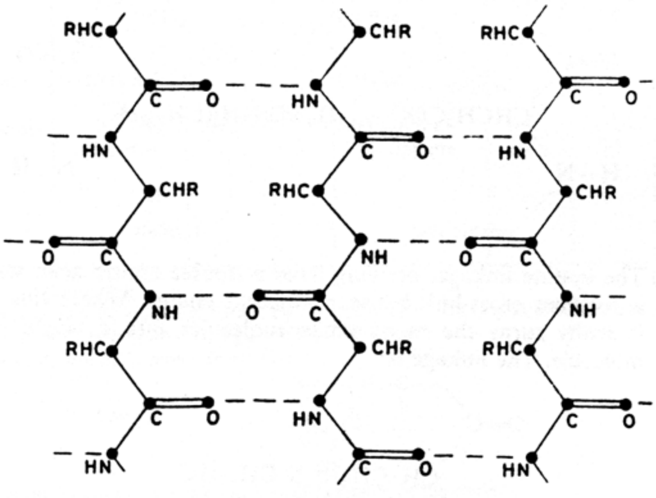


Figure 2.2: Structure of silk molecule

2.6.1 Physical properties of silk

Silk fibers are strong with moderate degrees of recovery from deformation. Silk has a dry tenacity of 3-6 g/d (27-54 g/tex) and a wet tenacity of 2.5-5 g/d (23-45 g/tex). Silk exhibits a recovery of 90% from 2% elongation and of 30%-35% from

20% elongation. Silk fibers are moderately stiff and exhibit good to excellent resiliency and recovery from deformation, depending on temperature and humidity conditions. Silk has a specific gravity of 1.25-1.30 and a moisture regain of 11% under standard conditions. Silk is soluble in hydrogen bond breaking solvents such as aqueous lithium bromide, phosphoric acid, and cuprammonium solutions. It exhibits good heat insulating properties and is little affected by heat up to 150°C. Silk has moderate electrical resistivity and tends to build up static charges.

Table 2.3: Amino Acid Contents in Fibroin

Amino Acid	Content in Fibroin (g/100 g Fibroin)	Amino Acid	Content in Fibroin (g/100 g Fibroin)
Glycine	36-43	Threonine	1-2
Alanine	29-35	Cystine	0
Tyrosine	10-13	Methionine	0
Serine	13-17	Arginine	0-2
Valine	2-4	Histidine	0-1
Leucine	0-1	Lysine	0-1
Proline	0-1	Aspartic acid	1-3
Phenylalanine	1-2	Glutamic acid	1-2
Tryptophan	0-1		

2.6.2 Chemical properties

Silk is slowly attacked by acids but is damaged readily by basic solutions. Strong oxidizing agents such as hypochlorite rapidly discolor and dissolve silk, whereas reducing agents have little effect except under extreme conditions. Silk is resistant to attack by biological agents but yellows and loses strength rapidly in sunlight. Silk is often weighted with tin and other metal salts. These salts make silk even more sensitive to 1ight-induced oxidative attack. Silk undergoes charring and oxidative decomposition when heated above 175°C in air over a prolonged period of time.

2.6.3 End-use properties

Silk possesses a combined set of aesthetic properties that make it useful for high-fashion luxury textile goods. Silk has a high luster and is translucent. Silk fabrics have pleasing appearance and drapability, and a characteristically pleasing crisp hand. Silk is highly moisture absorbent and has good to excellent resistance to wrinkling. It is a moderately strong fiber with moderate recovery properties. It exhibits fair abrasion resistance and good resistance to pilling. Silk is sensitive to chlorine bleaches and to alkalies and is easily damaged by sunlight. The fiber may be dyed with a wide variety of dyes to give dyed fibers with high colorfastness. Silk may be laundered under mild, nonalkaline conditions and dry cleans readily. Because of its high affinity for water, it dries slowly but may be dried or ironed safely up to 150°C. Silk burns slowly and self-extinguishes when removed from a flame. Silk is used extensively in luxury fabrics and apparel and home furnishings, and in accessories such as scarf.

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

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

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

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

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

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

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

$$-H, \quad -CH_3, \quad -CH_2OH, \quad -CH_2\,C_6H_4\,OH$$

The links between molecules will therefore be mostly main-chain hydrogen bond, with a few hydrogen bonds and salt linkages between side chains.

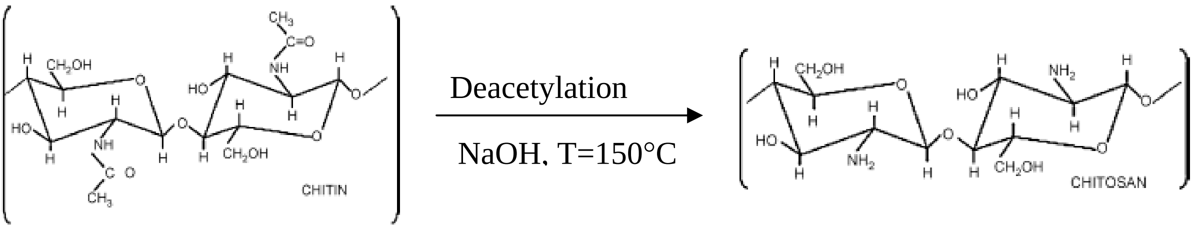
Silk is essentially used in very expensive luxury goods. It has been able to withstand competition from synthetic fibers in many high-quality textile applications because of its excellent dyeing characteristics, high moisture and absorbency, and heat-preserving property. It has one major drawback that it does not blend easily with other fibers (Sapchookul *et al.*, 2003; Janasak *et al.*, 2007).

2.7 Pretreatment

In the recent past, there has been an ever-increasing interest for the introduction of enzymes in wool processing. Areas of special interest are increased comfort, increased softness, surface appearance, and reduced pilling performance. Application of enzymes in degumming of silk and best fibers has also been reported. Recent research has shown the effectiveness of enzymatic action on processing of waste-silk fabric. Silk spun from waste silk posses some problems during processing because it contains many impurities in the form of broken chrysalis, straw, lignin, hair, and some cellulosic particles. Conventional processes are not effective in removing all the impurities but protease enzymes that are capable of hydrolyzing the peptide bonds are for silk degumming. Proteases have been reported to give the fabric a softer handle and reduced lousiness. The procedure recommended for scouring and bleaching of the spun silk is: soaping, treatment with enzyme degumming of suitable concentration at 50°C for 3 h, at pH 5.2, and bleaching with hydrogen peroxide. Such a process enhances the surface characteristics, wettability of the fabric, and removes the impurities as well. Some of the enzymes are used in processing of natural fiber fabrics. Hydrophilic coated and laminated fabrics transmit water vapor selectively by a molecular process, i.e., by absorption, diffusion, and desorption through the solid polymer layer. Such a polymer film or coating shows no evidence of voids or microporous structure, and thus is not susceptible to surface contamination by dirt, dust, etc. Thus, in this research, chitosan pretreatment shall be applied to the silk fabrics (Bajaj, 2002).

2.7.1 Chitosan

Chitosan is found in some fungi but in limited quantities. Hence, chitosan is commercially produced by alkaline deacetylation of chitin. The purpose of deacetylation is to produce chitosan that is readily soluble in dilute acetic acid. Deacetylation can be defined as a process that involves reaction of chitin with aqueous 40-50% NaOH solution at 100°C or higher for at least 30 minutes to hydrolyze the N-acetyl linkages (Figure 2.3). Repeating the process can give deacetylation values of up to 98% but it is difficult to achieve complete deacetylation with such a heterogeneous process.



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

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

Figure 2.3: Reaction of chitosan preparation

Different reviews of chitosan-based materials have appeared concerning separation and complexation, including membrane filtration and adsorption. Obviously, chitosan has also been investigated as a coagulant for the capture of contaminants from aqueous solutions in numerous articles. However, the studies mainly focused on the recovery of suspended solids (SS) and colloids; in the case of dissolved contaminants there are many fewer studies

2.7.2 Chitosan derivatives (*N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan chloride (HTACC))

Due to the loss of its cationic nature at pH above 6.5, chitosan exhibits poor solubility. Hence, its applicability, as well as antimicrobial activity is limited to acidic conditions. By utilizing the reactivity of the primary amino group and the primary and secondary hydroxyl groups of chitosan, various derivatives of chitosan were prepared with goals to dissolve it in water over the entire pH range and to broaden its applicability. *N*-(2-Hydroxy) propyl-3-trimethylammonium chitosan chloride (HTCC) was synthesized by the reaction of glycidyltrimethylammonium chloride (GTMAC) and chitosan (Figure 2.4). The reaction product was a water-soluble chitosan derivative, and showed excellent antimicrobial activity.

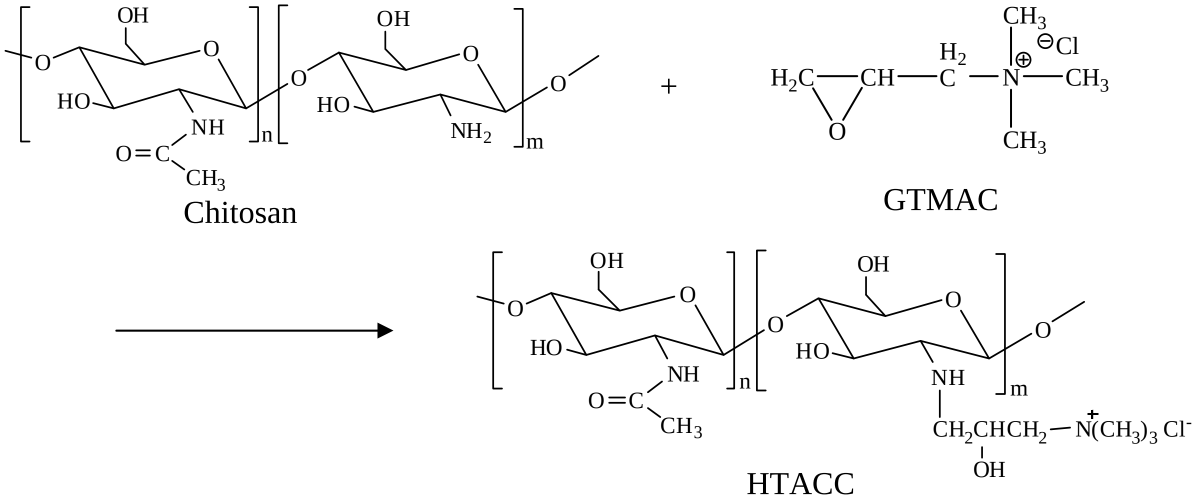


Figure 2.4: Reaction of HTACC preparation

2.8 Characterization of the printed silks

2.8.1 Color measurement

(1) Color space

There are several three-dimensional “color space” or “color order” systems that have been devised to classify colors (Figure 2.5). The color test chart of printed fabric was evaluated for CIELAB which was measured by a spectrophotometer (Gretag Macbeth Spectrolino, Switzerland), 45°/0°, using illuminant D50 and the 2° observer, based on CIE 1931. The stimulus of color dependence on the interaction is the proper combination of a light source, an object, and a standard observer (Leelajariyakul *et al*., 2008).

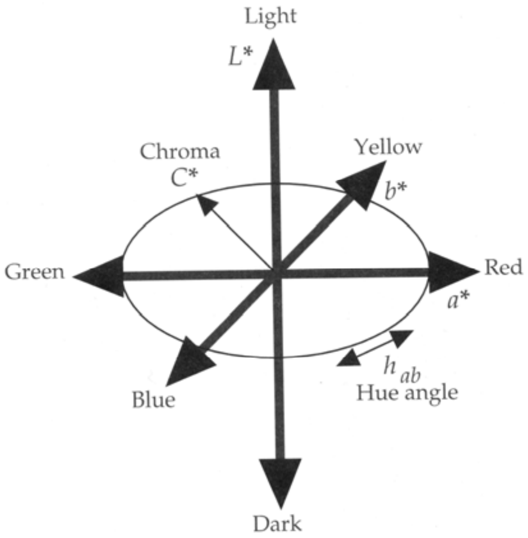


Figure 2.5: CIELAB color space.

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

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

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

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

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

$$L^* = 116 [f(Y/Y_n) - 16/116] \qquad (2.4)$$

$$a^* = 500 [f (X/X_n) - f(Y/ Y_n)] \qquad (2.5)$$

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

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

(2) Color strength (K/S)

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

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

$$\text{Degree of Fixation} = ((K/S)_{\text{after washing}} / (K/S)_{\text{before washing}})*100 \tag{2.8}$$

where R = the reflectance of printed silk fabric in the range of the highest absorption.

2.9 Literature review

Tincher and Yang (1999) carried out a study in which a range of silk fabrics were printed with the TOXOT Jamine™ 1000 S4 continuous inkjet printer using pigmented ink with sub-micron particle size lattices of polymer resins. C.I. Pigment Red 184 (Hostafine Rubine F6B) was used for this study. Two polymer compositions were selected and the polymer lattices were prepared by a proprietary process to give stable, nanometer range particles of acrylate copolymers with different ratios of butyl acrylate to methylmethacrylate to control glass transition temperature (T_g). The two resins prepared had T_g's of -10 and -21°C. The lattices showed viscosities in the range of 12-13 cps at approximately 30% solids. Results showed that inks with high pigment loading of 5-9% and resin content of 15-20% could be successfully jetted. Increase in solids level increased the viscosity, limiting good drop formation. Addition of urea (approximately 2.5%) to the ink formulation reduced the viscosity, improved jetting characteristics of ink and reduced the clogging of the recycle line by minimizing the rate of water evaporation. Printed silk samples were thermally cured and tested for bending rigidity and crock fastness properties. Inks with up to 20% solids and with resin to pigment ratios of 2.5 or above gave acceptable hand and crock fastness. To achieve good balance between hand and crock fastness for silk fabric printing, T_g of resins with -15°C were recommended.

Yu and Gottberg (2000) described a novel color pigment dispersion set for aqueous inkjet ink applications that comprised of surface modified copper phthalocyanine blue pigment (IJX™ 253, PB 15:4), Quinacridone red pigment (IJX™ 266, PR 122) and monoazo yellow pigment (IJX™ 273, PY 74). These dispersions were prepared using Cabot surface modification technology. It was demonstrated that surface modification of color pigments with ionic groups provides stable dispersions with favorable physical characteristics for formulation of aqueous inkjet inks.

Titration has been used as a quantitative tool to evaluate pigment particles bearing weak acid or base functional groups. The level of surface modification can be determined by measuring the value of total titratable groups in mmol/grams pigment. The dissociation constants (pK_a or pK_b) derived mathematically from the titration curve provide understanding about the colloidal stability as a function of pH. Poor determination of functional groups reported in previous studies about titration of pigment particles made the data interpretation difficult. Cabot's surface modification technology of introducing specific functional groups to the pigment particles has allowed for systematic investigation of stability of pigment dispersions. An understanding of the nature and concentration of surface charge groups and the charge density as a function of pH is helpful in formulation, troubleshooting and failure mode analysis of pigmented inks. Yu and Gottberg (2004) investigated surface modified carbon black pigments by potentiometric titration. The effect of ionic strength, inkjet ink components and nature of surface functional groups were studied and related to the pigment stability. The discrepancy between experimental pK and functional group pK was explained using a diffuse double layer (DDL) correction model. Potentiometric titration was found to be effective in order to understand the stability of pigment dispersions.

Daplyn and Lin (2003) reported preparation of three different pigment dispersions and formulations of inkjet inks from the prepared dispersions. The ink formulations comprised 2% pigment dispersion, 15% thermal curing binder, 5% ethylene glycol, 5% isopropyl alcohol and 73% water. The ink formulations were evaluated for their suitability for jet printing on textile fabrics. Results of this study showed that ink formulation containing a surface modified pigment (Cabot Magenta IJX 266) was most suitable for inkjet printing. This was attributed to the pigments smaller particle size, lower viscosity and stability to the freeze-thaw cycles and pH changes. It was suggested that the other two pigments viz., Clariant Toner Magenta E02 and the Microlith Magenta B-WA may cause blocking of print head nozzles due to relatively lower stabilities. Prints on cotton fabrics were found to have better image qualities compared to those on polyester fabrics, due to high absorbency of cotton.

Kiatkamjornwong *et al*. (2003) investigated print qualities of cotton fabric printed by inkjet printing and screen printing. The cotton fabric to be printed by ink jet printing was pretreated with 3%wt polyethylene oxide (2 to 3 million Dalton molecular weight) solution. Pigmented inkjet inks prepared in this study were composed of 4%wt of each pigment dispersion (cyan, magenta, yellow and black), 10%wt diethylene glycol, 15%wt glycerin, 16.49%wt acrylic binder with pigment to binder ratio of 1:2 and deionized water. The pH of the inks was adjusted to 9.0 using sodium hydroxide. The inks were filtered through a 0.5 micrometer pore size filter and printed on cotton using an Epson Stylus 3000 inkjet printer. The screen ink was composed of 10%wt pigment dispersion (cyan, magenta, yellow and black), acrylic binder with pigment to binder ratio of 1:2 and fume silica to increase the viscosity required for screen printing. The viscosity and flow behavior of both inkjet inks and screen inks were found to be acceptable. The particle size distribution and viscosity of inkjet inks were slightly increased during ambient storage of two months. It was found that both inks showed the same color saturation, color gamut and ink tone reproduction. The color gamut volume, stiffness, air permeability and crock fastness of inkjet printed fabrics were superior to those of fabrics printed with screen inks. The inkjet printed pre-treated fabric showed improved color gamut volume and color saturation compared to the untreated fabric. The three pass inkjet printing on pre-treated cotton fabric increased color gamut, color gamut volume and color saturation.

Xue *et al.* (2006) prepared the nanoscaled binders suitable for a pigment-based inkjet ink printing on fabrics. The polymer microemulsion with a high content of soft monomer of butyl acrylate (BA) was synthesized via a modified microemulsion polymerization method, where *N*-methylolacrylamide (NMA) served as the cross-linking monomer and monododecyl maleate (MDM) as the copolymerizable surfactant. The effects of the functional monomers (NMA, MDM), the weight ratios of monomers, and the solid contents on the microemulsion properties were investigated by TEM, DSC, particle size analysis, and fabric inkjet printing. The results indicated that the microemulsion had a number-average particle diameter less than 50 nm with a narrow particle size distribution. It was also found that the glass transition temperatures (T_g) of the film formed from the microemulsion could be lower than −30 °C. inkjet printing on fabric by the pigment-based inks formulated with the as-considered optimum microemulsion as a binder and commercial pigment dispersions demonstrated excellent printability of such inks, and good color fastness and softness of the printed fabrics.

Leelajariyakul *et al.* (2008) studied the effect of pigment dispersion techniques such as surface modification and micro-encapsulation on inkjet printing of silk fabric. Four color (cyan, magenta, yellow and black) surface modified pigment dispersions and microencapsulated pigment dispersions were used for inkjet ink formulations. The properties of both types of inks were: viscosity 3.5-5 mPa s, surface tension 38-45 mN m^{-1} and particle size 220-230 nm. To examine stability, inks were stored at ambient room temperature for 12 weeks. It was found that after storage, the particle size and viscosity of inks increased by 2-15% and 20-40% respectively. Silk fabric was pre-treated with 10% Sanfix 555 (cationic acrylate polymer) and 10% urea solution at 100% wet pick up and then dried at 80°C for 10 minutes. Both untreated and pre-treated silk fabrics were inkjet printed with both types of inks using an Epson Stylus color 3000 printer. The pre-treated silk fabrics showed high optical density compared to the untreated fabrics. When compared with microencapsulated pigment inks, the surface modified pigmented inks provided high optical density, good tone reproduction, better color gamut and gamut volume on both untreated and pre-treated silk fabrics.

Nam *et al.* (1999) was synthesized *N*-(2-Hydroxy)propyl-3-trimethylammonium chitosan chloride (HTACC) with the reaction of glycidyltrimethylammonium chloride (GTMAC) and chitosan. The reaction product was a water-soluble chitosan derivative, and showed excellent antimicrobial activity. HTCC was blended with polyacrylonitrile (PAN) using an NaSCN aqueous solution as a common solvent. The blend solution was transparent and stable up to 6 months without phase separation. The PAN/HTACC blend fibers were prepared via a wet spinning and drawing process. Thermal, electrical, and mechanical properties as well as antimicrobial activity were investigated. It was found that the antistatic property and antimicrobial activity of the blend fibers could be achieved by adding only a small amount of HTACC.

Bahmani *et al*. (2000) examined the performance of chitosan (MW 171,000) as a combined thickener and binder in pigment printing. Polyester/cotton and 100% polyester fabrics were printed with chitosan/pigment printing paste, dried at room temperature and cured at 150 °C for 6 minutes. They found that the fabrics printed with chitosan printing paste gave a comparable color fastness to the fabrics printed with commercial printing paste (Alcoprint system). However the fabrics printed with the chitosan printing paste showed poor color strength (K/S) and were stiff. It was proposed that the poor color strength was due to reduced stability of the pigment dispersion in chitosan paste at pH 4. It was suggested that the addition of appropriate auxiliaries could minimize the stiffness of the fabric and further studies would be necessary to improve the poor color strength.

Lim and Hudson (2004) studied antimicrobial activity of cotton fabric has been treated with a fiber-reactive chitosan derivative containing quaternary ammonium groups, *O*-acrylamidomethyl-*N*-[(2-hydroxy-3-trimethylammonium)-

propyl] chitosan chloride (NMA-HTACC). Cotton treated with NMA-HTACC has been dyed with direct and reactive dyes without the addition of salt. The color yield was higher than that on untreated cotton, despite the addition of a large amount salt in the latter case. After dyeing, cotton treated with NMA-HTACC gave better wash fastness than the untreated cotton. The light fastness was however inferior to that on untreated cotton. The antimicrobial activity of cotton treated with NMA-HTCC against *Staphylococcus aureus* was considerably lower after dyeing, probably due to the antimicrobial effect of the cationic group on NMA-HATCC being blocked by its combination with the anionic dye.

Lim and Hudson (2004) studied a fiber-reactive chitosan derivative, O-acrylamidomethyl-N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (NMA-HATCC), was applied to cotton fabrics by a cold pad-batch method in the presence of an alkaline catalyst to evaluate its use as a durable antimicrobial textile finish. The antimicrobial activities of the NMA-HTACC treated cotton fabrics were evaluated quantitatively against *Staphylococcus aureus*. The cotton treated with NMA-HTCC at a concentration of 1% on weight of fabric showed 100% of bacterial reduction. The activity was maintained over 99% even after being exposed to 50 consecutive home laundering conditions. The effect of an anionic surfactant on the antimicrobial activity of the NMA-HTACC treated fabric was discussed.

Abou-Okeil *et al*. (2005) studied the effect of chitosan pre-treatment on the printability of wool fabric. The wool fabric was pre-treated with chitosan of different molecular weights followed by mordanting with copper sulphate and then printing with a natural dye (2- hydroxy-1,4-naphthoquinone). The purpose of the chitosan pre-treatment was to increase the copper (II) binding of the wool fabric which would result in the reduction of metal ions in the effluent. It was found that copper (II) uptake increased with increase in the molecular weight and concentration of chitosan applied. The color strength (K/S) and the wash fastness of the chitosan pre-treated printed wool samples increased compared to the untreated wool samples.

Choi *et al.* (2005) investigated a medium viscosity (~150 mPa s) chitosan to replace sodium alginate in the pre-treatment print paste for digital inkjet printing of cotton fabric. Cotton fabric was padded (80% WPU) with pre-treatment print paste containing suitable amounts of chitosan, urea and sodium bicarbonate and cured at 150 °C for 90 seconds. The pre-treated fabric was inkjet printed with reactive dye based four color ink system using Mimaki Tx2-1600 digital inkjet printer. The printed fabrics were air dried and steamed at 110°C for color fixation. The color fastness properties of the printed fabrics were found to be satisfactory while the outline sharpness of the prints was enhanced by the chitosan pre-treatment. However, the color yield was not as good as that achieved with sodium alginate based pretreatment print paste.

Yuen *et al.* (2007) modified the pretreatment method by applying chitosan separately on the cotton fabric for digital inkjet printing with reactive dyes. The proposed two-bath method included (1) padding of cotton fabrics with chitosan solution (80% WPU) and curing at 170°C for 90 seconds. (2) padding of chitosan pre-treated fabrics with a pre-treatment paste containing 10 grams of urea and 8 grams of sodium bicarbonate in 150 grams of deionized water. The fabrics were padded with 80% WPU, dried at 80 °C and subsequently conditioned. High color yield was achieved with the developed two-bath method. However, chitosan slightly reduced the tensile strength of the digital inkjet printed cotton fabric.

Phattanarude *et al.* (2009) studied pretreatments of silk fabric with amino compounds for inkjet printing. The pretreating solutions were serine, glycine, aspartic acid, sericin, chitosan, and a commercial pre-treating chemical called Sanfix 555. Both untreated and treated fabrics were printed with in-house formulated pigmented inks and later steamed to fix the ink on the fabric surface. The pretreatments containing the amino compounds improved hydrophilicity of the silk fabric with the exception of chitosan. The color gamut from sericin, chitosan, and Sanfix 555 pretreatments was wider than that from the amino acid pretreatments. The chroma of the cyan color was most improved. The fabric, after pretreatment with sericin, showed a significant improvement in dry crock fastness while wet crock fastness was improved by serine and glycine. The chitosan slightly improved both dry and wet crock fastness. Wash fastness of all pretreated and printed fabrics including untreated and the printed fabrics was excellent because the pigmented ink was formulated with pigment and binder. Bending stiffness of the silk fabrics after chitosan pretreatment was significantly higher than those with other pretreatments. The ink penetration in sericin and chitosan padded layers was shallower than those for amino acids, enhancing ink deposition on the fabric surface. The amino compound pretreatments held and fixed additional ink on the fabric surfaces resulting in a wider color gamut of the inks.

Thanapongjongruay *et al.* (2009) studied color properties of silk fabrics that were pretreated with the solution of chitosan mixed with glycine or *N*-[(2-hydroxyl-3-trimethylammonium)propyl] chitosan chloride (HTACC) and printed with in-house formulated, water-based pigmented inkjet inks, followed by heat cured to fix the inks on the fabric surface. Based on the evaluation of color properties, it was found that the silk fabric pretreated with HTACC solution gave much better tone reproduction and wider color gamut than those pretreated with the mixed solution of chitosan and glycine and the untreated fabrics.

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Ink compositions

3.1.1.1 Colorants (cyan, magenta, yellow and black): surface-modified pigments from Cabot Corporation, Billerica, MA, U.S.A. were used as follows:

1) Cyan (CAB-O-JET® 250C): C.I. Pigment Blue 15:4;

2) Magenta (CAB-O-JET® 260M): C.I. Pigment Red 122;

3) Yellow (CAB-O-JET® 270Y): C.I. Pigment Yellow 74;

4) Black (CAB-O-JET® 200): C.I. Pigment Black 7.

3.1.1.2 Polymer binder: Printofix binder 710 (styrene-*co*-acrylate polymer dispersion) from Clariant Chemical Ltd., Bangkok, Thailand. Detailed information of pigment dispersion and binder is presented in Table 3.1.

3.1.1.3 Viscosity modifiers:

1) Diethylene glycol ($(CH_2OHCH_2)_2O$), laboratory reagent grade, MW = 106.12 g mol^{-1}, Ajax Finechem Pty, Ltd., New Zealand;

2) Glycerol, ($CH_2OHCHOHCH_2OH$), analytical reagent grade, MW= 92.09 g mol^{-1}, Ajax Finechem Pty, Ltd., New Zealand;

3.1.1.4 Solvent

1) Deionized water from a water purifier (Elga Lab water LA 611, Veolia Systems Ltd, Buckinghamshire, UK.

3.1.1.5 Additives:

1) Surfynol 104 (2,4,7,9-Tetramethyl-5-decyne-4,7-diol), a commercial non ionic surfactant was supplied by Air Products and Chemicals, Inc., Allentown,

PA, U.S.A. Surfynol104 is a non-ionic surfactant having an acetylenic diol surface active agent of 2, 4, 7, and 9-tetramethyl-5-decyne-4, 7-diol having inherently biodegradable that provides both dynamic wetting and defoaming in waterborne coatings, inks, and adhesives systems. The hydrophobic nature of the surfactant produces final ink properties with water sensitivity

2) Urea (NH_2CONH_2), laboratory reagent grade, MW = 60.06 g mol^{-1}, Ajax Finechem Pty, Ltd., New Zealand;

3) Sodium hydroxide (NaOH), MW = 40.00 g mol^{-1}, Merck KGaA, Germany.

Table 3.1: Properties of pigment dispersions and binder

	Pigment			Physical properties			
Materials	Color Index of pigment	Chemical class of pigment	Pigment concentration (wt. %)	pH	Viscosity (mPa s)	Mean particle size (nm)	Zeta potential (mV)
Cyan : C (CAB-O-JET® 250C)	PB 15:4	Copper phthalocyanine	10.03	6.11	2.40	98.71 ± 41.21	-54.60
Magenta : M (CAB-O-JET® 260M)	PR 122	Quinacridone	9.98	4.05	2.47	132.72 ± 47.73	-53.20
Yellow : Y (CAB-O-JET® 270Y)	PY 74	Monoazo	10.09	7.24	2.36	190.09 ± 89.00	-50.67
Black : Bk (CAB-O-JET® 200)	PBk 7	Carbon black	20.44	7.29	3.88	154.57 ± 64.89	-55.10
Printofix binder 710	-	Styrene- Acrylate copolymer	40.00	6.14	43.2	235.52 ± 71.21	-37.97

3.1.2 Pretreatment reagents:

3.1.2.1 Chitosan, MW = 57,000 g mol^{-1} with an *N*-deacetylation degree of 85, Seafresh Chitosan (Lab) Co., Ltd., Thailand;

3.1.2.2 Glycine (NH_2CH_2COOH), analytical reagent grade, MW = 75.07 g mol^{-1}, Sigma-Aldrich GmbH, France;

3.1.2.3 *N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan chloride (HTACC), Organic Synthesis Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Thailand. The HTACC was prepared from chitosan having an average molecular weight of 100,000 g mol^{-1} and the degree of deacetylation (DD) of 95%. The HTACC prepared contained 87.7% degree of substitution to result in the calculated molecular weight of 184,000 g mol^{-1} and the measure pH of the aqueous solution of 6.8.

3.1.3 Silk bleaching reagents:

3.1.3.1 Sodium carbonate (Na_2CO_3), MW = 105.99 g mol^{-1}, analytical reagent grade, Ajax Finechem Pty, Ltd., New Zealand;

3.1.3.2 Hydrogen peroxide (H_2O_2), laboratory reagent, Vidhyasom Co., Ltd., Thailand.

3.1.4 The locally woven silk fabric, the Ubon Ratchathani 60-35 worm species, The Queen Sirikit Institute of Sericulture, Thailand.

Description of the silk fabric: Plain weave style with a yarn number by counting the fibers removed from the fabrics directions (denier, warp × weft): 127.8 × 122.7; the number of threads per inch (warp × weft): 87 × 78; and the number of threads per square inch: 165.

3.2 Apparatus

3.2.1 Epson inkjet printer, model Stylus photo R230, Seiko Epson Corp., Japan.

3.2.2 X-Rite Spectrophotometer, model SP62, d/8, X-Rite. Inc., U.S.A.

3.2.3 X-Rite Spectrodensitometer, model 500 series, 45/0, X-Rite. Inc., U.S.A.

3.2.4 pH meter, model MP220, Mettler Toledo GmbH, Switzerland.

3.2.5 Brookfield viscometer, model DV-II+ Programmable with a UL adapter, Brookfield Engineering Laboratories, Inc., U.S.A.

3.2.6 Surface tensiometer, K6, Krüss, Germany.

3.2.7 Particle size analyzer with dynamic light scattering, Nanotrac U2124I, Microtac Inc., U.S.A.

3.2.8 Zeta-potential, Zeta nanosizer ZS model Zen 3600, Malvern Instrument Ltd., England.

3.2.9 Differential Scanning Calorimeter (DSC), DSC823e/700, Mettler Toledo GmbH, Switzerland.

3.2.10 UV-Visible spectrophotometer, HP-8453, Hewlett-Packard, Germany.

3.2.11 Fourier Transform Infrared spectrophotometer (FTIR), Spectrum GX, Perkin Elmer Life and Analytical Sciences, Inc., U.S.A.

3.2.12 Optical microscope, Nikon model eclipse 50i with cool pix MDC lens and Nikon E8400 camera, Nikon corp., Japan.

3.2.13 Padding machine, Labtec Newave Lab Equipment Co., Ltd., Taiwan.

3.2.14 Drying oven, R-3, Xiamen Rapid Co., Ltd., China.

3.3 Procedure

3.3.1 Preparation of pigmented inkjet inks

The six colors of pigmented inkjet inks comprised a surface-modified copper phthalocyanine blue pigment (CAB-O-JET® 250C, C.I. Pigment blue 15:4), quinacridone red pigment (CAB-O-JET® 260M, C.I. Pigment red 122), monoazo yellow pigment (CAB-O-JET® 270Y, C.I. Pigment yellow 74), and black pigment (CAB-O-jet 200,C.I. Pigment black 7). A commercial binder (Printofix binder-710) is self-crosslinking styrene/acrylate-based copolymer dispersion. The pigmented inkjet formulation is shown in Table 3.2. The pigment-to-binder ratio was prepared at 1:2, which is a typically selective ratio used in a general inkjet formulation (Leelajariyakul *et al.*, 2008). The viscosity of ink is the important property for jet ability and controlling the image quality. For the first part of the research, the formulated ink viscosity was adjusted and compared with the Epson original ink. The proportion of diethylene glycol and glycerol was adjusted for monitor the ink viscosity. The rest of the ingredients including binder, urea and surfactant were used as received. Each component was added individually to avoid any unfavorable inhomogeneity in the solution. Then, a dilute NaOH solution (10% w v^{-1}) was added to the ink in order to adjust the pH to be in the range of 7 to 9. After mixing, the inks were filtered through a cellulose acetate filter (pore size 0.45 μm) to prevent any coarse particles from clogging the orifice of the printer.

3.3.2 Characterization of the pigmented inkjet inks

3.3.2.1 pH of the inks

The pH of the ink was adjusted to a suitable range for printing by a good dispersion of binder and pigment, which was measured by a pH meter at room temperature.

3.3.2.2 Viscosity

The viscosity properties of the dispersed pigments and of the formulated inks were measured by a rotational type viscometer at 25 ˚C with varied shear rates (Brookfield viscometer, DV-II & programmable model). In addition, viscosities of the black inks made from several pigment-to-binder ratios were measured by the Cone and Plate viscometer (Bohlin rotational rheometer, Malvern instrument, Ltd., Worcestershire, UK.) at 25ºC with a cone and plate geometry with a radius of 55 mm, actual cone angle 2 degrees.

Table 3.2: A water-based pigmented Ink Formulation

Chemical	Weight (%)
Pigment dispersion (by solid weight)	
For process colors	5.00
For light colors	2.00
Diethylene glycol	2.5-10
Glycerol	1-12
Urea	5.00
Binder (by solid weight)	
For process colors	10.00
For light colors	4.00
Deionized water	volume was made up to 100 weight %

3.3.2.3 Surface tension

The surface tensiometer, a Du Noüy ring measuring method, was used for measuring surface tension of the dispersed pigments and formulated inks. The measurement was performed at room temperature with a platinum-iridium ring.

3.3.2.4 Printing behavior

The formulated inks were filled in the compatible ink cartridge. The filled ink cartridge was installed in the printer and cleaned for 5 times to obtain a completely filled print head with ink, by the head cleaning command in a printer program. The test pattern of each formulated ink sets were printed by the nozzle check order in the maintenance program of the printer.

3.3.2.5 Particle size dispersion of the dispersed pigments and pigmented inks

The dynamic light scattering, ultrafine particle size analyzer (Nanotrac U21241, Microtac Inc., U.S.A.) was used for the particle size analysis of the dispersed pigments, dispersed binder and formulated inks.

3.3.2.6 Differential scanning calorimetry

Thermal characterization of an emulsion polymer binder was measured by differential scanning calorimeter (DSC). The measurement temperature range was scanned from -40 to 300 ˚C, using the heating rate at 10˚C min^{-1} under liquid nitrogen with a flow rate of 30 ml min^{-1}.

3.3.2.7 Zeta-potential

The formulated inks were diluted with deionized water before measuring the zeta potential by Zeta nanosizer (Zeta nanosizer ZS model Zen 3600, Malvern

Instrument Ltd., England). The charges on the pigment surfaces were evaluated at 25°C.

3.3.3 The effect of Pigment –to-binder ratio

The rheological property of the formulated inks was further investigated with a cone and plate rotational rheometer at the high shear rate range (1-5000 s^{-1}). The pigmented inkjet formulation is shown in Table 3.3.

Table 3.3: Chemical composition of black ink

Formula	**Chemical concentration (%w w^{-1})**						
	Pigment	**Diethylene glycol**	**Glycerol**	**Urea**	**Printofix binder 710**	**Surfynol 104**	**Water**
1	25 (5 %pigment)	10	10	5	0	0.1	49.90
2	25 (5 %pigment)	10	10	5	6.25 (2.5% polymer)	0.1	43.65
3	25 (5 %pigment)	10	10	5	12.50 (5% polymer)	0.1	37.4
4	25 (5 %pigment)	10	10	5	18.75 (7.5% polymer)	0.1	31.15
5	25 (5 %pigment)	10	10	5	25.00 (10% polymer)	0.1	25

The pH of the inks was adjusted with 10 %w v^{-1} NaOH in a range of 8-9.

3.3.4 Preparation of the silk fabrics

The silk fabrics were bleached to remove wax and impurities, and to improve the fabric whiteness. The fabric was cut into a rectangle shape with a dimension of 23 cm × 33 cm. The silk fabrics were bleached in the mild oxidizing solution, 10 g L^{-1} hydrogen peroxide and 2 g L^{-1} sodium carbonate, with 1/50 of a silk fabric-to-solution ratio, at the temperature of 95°C for 45 min. Then, the bleached silks were soaked to boiling water for 10 min, passed to the filtered tap water 10 min, and dried at ambient condition.

3.3.5 Preparation the pretreatment solutions

1) The 0.1% w v^{-1} chitosan solution was prepared by dissolving the chitosan flake with 0.5% v v^{-1} acetic acid solution and stirred using a magnetic stirrer until a clear solution was obtained.

2) The 1% w v^{-1} chitosan and 15% w v^{-1} glycine solution were prepared by individually dissolved chitosan and glycine in 0.5% v v^{-1} acetic acid solution and stirred using magnetic stirrer until a homogeneous solution was obtained.

This pretreatment solution was selected based on the previous experimental result (Kiatkamjornwong *et al*., 2007) that the mixed solution produced the best color saturation and color gamut in cyan and yellowish green regions.

3) 0.1% w v^{-1} HTACC solution was prepared by dissolving the newly synthesized HTACC with deionized water and stirring by using a magnetic stirrer until a homogeneous solution was obtained.

3.3.5.1 Characterization of the pretreatments

Three pretreatment solutions: 0.1% w v^{-1} chitosan, 0.1% w v^{-1} HTACC and mixture of 1% w v^{-1} chitosan and 15% w v^{-1} glycine, were each measured in terms of viscosity, surface tension, pH and zeta potential. Each pre-treating material was blended with the dried KBr powder, pressed into a disc, and characterized by FT-IR.

3.3.6 Silk pretreatments and pretreated fabric stiffness

The bleached silk fabrics were padded (Padding machine, Labtec Newave Lab Equipment Co., Ltd., Taiwan) by the mentioned pretreatment solutions with a 100% pick up. The padded fabrics were dried later in an oven (drying oven, R-3, Xiamen Rapid Co., Ltd., China) at 80 ºC for 5 min and 100 ºC for 2 min.

3.3.6.1 Stiffness test of the pretreated silk

Flexural rigidity or stiffness of fabrics relates to their overall mechanical integrity and comfort. Drape, the ability of a fabric to orient itself into folds which is influenced by gravity, is markedly dependent on the stiffness and bending length. Thus, test methods have focused on the mechanics of bending stiffness and the measurement and prediction of fabric drape (Vigo, 1997). The testing method for woven fabrics (JIS L 1096:1999, 45°) cantilever method was used for evaluating the stiffness of fabric sized 2 cm × 15 cm. The average bending length in the warp and weft directions obtained from 5 measurements was used to determine the stiffness. The flexural rigidity or stiffness is correlated with the bending length as shown in the equation 3.1 (Kiatkamjornwong *et al.*, 2005; Phattanarudee *et al.*, 2009).

$$G = W \text{ x } C^3 \qquad (3.1)$$

Where G is the flexural rigidity (mg cm), W is the fabric mass per unit area (mg cm^{-2}) and C is the bending length (cm).

3.3.7 Printing process

The silk fabric was supported by A4 adhesive paper to give a stable dimension of fabric for inkjet printing. Both the untreated and treated silk fabrics were printed with in-house formulated inkjet inks by Epson Stylus Photo R230 (North Ryde, Sydney, NSW, Australia) with a best photo print quality mode at a resolution of 5760×1440 optimized dpi.

For printing of the light cyan and light magenta inks on the fabrics, the light cyan and light magenta ink cartridge were installed in the place of the cyan and magenta ink slots for the fastness experiments.

The printed silk was heat cured to fix the printed inks at 120 ºC for 8 min. The Gretag Macbeth test chart composed of 294 color batches (Figure A1) and solid tone patterns, black, cyan, light cyan, magenta, light magenta and yellow inks printed fabrics (3 pieces for each color) were used for evaluation of the color properties and color fastness test, respectively.

3.3.8 Evaluation of the printed fabric

3.3.8.1 Color gamut and color gamut volume

The color value of the test chart was evaluated by CIE L*a*b* (1976) color system, which was measured by a spectrophotometer (X-Rite Spectrophotometer, model SP62, d/8, X-Rite. Inc., U.S.A) with d/8˚ measuring geometry, a specular excluded mode, using D50 illuminant and 2˚ observer, (CIE 1931). The L*, a*, b* values were used to calculate a gamut volume, and the chroma, C* was calculated from a* and b* value. The gamut volume was then calculated by a color gamut volume program (SHIPP program) provided by the Imaging Society of Japan (Tokyo, Japan) as shown in the calculation method in appendix B.

3.3.8.2 Optical density and tone reproduction

The pattern of grey levels was printed onto the silk fabrics for evaluating the optical density and tone reproduction. The printed pattern was measured by a spectrodensitometer with 45/0 measurement geometry.

3.3.8.3 Sharpness

The sharpness of printed fabric was measured by optical microscope, (Nikon, model eclipse 50i with cool pix MDC lens and Nikon E8400 camera, Nikon corp., Japan). The inter-color bleeding area and the printed “E” character were assessed on various pretreatment fabrics.

3.3.8.4 Light fastness

Light fastness was assessed according to ISO 105-B02:1994(E), a xenon arc fading lamp test. The specimens and blue wool standards (at less 45 mm × 10 mm dimension) were partly covered with a card. They were exposed simultaneously to a xenon arc lamp under a humidity control box. The exposure was usually continued until a color contrast equivalent to grade 3 on the grey scale was obtained. The light fastness of sample is the number of the blue wool standard that has faded to the same extent as the exposed area of the sample.

3.3.8.5 Wash fastness

Wash fastness was assessed according to ISO 105-C10:2006(E), test number A (1). A specimen of 100 mm × 40 mm dimension was attached between the two single-fiber adjacent fabric (silk and cotton) by sewing along one of shorter edges. The composite specimen was washed at 40 ± 2 °C for 30 min in the 5 g L^{-1} standard soap solution (fluorescent brightening agents free) with a liquor ratio of 50:1 (ml g^{-1}). After the washing, the composite specimen was rinsed with water at ambient temperature. Then the specimen was dried by hanging it in air at a temperature not exceeding 60 ˚C. Changes in color of the specimen and the staining of the adjacent fabric with reference to the original specimen were assessed by using the grey scales. The printed fabrics obtained before and after washing were also reported in terms of changes in color strength (K/S) and degree of fixation as shown in Equations 2.7 and 2.8.

The fabrics were printed with a solid tone pattern in six colors (cyan, light cyan, magenta, light magenta, yellow, and black). The K/S value was calculated by the reflectance value of the printed fabric measured by the spectrophotometer.

3.4 Interaction of the pretreatment reagent and the pigmented inkjet inks

The pigmented inks (Cyan, Magenta and Yellow) were each diluted with deionized water to 0.03% w v^{-1} concentration to obtain an absorbance not larger than 1 unit. Then, 10 ml of the diluted inks were mixed with 0.50, 1.00, 2.00, 3.00 and 4.00 ml of the pretreatment solution. After the mixtures were left for 24-h sedimentation at room temperature, the mixtures were then centrifuged for 20 min at 3000 rpm to sediment the precipitate and the supernatant was carefully pipetted and this clear solution was measured by the UV spectrophotometer (Jocic *et al.*, 2005). The absorbance values of the supernatant aliquot were measured in the visible region of a UV-Vis spectrophotometer (HP-8453, Hewlett-Packard, Germany).

CHAPTER IV

RESULTS AND DISCUSSIONS

In this chapter, four main sections consisting of the ink formulation property, color appearance of the printed silk fabric, the image permanence, and the fabric performance and usage are presented and discussed. The general properties of pigment dispersion and binder have already presented in Table 3.1 in Chapter 3. The general guideline of the pigmented inkjet formulation has already been presented in Table 3.2 of Chapter 3.

4.1 Properties of pigmented inkjet inks

For pigmented textile ink development, the rheological property of an ink is a critical factor for jet ability and controlling the image quality. The ink formulation depends mainly on the print head technology being used (Hees *et al.*, 2003). Inks must have physico-chemical properties suitable for drop formation and capable for producing sharp images. For this section, the six color inks composed of the black, cyan, light cyan, magenta, light magenta and yellow colors were prepared and measured for the physical properties. The rheological property was presented in the terms of viscosity. The formulated ink viscosity was adjusted and compared with the Epson commercial ink. The concentration of rheology modifier (diethylene glycol and glycerol) was adjusted for monitoring the ink viscosity, and the other physical properties were measured for pH, and surface tension. The jet ability of the formulated ink sets was shown in the test pattern images.

4.1.1 Ink formulation and physical properties

As the good for appearance and color properties of the printed silk fabric: optical density, tone reproduction, color gamut and color gamut volume, the surface-modified pigments with the sulfonic acid group were used for ink formulation (Leelajariyakul *et al.*, 2008). The surface-modified pigments are made from copper phthalocyanine blue (C.I. Pigment Blue 15:4), quinacridone red (C.I. Pigment Red 122), monoazo yellow (C.I. Pigment Yellow 74), and carbon black (C.I. Pigment Black 7). A rheology modifier is an ingredient used to control the viscosity of the ink or more precisely the rheological profile of the ink. For the ink formulation, diethylene glycol and glycerol are performed as a rheology modifier because solvents are not rheology modifier, in common. The proportion of diethylene glycol and glycerol was adjusted for monitoring the ink viscosity at a low shear rate. The pH, viscosity, and surface tension of the formulated inks are shown in the Table 4.1 - 4.6, and the rheological behavior is shown in the Figures 4.1 - 4.6.

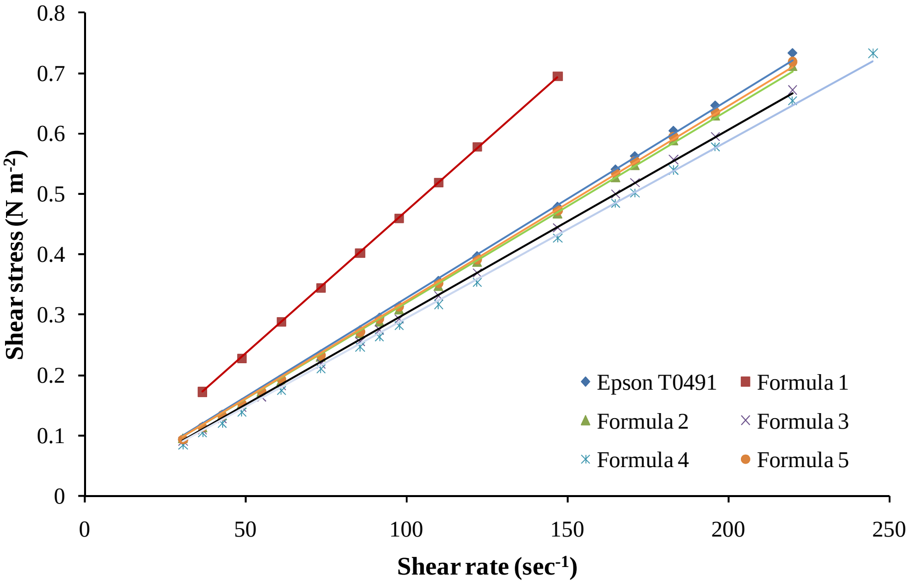
4.1.1.1 Black ink formulation

The five black inks in each ink formulation, which include a pigment dispersion of Black (CAB-O-JET® 200): C.I. Pigment Black 7, are shown in the Table 4.1 which presents the ink ingredients and concentrations. Figure 4.1 shows the rheological property of the black ink formulations. All inks exhibit the Newtonian fluid property, i.e., shear stress is in a linear proportion to shear rate and viscosity is constant at all shear rates. The high ratio of diethylene glycol-to-glycerol content in ink formulation 1 had the highest viscosity (4.74 mPa s) whereas the low ratio of diethylene glycol-to-glycerol content in ink formulations 3 and 4 had the lowest viscosity (3.00 and 3.27 mPa s). The viscosity of the commercial ink is similar to those of ink formulations 2-5 (3.00-3.33). The pHs of the ink formulations 1-3 are higher because of the effect of alkaline solution added (10% w v^{-1} NaOH) and the lower pH in the ink formulations 4-5. The commercial ink (Epson T0491) has the highest pH (8.48). Surface tensions of the black inks formulations 1 and 2 are higher (44.2-44.9) than the other ink formulations 3-5 and the commercial ink. The lower surface tension of ink formulations 3-5 was caused by the addition of surfactant, Surfynol 104. The commercial black ink has the lowest surfactant tension of 30 mN m^{-1}.

Table 4.1: Chemical composition and properties of the formulated black inks

	Chemical concentration (%w w^{-1})			**Properties**		
Formula	**Diethylene glycol**	**Glycerol**	**Surfactant**	**pH**	**Viscosity (mPa s)**	**Surface Tension (mN m^{-1})**
1	10	10	-	7.25	4.74*	44.2
2	5	5	-	7.22	3.23**	44.9
3	5	5	0.1	7.27	3.05**	38.7
4	5	6	0.1	6.79	3.00**	40.6
5	5	8	0.1	6.89	3.27**	38.9
Epson T0491				8.48	3.33**	30.15

For the ink formula 1-3, the pHs were adjusted with 10% w v^{-1} NaOH; viscosity at 25 °C, spindle #S00; rotational speed, *150 s^{-1}, **220 s^{-1}.



(a)

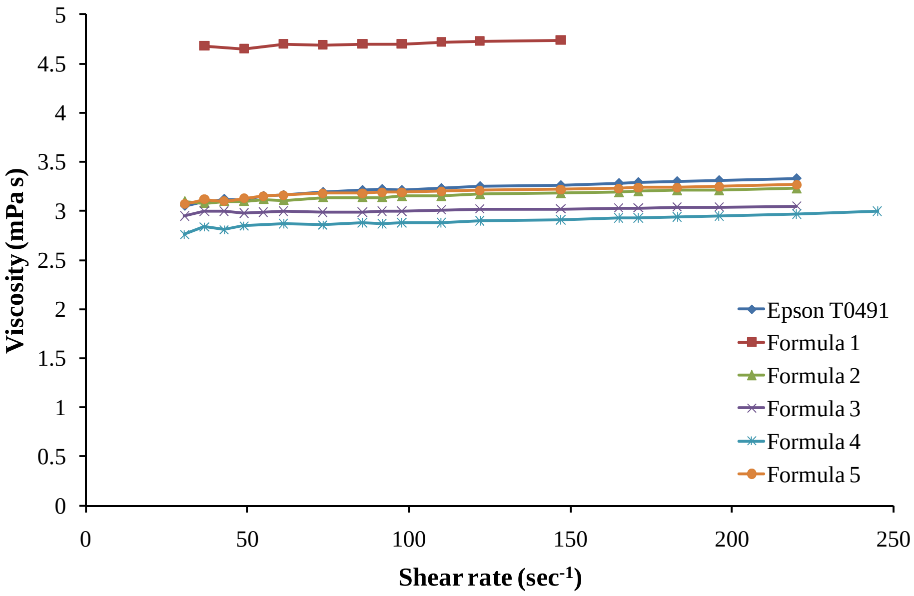


Figure 4.1: Comparison of the black formulated inks and Epson ink; (a) The relationship of shear stress – shear rate, (b) Viscosity

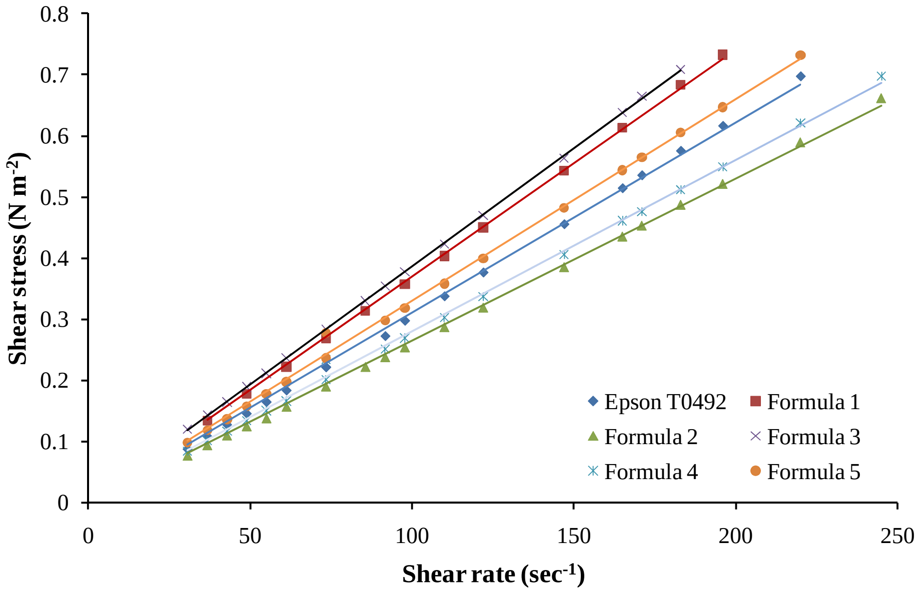
4.1.1.2 Cyan ink formulation

The five cyan inks in the ink formulations are shown in Table 4.2. The ink viscosities and pH of the cyan inks are relatively lower. The pH of the commercial ink is much higher than the cyan inks. In contrast, the ink surface tensions are in the range of 43-51 mN m^{-1}. Figure 4.2 (a) – (b) show that all inks have the Newtonian fluid property. The proportion of diethylene glycol-to-glycerol ratio of 5/10 in formulation 5 is relatively high and close to that of Epson cyan ink.

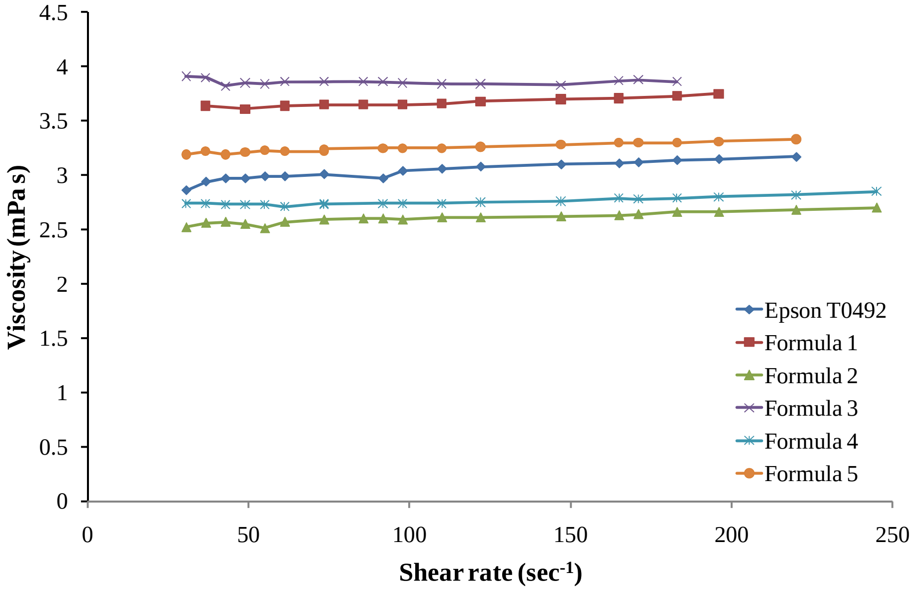
Table 4.2: Chemical composition and properties of the formulated cyan inks

	Chemical concentration (%w w^{-1})			**Properties**		
Formula	**Diethylene glycol**	**Glycerol**	**Surfactant**	**pH**	**Viscosity (mPa s)**	**Surface Tension (mN m^{-1})**
1	10	10	-	7.07	3.75*	51.0
2	5	5	-	7.24	2.68**	49.8
3	10	5	0.1	7.58	3.86*	42.3
4	5	5	0.1	6.68	2.85**	44.4
5	5	10	0.1	6.76	3.33**	43.1
Epson T0492				9.45	3.17**	30.80

For the ink formula 1-3, the pHs were adjusted with 10% w v^{-1} NaOH. Viscosity was measured at 25 °C, spindle #S00, rotational speed, *180 s^{-1}, **220 s^{-1}.



(a)



(b)

Figure 4.2: Comparison of the cyan formulated inks and Epson ink; (a) The relationship of shear stress - shear rate, (b) viscosity

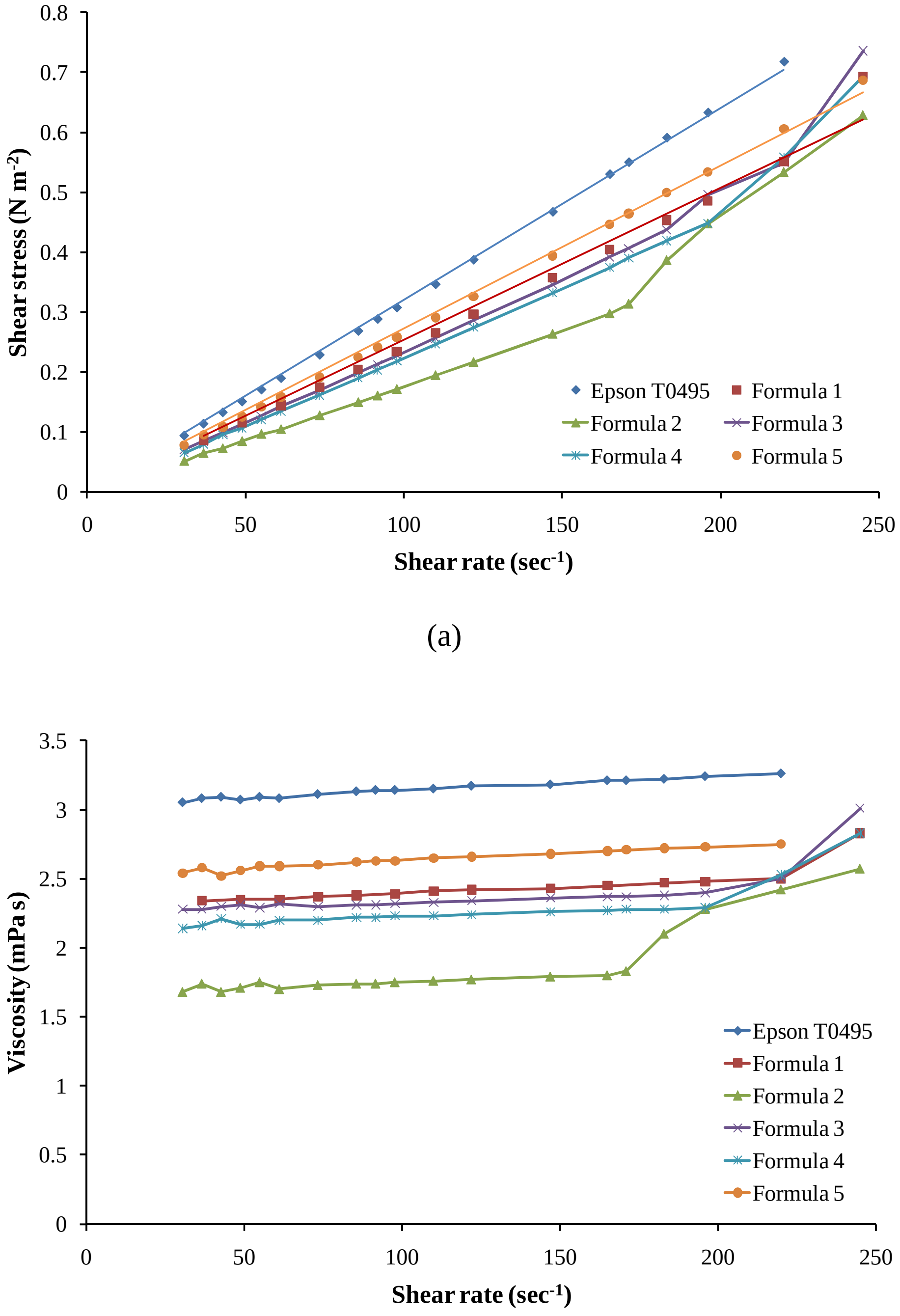
4.1.1.3 Light cyan ink formulation

The five light cyan inks in the ink formulations are shown in the Table 4.3. Figure 4.3 shows the rheological property of the light cyan ink formulation. The ink formulation prepared with the diethylene glycol-to-glycerol ratio of 10/15 can also produce the Newtonian fluid. The ink rheological property shows the shear-thickening behavior in the ink formulations 2, 3 and 4 at a shear rate higher than that at 150 s^{-1}.

Table 4.3: Chemical composition and properties of the formulated light cyan inks

	Chemical concentration (%w w^{-1})			**Properties**		
Formula	**Diethylene glycol**	**Glycerol**	**Surfactant**	**pH**	**Viscosity (mPa s)**	**Surface Tension (mN m^{-1})**
1	10	10	-	7.70	2.83	50.4
2	5	5	-	7.46	2.57	51.5
3	10	10	0.1	8.33	3.01	39.9
4	10	10	0.1	6.90	2.83	42.3
5	10	15	0.1	6.99	2.81	40.1
Epson T0495				9.08	3.26	32.90

For the ink formula 1-3, the pHs were adjusted with 10% w v^{-1} NaOH. Viscosity was measured at 25 °C, spindle #S00, rotational speed 220 s^{-1}.



(a)

(b)

Figure 4.3: Comparison of the light cyan formulated inks and Epson ink; (a) The relationship of shear stress – shear rate, (b) Viscosity

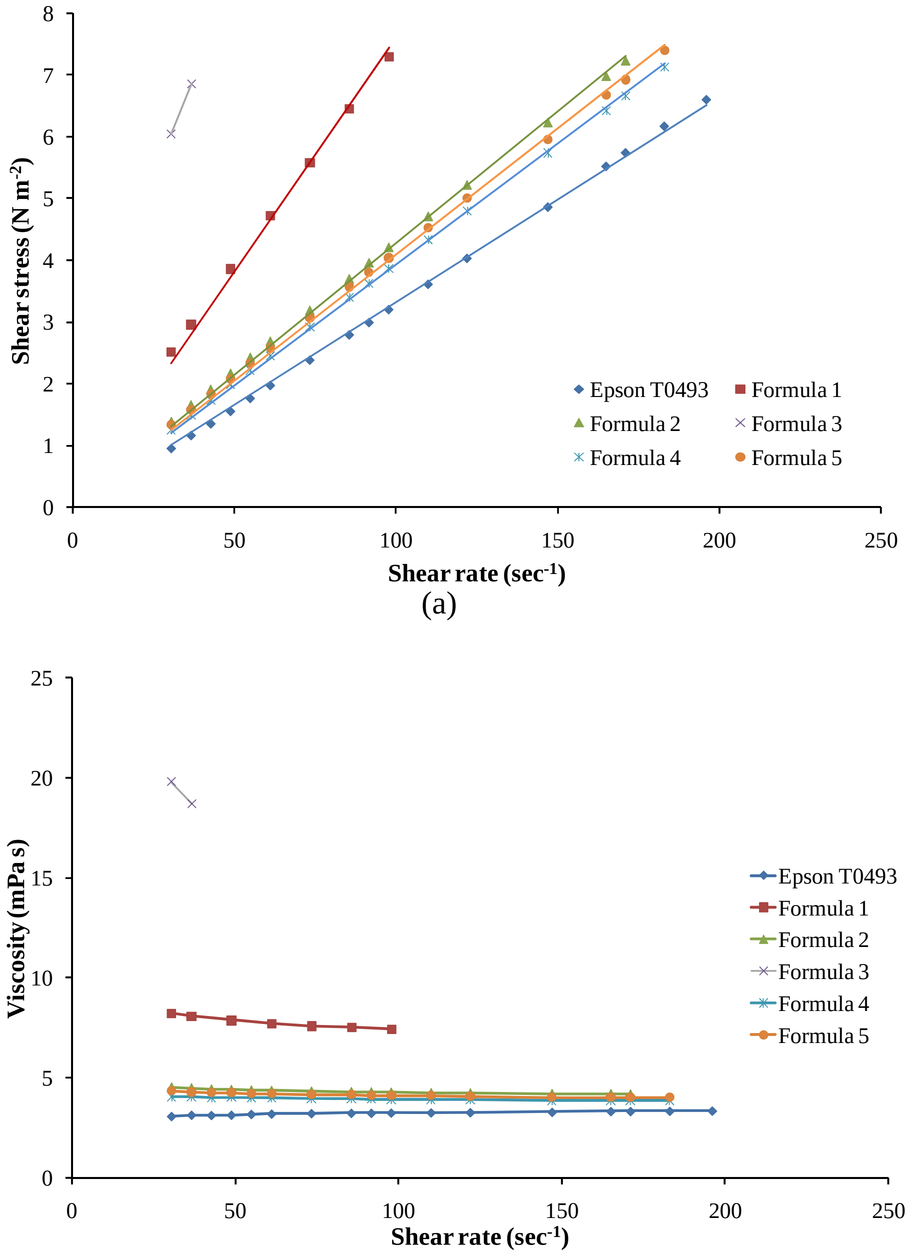
4.1.1.4 Magenta ink formulation

The five magenta ink formulations are shown in the Table 4.4. One can see in Table 4.4 and Figure 4.4 that the viscosity of the magenta ink formulation 1 is very high (7.45 mPa s). Comparison between the ink formulations 1 and 3, it is seen that the high viscosity inks with shear-thinning behavior were found in the alkaline adjusted inks. All other inks showed the Newtonian fluid property. The surface tensions of the prepared inks were relatively high when comparing with the commercial ink.

Table 4.4: Chemical composition and properties of the formulated magenta inks

	Chemical concentration (%w w^{-1})			**Properties**		
Formula	**Diethylene glycol**	**Glycerol**	**Surfactant**	**pH**	**Viscosity (mPa s)**	**Surface Tension (mN m^{-1})**
1	10	10	-	7.27	7.45*	50.9
2	5	5	-	7.10	4.22**	52.7
3	5	2.5	0.1	7.47	18.7*	43.3
4	5	2.5	0.1	6.65	3.89**	45.1
5	5	1	0.1	6.73	3.44**	42.1
Epson T0493				9.33	3.37**	34.1

For the ink formula 1-3, the pHs were adjusted with 10% w v^{-1}NaOH. Viscosity was measured at 25 °C, spindle #S00, rotational speed, *100 s^{-1}, **170 s^{-1}.



(a)

(b)

Figure 4.4: Comparison of the magenta inks and Epson ink; (a) The relationship of shear stress – shear rate, (b) Viscosity

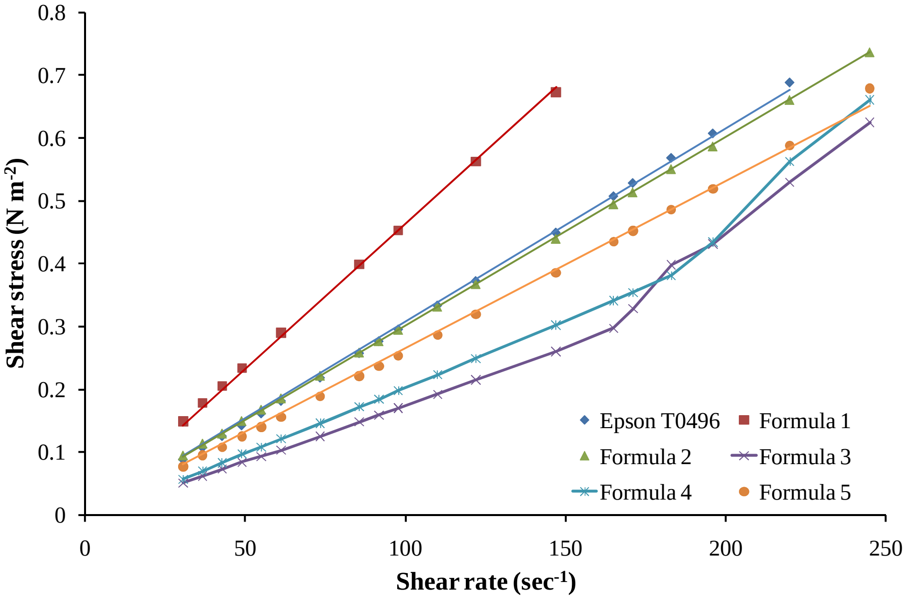
4.1.1.5 Light magenta ink formulation

The five light magenta inks in the ink formulations are shown in Table 4.5 and Figure 4.5. The ink viscosities of ink formulations 2 to 5 are relatively low than the standard commercial ink. The Newtonian fluid property is observed in the ink formulations 1, 2 and 5 while in the ink formulations 3 and 4 shows the shear-thickening fluid. The surface tensions of all inks are very high in the non-surfactant loaded inks 1 and 2, and relatively high in the ink formulations 3-5 with 0.1% w w^{-1} addition while the commercial ink has the lowest surface tension of 29.7 mN m^{-1}.

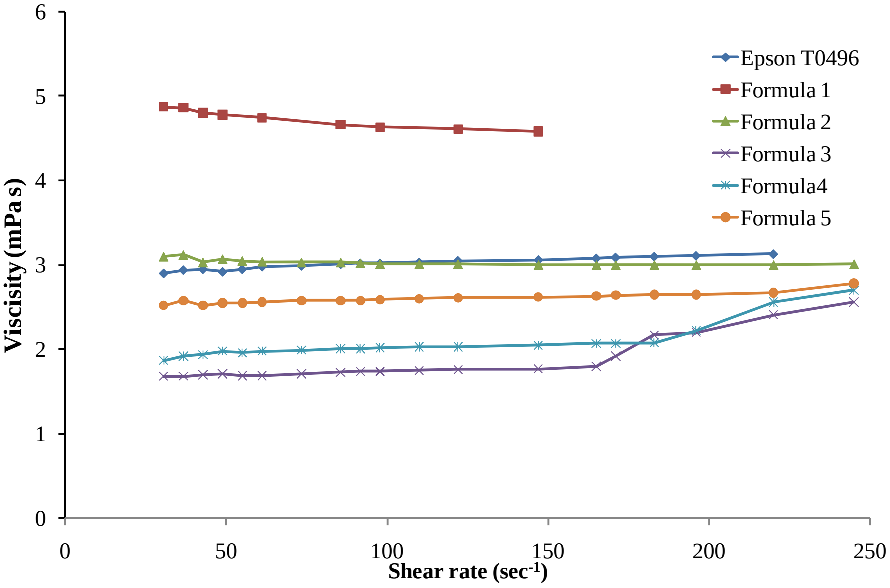
Table 4.5: Chemical composition and properties of the formulated light magenta inks

	Chemical concentration (%w w^{-1})			**Properties**		
Formula	**Diethylene glycol**	**Glycerol**	**Surfactant**	**pH**	**Viscosity (mPa s)**	**Surface Tension (mN m^{-1})**
1	10	10	-	7.78	4.58	50.75
2	5	5	-	7.79	3.01	52.1
3	5	5	0.1	8.18	2.56	40.7
4	5	10	0.1	6.89	2.7	41.8
5	10	12	0.1	7.13	2.78	41.3
Epson T0496				9.05	3.13	29.7

For the ink formula 1-3, the pHs were adjusted with 10% w v^{-1}NaOH. Viscosity was measured at 25 °C, spindle # S00, rotational speed, *100 s^{-1}, **170 s^{-1}.



(a)



(b)

Figure 4.5: Comparison of the light magenta inks and Epson ink; (a) The relationship of shear stress - shear rate, (b) Viscosity

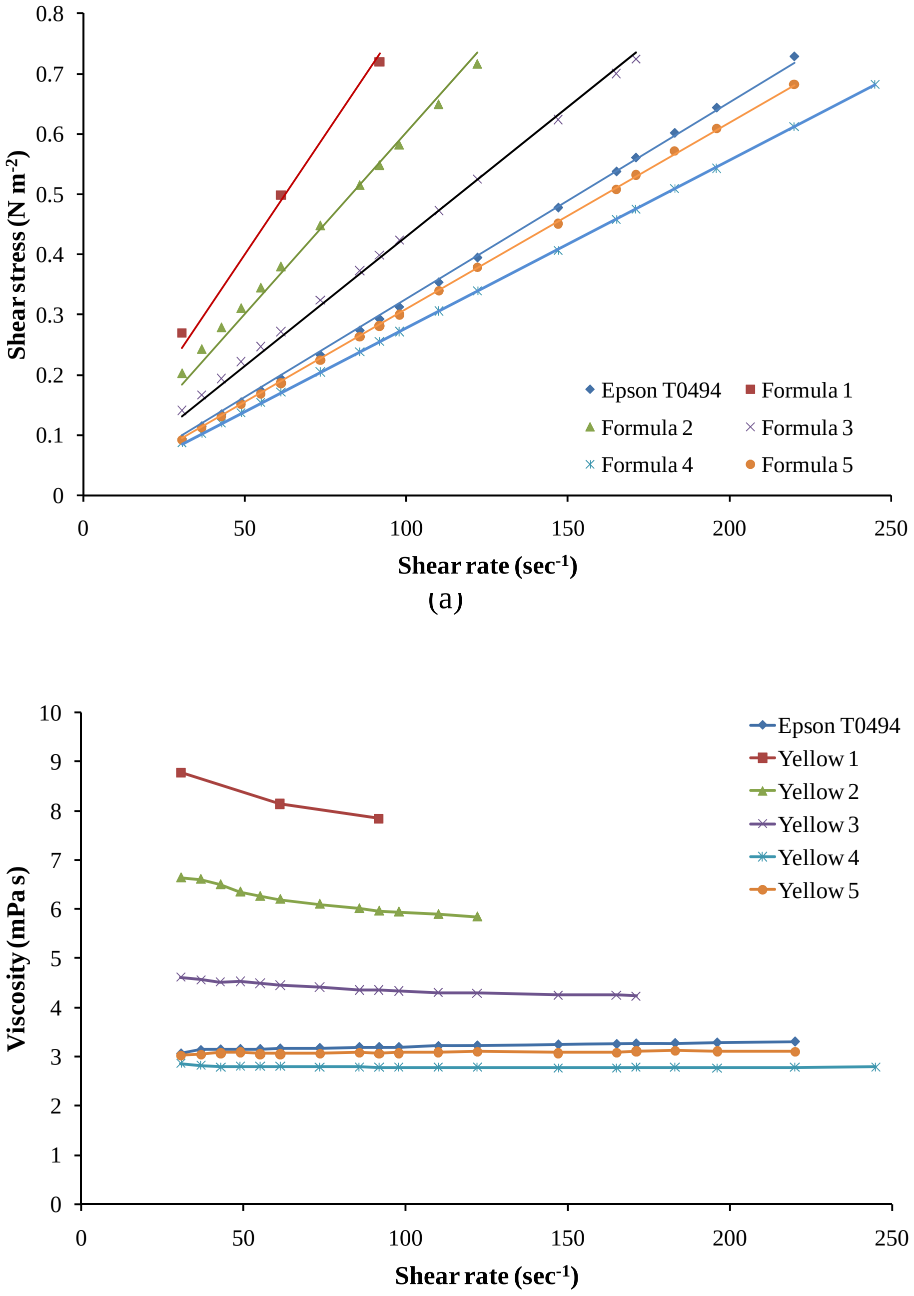
4.1.1.6 Yellow ink formulation

The five yellow ink formulations are shown in the Table 4.6 and Figure 4.6. The inks formulations 3-5 showed the Newtonian fluid property. Comparison between the ink formulations 3 and 5 showed that the high viscose inks were found in the alkaline-adjusted inks formulations 1-3. One thing is observed that the ink formulations 1 and 2 exhibit the inevitable shear thinning behavior. The non-adjusted pH inks had very low ink viscosity (around 3 mPa s). The ink formulation 5 containing the diethylene glycol-to- glycerol ratio of 1/2 had the similar viscosity with the commercial ink. The surface tensions of the inks without surfactant were very high (51-54 mN m^{-1}) while the surfactant added inks had much lower ink surface tension.

Table 4.6: Chemical composition and properties of the formulated yellow inks

Formula	**Chemical concentration (%w w^{-1})**			**Properties**		
	Diethylene glycol	**Glycerol**	**Surfactant**	**pH**	**Viscosity (mPa s)**	**Surface Tension (mN m^{-1})**
1	10	10	-	7.25	7.88*	51.5
2	5	5	-	7.32	5.85*	53.5
3	5	2.5	0.1	7.88	4.23**	42.8
4	2.5	2	0.1	6.77	2.97**	45.6
5	5	2.5	0.1	6.89	3.1**	45.5
Epson T0494				9.19	3.31**	32.9

For the ink formula 1-3, the pHs were adjusted with 10% w v^{-1}NaOH. Viscosity was measured at 25 °C, spindle #S00, rotational speed, *120 s^{-1}, **220 s^{-1}



(a)

(b)

Figure 4.6: Comparison of the yellow inks and Epson ink; (a) The relationship of shear stress – shear rate, (b) Viscosity

Among the five ink formulations, the effect of the pH on the ink viscosity was found. A nonlinear relation between pH and viscosity was found. The higher ink viscosity was found in the magenta and yellow inks having the higher pHs in general.

The yellow inks No.3 ink has pH = 7.88, viscosity = 4.23 mPa s while the no.1 ink has pH = 7.23, viscosity = 7.88 mPa s. In theory, increases in the ink viscosity could possibly be caused by the emulsion binder in the ink. The binder used, Printofix binder 710, is a self-crosslinking acrylate-based copolymer dispersion with butadiene. The emulsion polymer contains the large fractions of hydrophilic (typically carboxyl-rich) monomers. This high degree of hydrophilicity means that the particulate nature of the dispersion is lost when the acidic dispersion (pH<7) is added to alkaline environment of the ink formulation (pH>7). That means, when the emulsion polymer binder is in the acidic condition, the polymer can coagulate and then precipitate. When NaOH solution was added to the emulsion inks, the emulsion polymer chains can better disentangle and disperse which allow the pigment particles to be dispersed in the emulsion system. The resulting structures, which range from massively swollen polymer networks to polymer chain dissolved in the aqueous phase, influence the rheology of the ink formulation. Apart from the increase in the viscosity of aqueous phase due to dissolved polymer molecules, which are stiff chain at the pH of the ink formulation, polymer bridges also form between the pigment particles (Urban and Takamura, 2002). Because of the acrylate emulsion polymer having the pH of 6.14 and the addition of alkaline solution (10% w v^{-1}NaOH) to make the pH of the inks to be greater than 7, both conditions affect pH and viscosity of the inks, therefore, the formulations 4 and 5 were not adjusted with the alkaline solution (10% w v^{-1}NaOH) for comparison of the ink properties The ink formulations No.1 and No.2 gave very high viscosity in all 6 color formulations. The variables so designed generate high viscosity and reduce the extent of jettability upon which shall be discussed in the later sessions. In the same manner, ink formulations No.3, 4, 5 are also to be discussion about their jettability more precisely later.

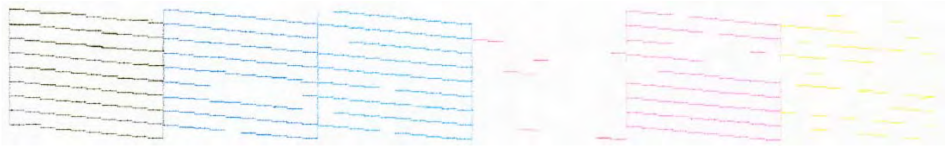
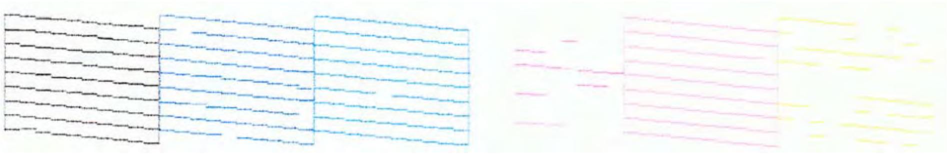
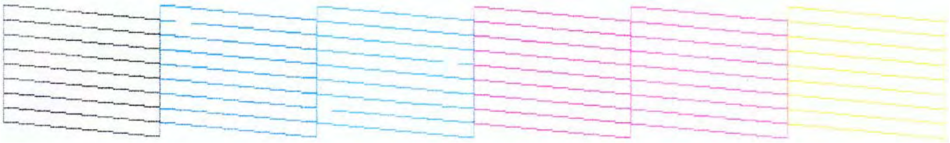
Surfactant is one ingredient for delivering the pigment and the binder from the ink to substrate through the print head. The commercially low HLB surfactant is used to lower the surface tension, so the ink can wet the nozzle capillary to establish and maintain the meniscus at the nozzle tip. The low HLB surfactant is also a major factor which determines the interaction between the ink and the substrate; therefore it controls or affects wetting, bleeding, dot-gain, dot quality and ultimately the image quality (Fu, 2006). The commercially low HLB surfactant, surfynol 104 (HLB = 5), 0.1% by weight is used to reduce the surface tension of the ink system as shown in the result with a range 39 to 46 mN m^{-1}.

Printofix 710, the binder for the current inkjet ink controls the viscosity of the system and promotes droplet formation. The polymer also serves to bind the colorant and provides the adhesion to the surface. It is also responsible for the properties of the application of the inks. In common with other ingredients in ink, the binder must exhibit good stability upon storage and during use. The binder rheological properties influence jet break-up and high end use performance, such as good adhesion, is constrained by the low viscosity requirements of the fluid required for printer operation. When this is combined with the application of a thin film in a form of a dot, it proves to be an extremely demanding set of properties required for the polymer.

4.1.2 Printing behavior

The jetting patterns of each ink color (black, cyan, light cyan, magenta, light cyan and yellow) of the ink formulations 3, 4 and 5 are shown in Table 4.7.

Table 4.7: The print pattern of the ink formulations

<table>
<tr><th rowspan="2">Ink formulation</th><th colspan="6">Ink color</th></tr>
<tr><th>Black</th><th>Cyan</th><th>Light cyan</th><th>Magenta</th><th>Light magenta</th><th>Yellow</th></tr>
<tr><td>3</td><td colspan="6"></td></tr>
<tr><td>4</td><td colspan="6"></td></tr>
<tr><td>5</td><td colspan="6"></td></tr>
</table>

Assessment of the jettability of inks is essential in the process of developing ink formulations and in the process of verifying suitability of inks for print-head assemblies. Currently, evaluation of jettability of inks has largely relied on testing the inks in the print-head assemblies concerned, which, whilst being a reliable method, does have its drawbacks. Thus, there is a high level of risk of the inks of poor performance properties damaging the printhead. Lin and He (2008) suggested that assessment of the jettability of inks through the creation of a “jettability plot” using easily measurable properties such as viscosity and surface tension of the ink. Thus, for each print-head assembly, a jettability plot can be created which contains jettable and un-jettable regions. Consequently, the assessment of the jettability of an ink can be achieved by measuring the viscosity and surface tension of the ink followed by determination of the region the viscosity/surface tension combination falls in.

The jetting failure of the black ink formulation was not detected for the ink viscosity and surface tension in the range 3.00 to 3.27 mPa s and 38.7 to 40.6 mN m^{-1} which possessed the Newtonian fluid.

For the cyan ink formulation, the jetting failure was, however, detected in the ink formula 3 with the ink viscosity equaling to 3.86 mPa. The printed pattern showed a nearly complete jetting pattern for the ink viscosity and surface tension in the range of 2.85 - 3.33 mPa s and 43.1 - 44.4 mN m^{-1}, a Newtonian fluid.

The jetting failure in the light cyan ink formulation was detected for all ink formulations except ink formulation 5. However, the complete jetting and printed pattern was found in ink formulation 5 with the ink viscosity and surface tension, in a range of 2.81 to 3.01 mPa s and 39.9 to 42.3 mN m^{-1} as mentioned earlier. The complete failure of the jetting and printed pattern of ink formulation 3 could be caused by clogging resulted from the pH effect.

The jetting failure of the magenta ink was detected in ink formulations 3 and 4. The magenta ink color in ink formulation No.3 had pH = 7.47 and viscosity =18.7 mPa s, a very high value and this causes jetting problem. Both magenta ink formulations showed the higher viscosity which made both inks an injection problem from the nozzle. The ink formulation 5 showed the complete jetting and printed pattern with an ink viscosity = 3.44 mPa s and surface tension = 42.1 mN m^{-1}, the Newtonian fluid.

The jetting failure of the light magenta ink formulation was detected in the ink formulation 3 and a large amount of jetting failure found also in the ink formulation 4. Both ink formulations showed the shear-thickening fluid property. The ink formulation 5 showing the complete jetting and printed pattern with ink viscosity =

2.78 mPa s and surface tension = 41.3 mN m^{-1} was found with the Newtonian fluid property.

Likewise, the jetting and printed failure pattern was detected in the yellow ink for the ink formulations 3 and 4. The jetting failure of the ink formulation 3 could possibly be caused by a flow problem of its ink. The complete jetting and printed pattern in the ink formulation 5 was obtained with the ink viscosity = 3.1 mPa s and surface tension = 45.5 mN m^{-1} with the Newtonian fluid.

Viscosity and surface tension are the controlling physical properties for drop formation. With respect to the latter, its dynamic value is important because of the very short time of flight available for chemical species to migrate to the surface of the drop. Thus its value tends to be near that of water. The static value plays a role in preventing the ink from weeping out of the print head when not jetting and the wetting the medium for good penetration. Viscosity affects jet dynamic via (1) viscous damping of the generated capillary wave, (2) the jet's velocity, which in turn changes its break-off length, and more importantly (3) the voltage window over which stable stimulation occurs without satellite formation of ink drop.

The criteria used to identify the two regions are based on the results as shown in Table 4.7. Figure 4.7 illustrates the plots of ink viscosity vs. ink surface tension to determine jettable region as shown by the two oval boundaries and un-jettable region outside the two oval boundaries. The big oval is for the six experimental ink sets while the small oval is for Epson commercial ink set. One can see that within the regimes of viscosity, the commercial ink set has a narrow map while the experimental ink sets have the wide map. Interestingly, the jettable experimental ink sets within the map can be used interchangeably.

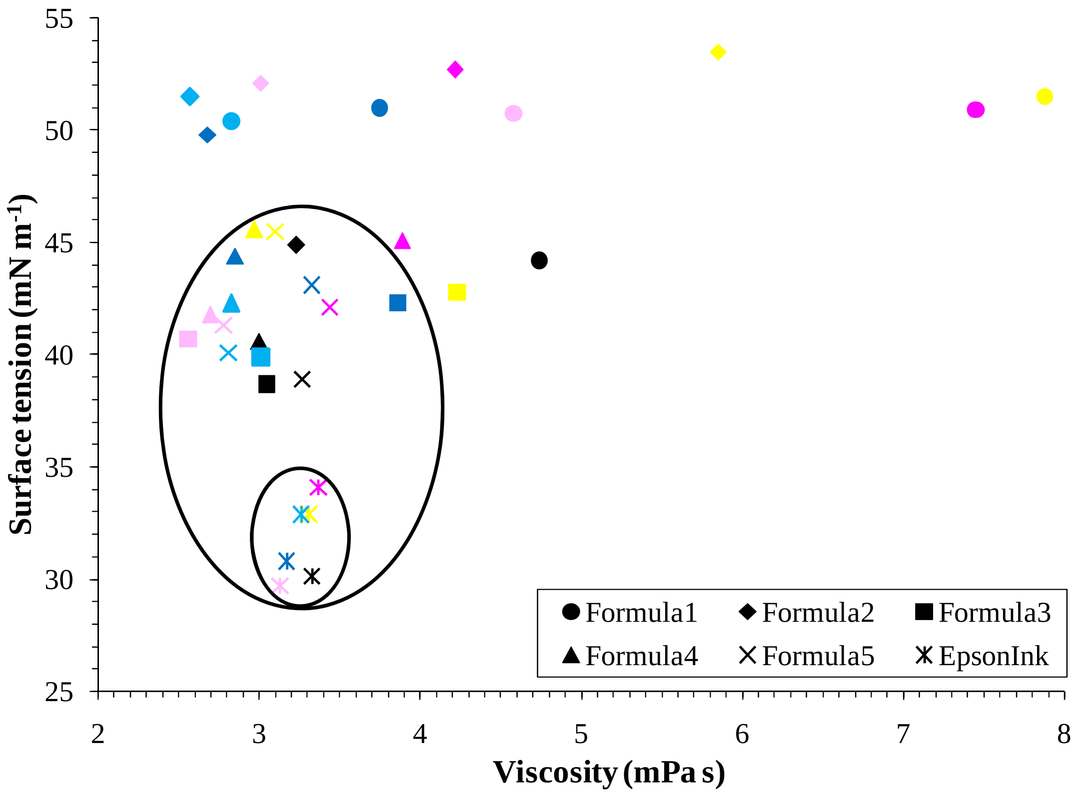


Figure 4.7: Plots of ink viscosity vs. ink surface tension to determine jettable and un-jettable regions (the color legends represent the ink colors)

Considering velocity and jettability of the ink, it is observable from the experiment that drop velocity produced by a pressurized ink-jet nozzle is expressed by two empirical constants; the fluid parameters of pressure, viscosity, and density; and the nozzle parameters. Le (1999) stated that the research and commercial inkjet print head eject at the rate of faster than 6000 drops s^{-1} with a measured ink channel of 0.001 inch in length and 25-30 µm in diameter. It is anticipated that at the current technology, the speed of drop ejection rate is far faster with finer droplet size in the femto scale. Even the latest piezo and thermal printing for graphic arts, the smallest size is one picoliter, they are 1000 times larger than the femto range. On the speed or frequency, the highest level is 25 KHz.

Applied pressure to the drops depends primarily on the shape and size of the nozzle and on fluid viscosity. In addition, the forced oscillation to cause a separation length of a jet is related to the voltage applied to a piezoelectric crystal, to disturbance growth rate, and to velocity. This condition is applicable to “normal” liquids (those having good stream stability) in this study having viscosities between 2–4 mPa s and dynamic surface tensions between 25 and 45 mN m^{-1}. Furthermore, the stream stability of the polymer solutions depends inversely on concentration and molecular weight which is related with the polymer viscoelastic character. However, measurements of jet velocity, separation length, and stream stability are not in the scope of current study.

4.1.3 Particle sizes and Zeta potential

Besides, viscosity and surface tension are found to be the controlling physical properties for drop formation and ejection, other physical parameters, such as, particle size and zeta potential are also the important factors for inkjet ink. The particle sizes of the inks must be measured after filtration to check for the oversized ink particles in a cartridge. The ink large particle sizes may clog the orifice of the printer during printing therefore filtration is a necessary requirement before printing. Table 4.8 shows that the six color inks have different average particle diameters depending on the types of pigments. The average particle sizes of the resulting inks and the binder are in the range of 100–300 nm and 160–300 nm, respectively. The zeta potential values of the ink formulations are in the range of (-35) to (-50) mV in that the inks have been charged negatively resulting from the presence of the sulphonic acid group ($-SO_3^-$). Zeta-potential of acrylate/styrene copolymer emulsion binder is also negative having a value of (-38) mV. Moreover, a dispersant on the pigment surface can migrate from the pigment surface during the ink preparation as indicated by a decrease in a zeta-potential from (-35) to (-50) mV compared to the zeta-potential of pigment dispersions (-50) to (-55) mV. The density of the ink was 1 g cm^{-3}. The square root of surface tension to viscosity ratios of the inks is relatively constant except that of magenta color. With the same ink chemistry, the penetration of the five inks is similar. In summary, the ink properties mentioned above confirm the acceptable behavior of the inkjet ink for a textile printing system**.**

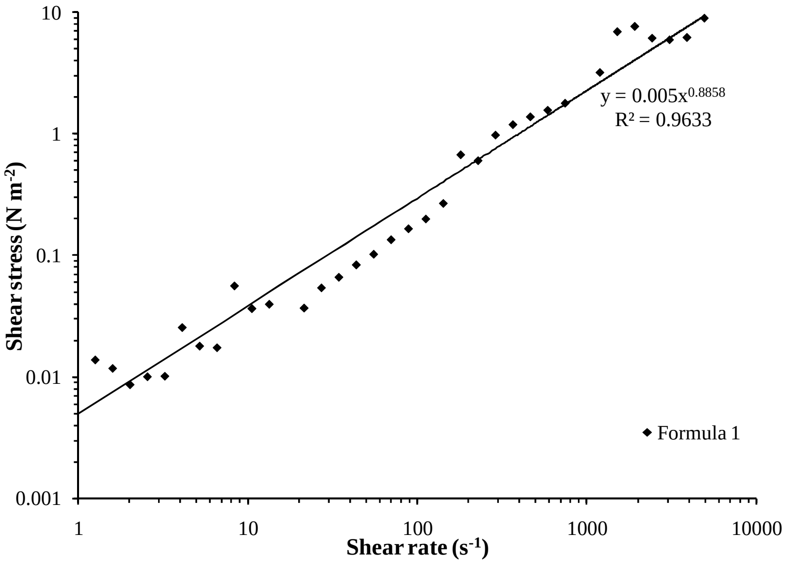
Table 4.8: Particle sizes and Zeta potential of ink formulation 5 and the binder

Color	**Properties**					
	Mass density (g cm^{-3})	**Viscosity (mPa s)***	**Surface Tension (mN m^{-1})**	$\sqrt{\frac{\gamma}{\eta}}$	**Particle size (nm)**	**Zeta-potential (mV)**
Black	1.07	3.27	38.9	3.50	173 ± 72	-49.4
Cyan	1.07	3.33	43.1	3.60	152 ± 78	-49.3
Light cyan	1.07	2.81	40.1	3.78	148 ± 77	-50.7
Magenta	1.04	3.44	42.1	3.23	207 ± 72	-44.6
Light magenta	1.06	2.78	41.3	3.85	197 ± 76	-35.3
Yellow	1.05	3.1	45.5	3.83	223 ± 88	-44.6

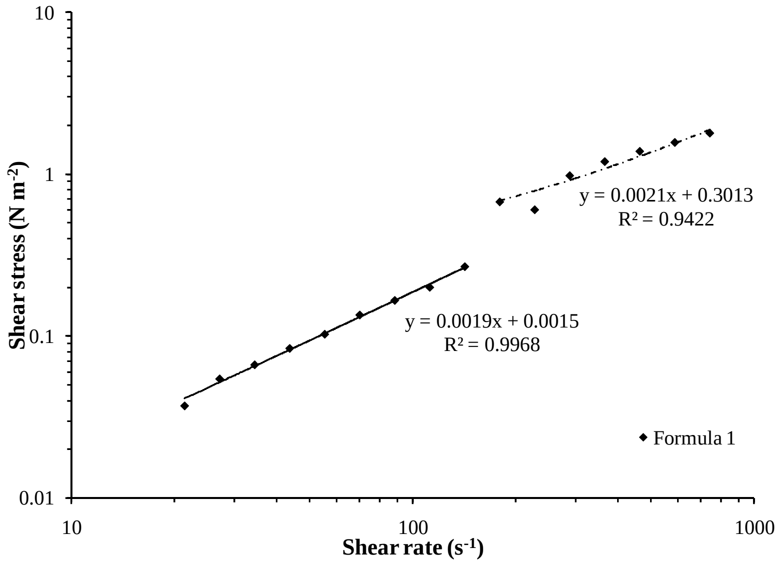
*at a shear rate of 220 s^{-1} and at 25 °C.

4.1.4 Effect of pigment-to-binder ratio on ink rheological property

Five experimental black inks with the pigment-to-binder (P/B) ratios of 1/0, 1/0.5, 1/1, 1/1.5, and 1/2 were prepared and measured for their viscosities at low and high shear rates. Adopting that the black inks are Newtonian fluid at low shear rates, the results are shown in Figures 4.8 to 4.12, and Table 4.9.

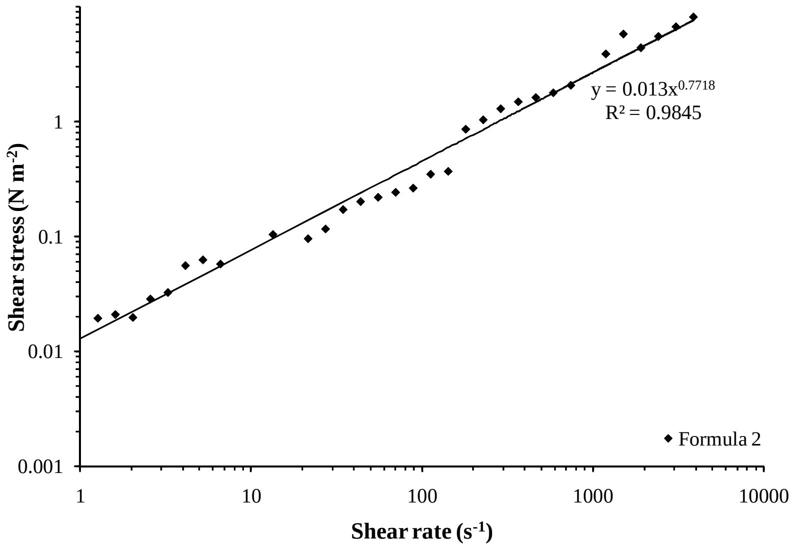


(a)

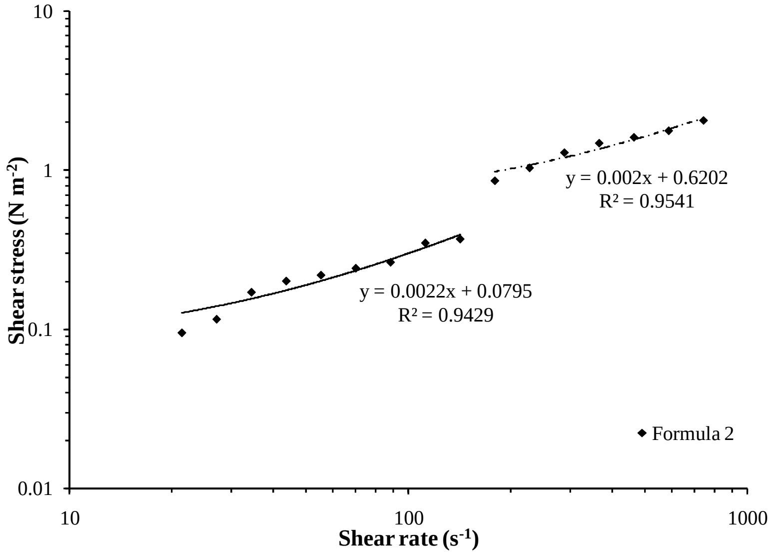


(b)

Figure 4.8: Rheological behavior of the ink formulation 1 with the P/B ratio 1:0; (a) at high shear rates (1-5000 s^{-1}), and (b) at low shear rates (21-741 s^{-1})

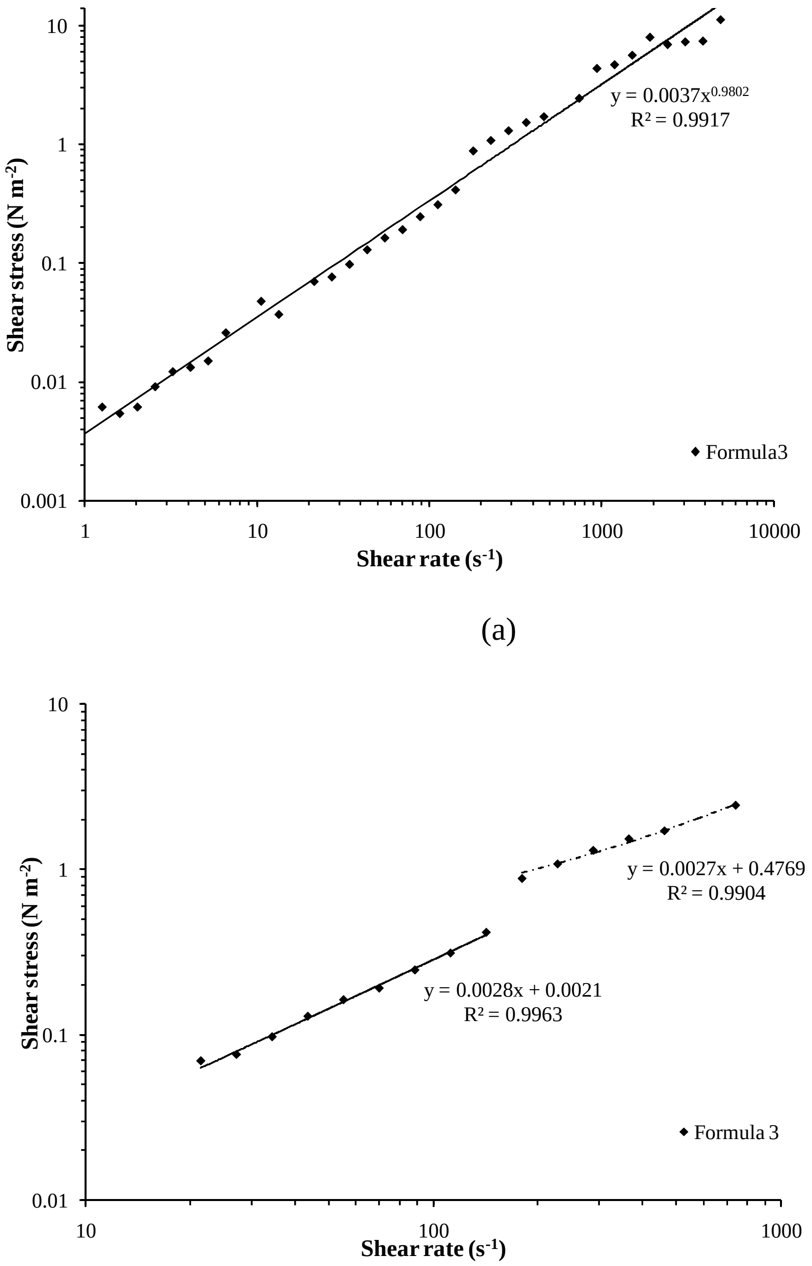


(a)



(b)

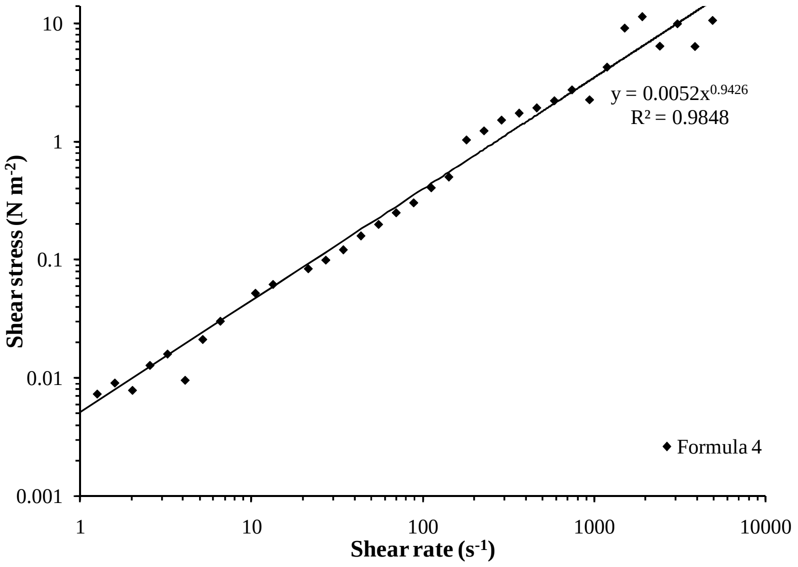
Figure 4.9: Rheological behavior of the ink formulation 2 with the P/B ratio 1:0.5; (a) at high shear rates (1-5000 s^{-1}), and (b) at low shear rates (21-741 s^{-1})



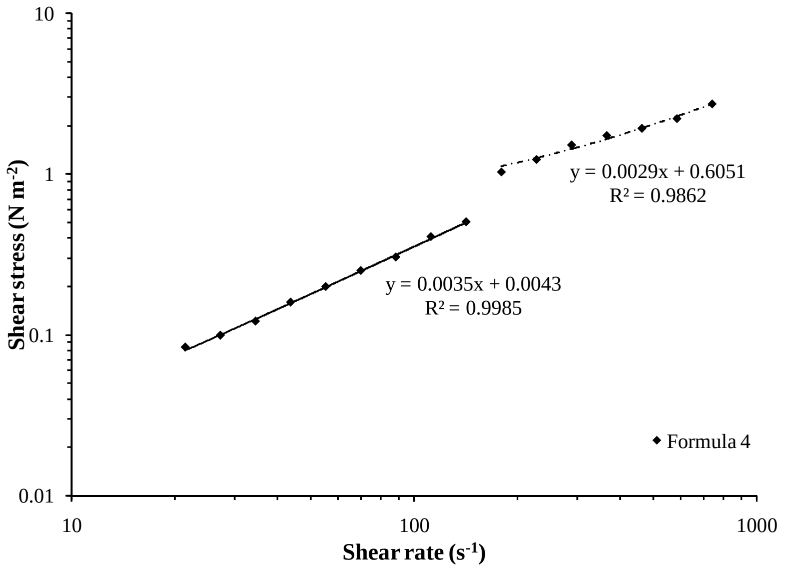
(a)

(b)

Figure 4.10: Rheological behavior of the ink formulation 3 with the P/B ratio 1:1; (a) at high shear rates (1-5000 s^{-1}), and (b) at low shear rates (21-741 s^{-1})

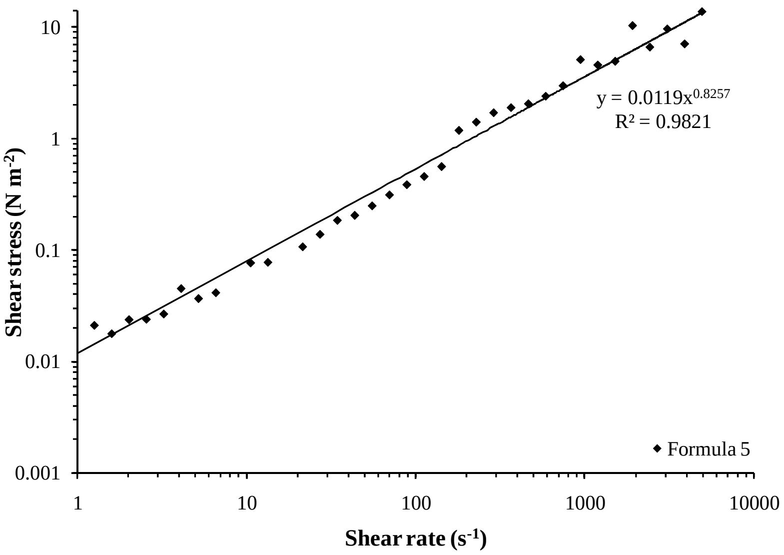


(a)

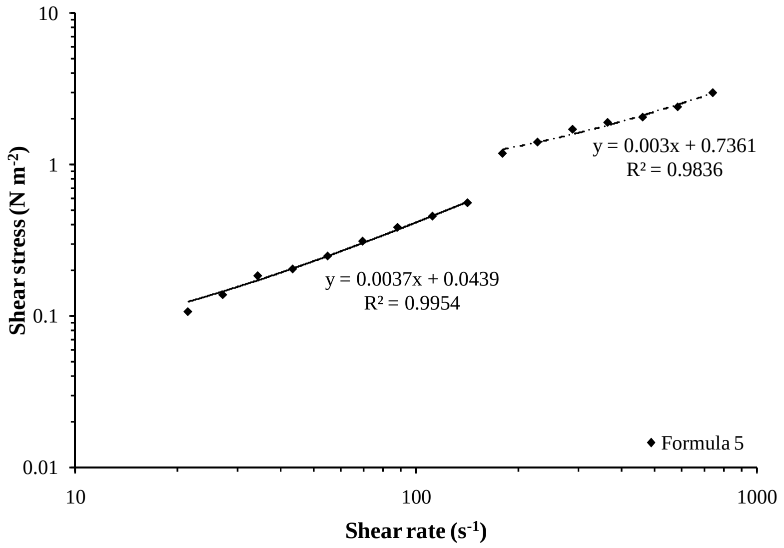


(b)

Figure 4.11: Rheological behavior of the ink formulation 4 with the P/B ratio 1:1.5; (a) at high shear rates (1-5000 s^{-1}), and (b) at low shear rates (21-741 s^{-1})



(a)



(b)

Figure 4.12: Rheological behavior of the ink formulation 5 with the P/B ratio 1:2: (a) viscosity vs. shear rate; the relationship of shear stress – shear rate (b) at high shear rates (1-5000 s^{-1}), and (c) at low shear rates (21-741 s^{-1})

Table 4.9: Pigment-to-polymer binder ratio and properties of the formulated black inks

Formula	Pigment-to-binder ratio	pH	**Properties**				
			Mass density (g cm^{-3})	**Surface Tension (mN m^{-1})**	**Viscosity (mPa s)**		
					High shear rate (s^{-1})	**Low Shear rate (s^{-1})**	
						21-142	**180-741**
1	1:0	8.84	1.07	31.2	2.1	1.9	2.8
2	1:0.5	8.33	1.07	34.9	2.4	3.1	3.3
3	1:1	8.22	1.08	36.6	2.6	2.9	3.7
4	1:1.5	8.17	1.08	38.4	2.7	3.6	4.1
5	1:2	8.43	1.08	39.6	2.9	4.2	4.5

The inks contained the fixed ingredients of diethylene glycol, 10.0; glycerol, 10.0; urea, 5.0; surfynol 104, 0.1; Deionized water, the volume was made up to 100% weight. The pH of the formulated inks is adjusted with 10 % w v^{-1} NaOH.

The high shear rate measurement, at 1-5000 s^{-1}, of the black ink sets gave further interesting data as follows. In essence, all the formulated inks exhibited a similar behavior, i.e., a Newtonian plateau at the low shear rate from the shear rate of 21 to142 s^{-1}, followed by a shear-thinning region between 180 to 741 s^{-1}shear rate. The rheological behavior of the formulated inks seemed to illustrate the Newtonian fluid with P/B ratios of 1:0.5 and 1:1. The shear thinning behavior of the inks, a common characteristic of polymer solution, are caused by the influence of polymer in the dispersion (Tielemans, 2008).

The black ink color is chosen as a model of pigment-to-binder study. Printofix 710 binder is used in a form of dispersion with the solid content of 40%. Increasing the binder content decreases pH of the ink slightly and cannot increase the mass density even more binder content is added. On the other hand, viscosity and surface tension are increased significantly. Higher contents of the binder in the ink increase shear rate and shear stress of the fluid, i.e., the higher viscosity of the black inks. Surface tension of the ink fluid is increased due to the increase of the acrylate content.

4.1.5 Thermal property of the binder

DSC thermograms of the binder measured in a dispersion form are shown in Figure 4.13. The first heating process had two sharp endothermic peaks. The onset of the first peak exhibited the endothermic reaction at -1.39 °C and 1.72 °C. The thermogram did not give a slope to the glass transition temperature (T_g). However, Szafran *et al.* (2001), reported that a T_g = 1.7 °C was found for acrylate/styrene emulsion binder at the butyl acrylate-to-styrene-to-acrylic acid ratio of 65: 28.5: 6.5 %weight.

The T_m of the present binder found at 1.7 °C suggests that the binder is elastic and exhibits a viscous deformation at room temperature (Sapchookul *et al.*, 2003). The second peak was for the cross-linking reaction that is onset at 91.16 °C, suggesting that the printed fabrics should be subjected to heat treatment at 92 °C, or higher, for a strong pigment fixation with polymer binder. Printofix 710 binder is a self-crosslinking copolymer which can crosslink without the addition of an external crosslinking agent in the ink ingredient because its molecule contains crosslinkable functional groups to crosslink at an appropriate condition. The thermal property mentioned above is for the purpose for a confirmation that the heat treatment used to perfectly fix the printed fabric in this study should be at 120 °C. We investigated the fixing time and found that the appropriate fixing time of 8 min is a time for the current pigment-binder ink film to fix and adhere to the silk fabrics.

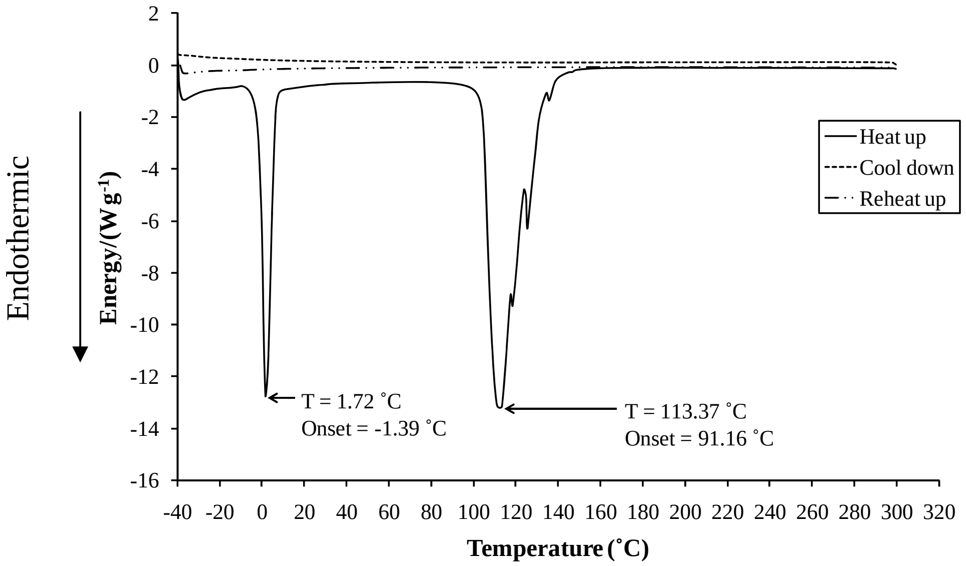


Figure 4.13: DSC diagrams of the binder

4.2 Characterization of the pretreated and printed silk fabrics

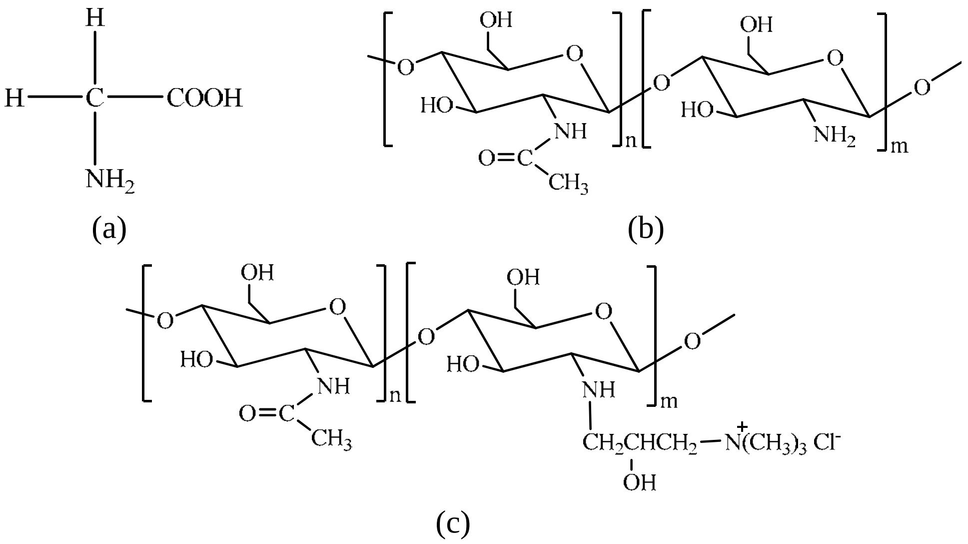


Figure 4.14: Chemical structures of (a) glycine, (b) chitosan, (c) *N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan chloride (HTACC)

Chemical structures of the three pretreatment reagents are presented in Figure 4.14. Their structures, molecular weight and loading shall be considered as some influencing factors for fabric stiffness.

4.2.1 Effect of the pretreatment solution on stiffness of the treated fabrics

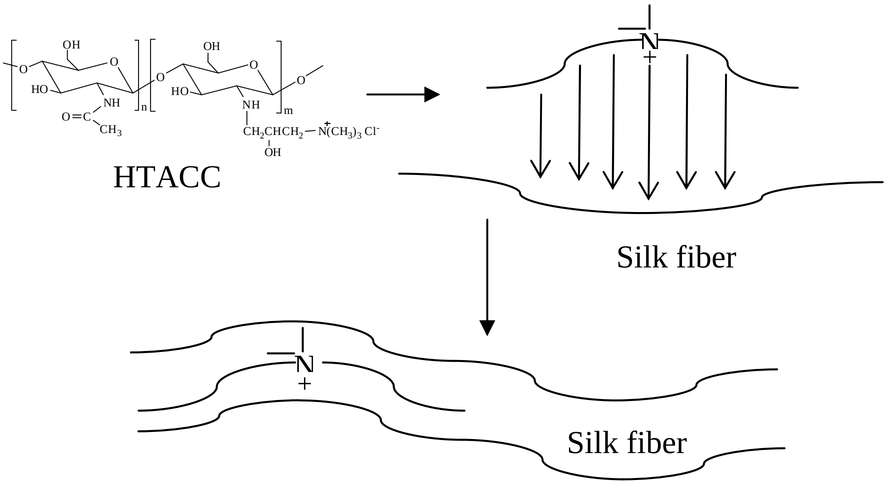
Bending stiffness is generally regarded as the ability of a material to drape and evaluated by bending length measurement. JISL 1096:1999 Stiffness (45°cantilever method) was used to determine the stiffness of the fabric sized 2 cm x15 cm. The average bending lengths in the warp and weft directions obtained from five measurements were used to determine the bending stiffness. The flexural rigidity or stiffness is correlated with the bending length as shown in the equation 3.1 (Kiatkamjornwong *et al*., 2005).

Table 4.10: The properties of the pretreatment solutions

Pretreatment solution	**Viscosity (mPa s)**	**Surface Tension (mN m^{-1})**	**pH**	**Zeta-potential (mV)**
0.1% w v^{-1}chitosan	2.59	69.1	4.45	+51.8
1% w v^{-1} chitosan and 15% w v^{-1} glycine	12.30	56.9	4.86	+47.4
0.1% w v^{-1} HTACC	2.00	56.8	6.76	+36.6

The viscosity of the pretreatment solutions as shown in Table 4.10 plays a significant role in the stiffness of the fabrics because the higher viscous padding solution contained more padding mass. The higher bending length reflects the higher bending stiffness of the fabric. The effect of the pretreatment on fabric flexural rigidity (stiffness) of fabric is given in Table 4.11 and Figure 4.15.Generally, the higher molecular mass generates a high stiffness of the fabric. In this work, the molecular weight of CH is 57,000 g mol^{-1} and the calculated MW for HTACC synthesized at approximately 184,000 g mol^{-1} was used. It is generally known that chitosan pretreatment increases fabric stiffness. The main point is that the relatively high content of 1% chitosan causes the remarkably high viscosity of the pretreatment solution. The solution viscosity of 1% chitosan mixed with 15% glycine is very high due to their contents. One possible cause is that the ionic interaction (H-bonding) between the amino group of chitosan with the carboxylic acid group of glycine to result in a larger molecular size of pretreatment reagent to increase stiffness of the treated fabrics when it was cured at higher temperatures.

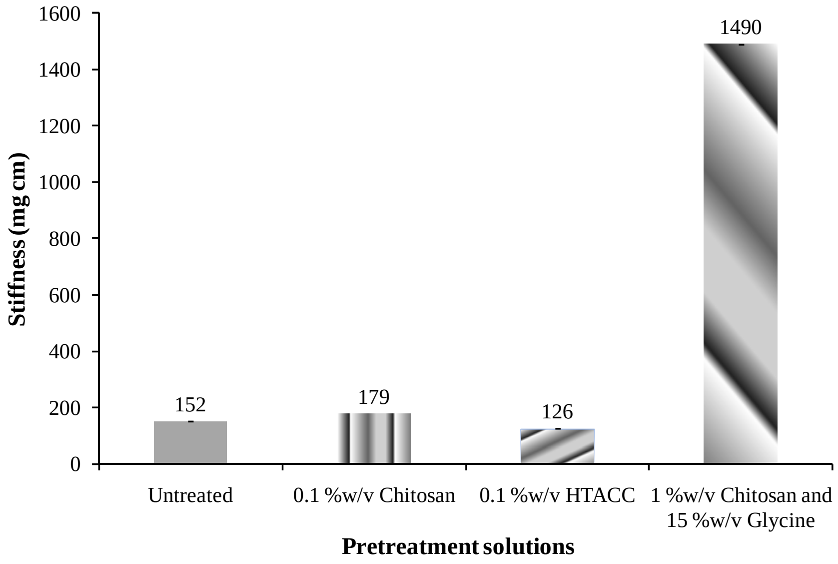
Although the number of threads per inch (warp × weft) is 87 by 78; the bending stiffness in the weft direction was remarkably higher than that of the warp direction as shown in Table 4.11. Bending stiffness of the silk fabrics treated with 0.1% HTACC decreased more than those of the untreated silk fabric. The HTACC produced a softer touch than those pretreated with chitosan at the same concentration even though the HTACC molecular weight is threefold higher. As expected, the bending stiffness of silk fabrics treated with 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine increased much more than the untreated silk fabric because the higher viscosity of chitosan and glycine pretreatment solution bundled the silk fiber together to become thicker and less flexible (Phattanarudee *et al*., 2009). The pretreatment generally increases the bending stiffness of the fabric since the bending stiffness depends on the amount of treating chemicals that deposit on the fabric surface. The fibers being grouped possess less flexibility and tend to resist bending. The long side chain of (2-hydroxyl-3-trimethylammonium) propyl chloride attached with the nitrogen atom of the amine occupies more spaces on the fabric which behaves somewhat like the cationic softener. Based on this proposed concept, the HTACC pretreated fabric rendered a soft touch to hand. Crutzen (1995) proposed the hydrophobic model of ditallow dimethyl ammonium chloride deposition on cotton along with the softening power of quaternaries, an adopted model for the current HTACC pretreatment can be given in Scheme 1 based on Crutzen proposal.



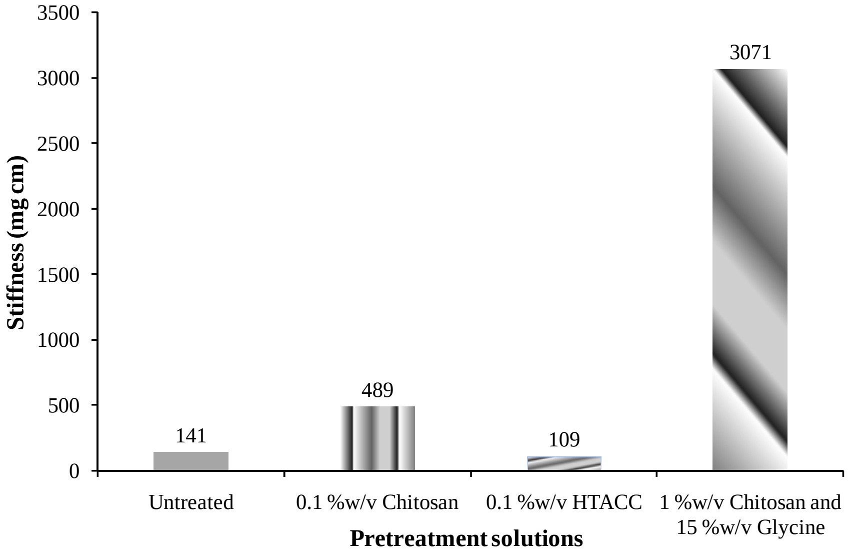
Scheme 1 Adopted Crutzen’s hydrophobic model for interaction of HTACC and the silk fabric

Table 4.11: Stiffness of the pretreated, unprinted silk fabrics

Pretreated fabrics	**Fabric mass per unit area (mg cm^{-2})**	**Stiffness (Bending length, cm)**		**Flexural rigidity (mg cm)**	
		Warp direction	**Weft direction**	**Warp direction**	**Weft direction**
Untreated	11.89±0.46	2.34±0.07	2.27±0.12	152±13	141±22
0.1 %w v^{-1} chitosan	10.89±0.30	2.54±0.09	3.54±0.26	179±19	489±103
0.1 % w v^{-1} HTACC	11.73±0.48	2.20±0.12	2.10±0.04	126±21	109±7
1 %w v^{-1} chitosan and 15 % w v^{-1} glycine	13.50±0.52	4.80±0.09	6.10±0.17	1490±87	3071±250



(a)



(b)

Figure 4.15: Stiffness of the untreated and pretreated silk fabrics in (a) the warp direction, and (b) the weft direction

4.3 Effect of the pretreatment solution on the print qualities

The color saturation of the inkjet ink depends greatly on the prior occurrence of capillary flow into the fiber and ink absorption on the fabric. Therefore, the chemical and physical properties including the environment are the two important prerequisite factors governing the color strength on the fabric surfaces.

4.3.1 Color and color gamut volume

The diagrams of a* b*, L* a*, and L* b* (Figure 4.16) of the printed silk fabrics indicate that the color gamut of the pretreated fabrics provided a wider color area than the printed colors on the untreated fabrics. The chroma of the printed silk fabrics in the L*C* diagram (Figure 4.17) shows the similar trend with the color gamut. The 1% $w\ v^{-1}$ chitosan mixed with 15% $w\ v^{-1}$ glycine, and HTACC pretreatments highly improved the chroma which is in agreement with the result of Kiatkamjornwong *et al.* (2007), while the color strength of the fabrics with HTACC pretreatments was the highest. The HTACC pretreatment can improve the color gamut of the printing inks because the HTACC molecule contains quaternary ammonium group from the conjugation of glycidyltrimethylammonium chloride to chitosan molecule to interact with the anionic pigments in the inks. The chitosan and glycine pretreatment could improve the color gamut of the printing ink because both of pretreatment molecules contain amino group (NH_2) which can be protonated to NH_3^+ groups in acetic acidic solution that increased the active sites on the silk fabric surface by reacting with the sulfonic acid groups on the pigment surface (Phattanarudee *et al.*, 2009) and to hold the pigmented inks on the printed areas.

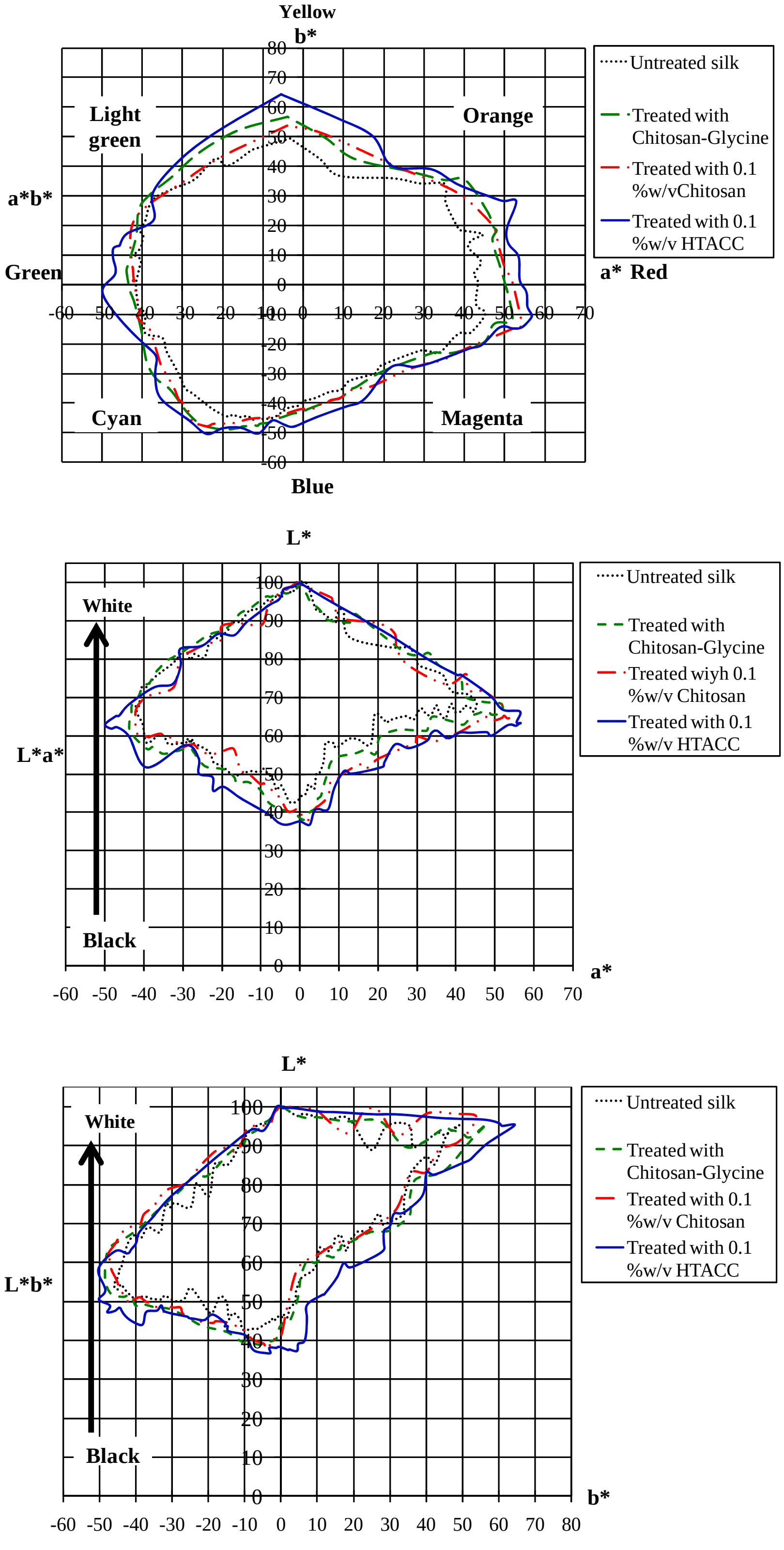


Figure 4.16: a*b*, L*a* and L*b* of the untreated and treated silks with various pretreatments

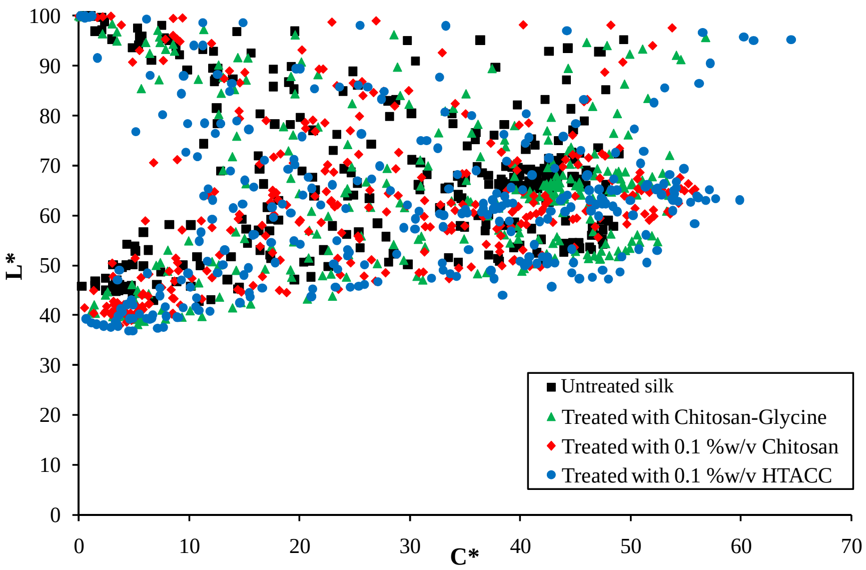


Figure 4.17: L*C* of the untreated and treated fabrics with various pretreatments

Table 4.12: Color gamut volume of the untreated and treated fabrics with various pretreatments

Pretreated fabrics	Gamut volume
Untreated	6099
0.1% w v^{-1} chitosan	6484
1% w v^{-1} chitosan and 15% w v^{-1} glycine	8098
0.1% w v^{-1} HTACC	9525

The color gamut volume of the printed silk fabrics pretreated with the three pretreatment agents is listed in Table 4.12. The untreated fabric and treated fabrics with 0.1% w v^{-1} chitosan, 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine solution, and HTACC solution gave the color gamut volumes of 6099, 6484, 8098 and 9525, respectively. The pre-treated silk fabrics with 0.1% w v^{-1} chitosan 1% w v^{-1}, chitosan mixed with 15% w v^{-1} glycine solution, and HTACC solution increase its individual gamut volume by 6.31%, 24.9% and 46.9%, respectively. The plausible reasons for the increase in gamut volume are the interaction of the positive charges in the pretreatment reagents with the anionic charges of the pigment.

4.3.2 Tone reproduction

A halftone pattern consisting of percent dot areas from 7% (highlight) to 91% (solid tone) at the grey level was printed onto the silk fabrics. The tone reproduction of the pretreated silk fabrics was higher than untreated silk fabric as shown in Figure 4.18. The plots indicate that the reproduced optical densities were higher for the pretreated silk fabrics. The pretreated fabrics with HTACC exhibited the higher optical densities than the other pretreated fabrics in the regions of highlight, mid tone and solid tone. The pretreated fabrics with chitosan exhibited the higher optical density than the other pretreated fabrics in the mid tone area from 30% to 70% dot area. The observed results can be explained by the ionic interaction between the cationic moiety of the pretreatment reagents with the anionic part of the pigment, i.e., the higher the interaction, the greater the color qualities.

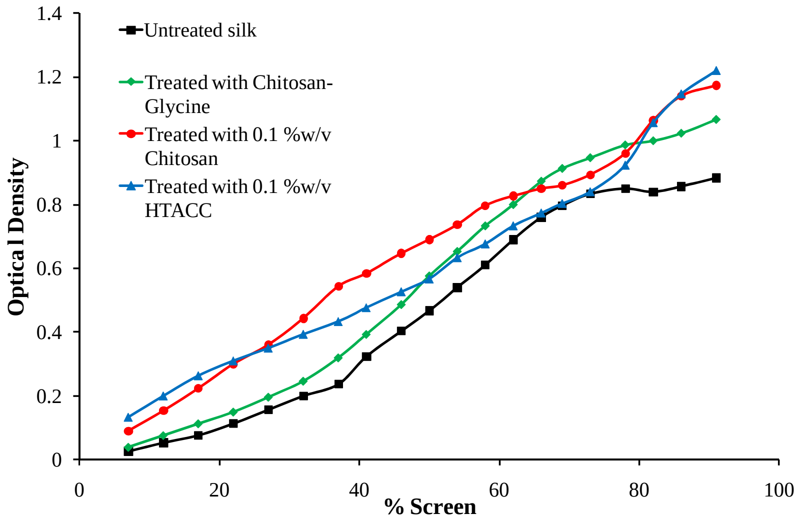
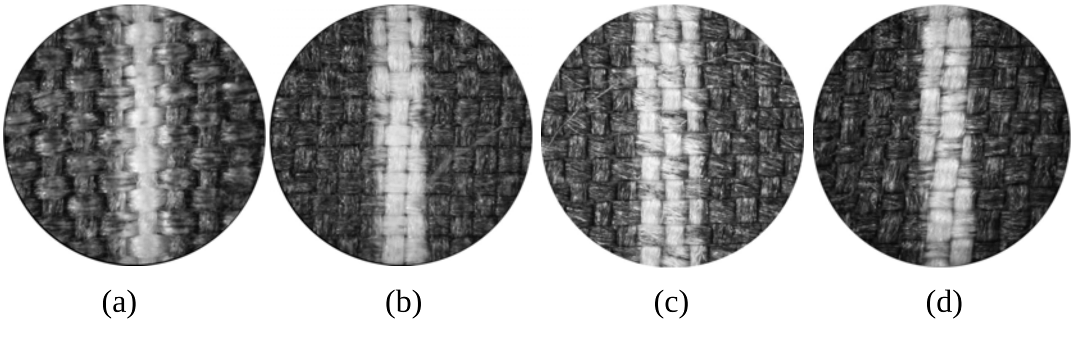


Figure 4.18: Effect of the pretreatments on tone reproduction of the untreated and treated silk fabrics

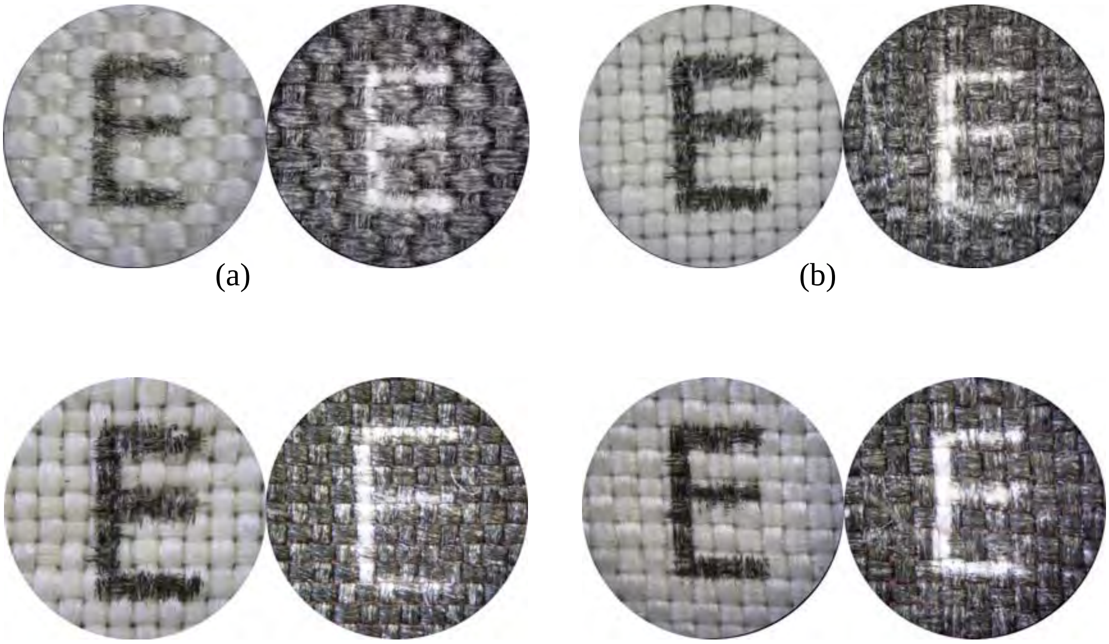
4.3.3 Inter-color bleeding and outline sharpness of the printed fabrics

The sharpness appearances of the printed silk fabrics assessed with inter-color bleeding of the yellow line printed on the black color background and the character "E" outline sharpness on the Gretag Macbeth test chart are shown in Figures 4.19 and 20. The results suggest that the bleeding occurs and spreads more in the untreated fabric. The surface of the pretreated silk fabrics has the tighter yarn and gives a smooth surface than that of the untreated fabric. The sharpness of the printed character "E" was evaluated in both the positive and negative characters pretreated with various pretreatment solutions. In principles, the good printed qualities are sharpness, even ink deposition and legibility. The sizes of the positive characters are larger and shaper than those of the negative characters. The ink spreading in both vertical and horizontal directions was observed more in the untreated fabric and less in all the treated fabrics. The printed positive and negative characters by HTACC pre-treatment gave much better legibility with the sharper edges, evenly printed color densities and higher contrast between the letter and the background than the other printed silk fabrics. It is anticipated that the ionic interaction as mentioned above may play a role in controlling the inter-color bleeding and outline sharpness properties.



(a) (b) (c) (d)

Figure 4.19: Optical photographs of the printed silk fabric with three pretreatment agents: (a) without pretreatment, pretreated with (b) 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine, (c) 0.1% w v^{-1} chitosan, and (d) 0.1% w v^{-1} HTACC (x4)



(a) (b)

(c) (d)

Figure 4.20: Optical photographs of the outline sharpness of printed character “E” on the printed fabrics with three pretreatment agents: (a) without pretreatment; pre-treated with (b) 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine, (c) 0.1% w v^{-1} chitosan, and (d) 0.1% w v^{-1} HTACC (x4)

4.4 Effect of the pretreatment solution on the fabrics color fastness

4.4.1 Light fastness

Table 4.13 shows the results for the light fastness of the formulated ink colors printed on the pretreated fabrics. The pretreatment reagent did not affect the light fastness of the fabrics at all. The light fastness for all the printed silk was acceptable with the commercial standard, i.e., the industry generally accepts light fastness at level 5 for the pigment printed fabrics. In addition, the result did not indicate the effect of pigment concentration on light fastness property in comparison with those occurred in the dye-based inks (Kobayashi, 2006). The yellowing by the cationic polymer is a known disadvantage. However, Our result cannot conclude this negative phenomenon, because the amount of cationic polymer loading is relatively low. The excellent light fastness property can be due to the strong interaction of the pretreatment agent with the anionic surface-modified pigmented inks besides the better endurance of pigment particles with light. In addition, the pigment classes used in inkjet inks are the high performance pigments which generally inherent the better light fastness by the pigment itself. In addition, the crosslinkable binder (Printofix 710) can synergistically absorb the UV energy to extend the light fastness of the pigments.

Table 4.13: Light fastness of the printed silk fabrics

Pretreated fabrics	**Color change (Rating)**					
	Black	**Cyan**	**Light cyan**	**Magenta**	**Light magenta**	**Yellow**
Untreated	>6	>6	>6	>6	>6	>6
0.1% w v^{-1} chitosan	>6	>6	>6	>6	>6	>6
1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine	>6	>6	>6	>6	>6	>6
0.1% w v^{-1} HTACC	>6	>6	>6	>6	>6	>6

Blue wool references range from 1 (very low light fastness) to 8 (very high light fastness). Due to limitation in lamp availability, the higher rating cannot be obtained

4.4.2 Wash fastness

Table 4.14 shows the color fastness to washing of the printed silk with various pretreatments. All of the printed silks were found to be acceptable. The color change ratings of wash fastness with all pretreatments were improved based on the grey scale assessment. The color strength (K/S) of the printed silk fabrics measured before and after the washings is presented in Table 4.15. The K/S values of the process pigment colors for the pretreated silk were higher than those of the untreated silk, and those pretreated with 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine gave the higher K/S value than HTACC pretreated fabrics. The degree of fixation results as shown in Table 4.16 gives a similar trend line with the K/S values. The degree of fixation retains at a higher level than 90% of color for the process colors with the pretreatment with 1% w v^{-1} of chitosan mixed with 15% w v^{-1} glycine solution, and 0.1% w v^{-1} HTACC solution. The reason for the high color fixation can be caused by mainly the binder (Printofix 710) which can self-crosslinking polymerization (covalent bonding) when it is cured by heat. It is anticipated that interaction with the pretreatment reagents or the interaction between the pretreatment agent and the surface modified anionic pigments via ionic bonding, a weak bonding, cannot synergistically increase the fastness significantly. The covalent bonding between the fabric and the ink binder is reflected in the untreated fabrics because the binder can self polymerize and protect the pigments in its polymerized film.

The current research found that the extent of washing fastness and the K/S values reflected the degree of fixation as it directly interrelated, i.e., the higher the washing fastness, the greater the degree of washing fixation became. The degree of fixation of the printed cyan color on the treated fabrics is lower than that of the untreated fabrics, possibly be caused by the solubility of pretreatment reagents in the water. When the printed fabrics were fixed by heat cure and washed in the detergent solution, some of the unfixed pretreatment reagent that bind with the ink particles can dissociate from the surface of the printed fabric. However, the wash fastness for all the printed fabrics was acceptable within the commercial standard scale, that is, the industry generally accepts wash fastness at the level 4 for the printed fabrics.

Table 4.14: Wash fastness of the printed silk fabrics

Pretreatment	Ink color	Rating		
		Color change	Wash fastness	
			Cotton	Silk
Untreated	Black	4	3-4	4
	Cyan	4	4	4
	Light cyan	4	4	4
	Magenta	4	4-5	4-5
	Light magenta	4	4-5	4-5
	Yellow	4	4	4
0.1% w v^{-1} chitosan	Black	4	3-4	4
	Cyan	4-5	4	4-5
	Light cyan	4-5	4	4
	Magenta	4-5	4	4
	Light magenta	4-5	4-5	4-5
	Yellow	4-5	4	4
1% w v^{-1} chitosan and 15% w v^{-1} glycine	Black	4-5	3-4	4
	Cyan	4	4	4
	Light cyan	4-5	4-5	4
	Magenta	4-5	4-5	4-5
	Light magenta	4-5	4	4
	Yellow	4-5	4	4
0.1% w v^{-1} HTACC	Black	4-5	3-4	4
	Cyan	4-5	4	4
	Light cyan	4-5	4	4
	Magenta	4-5	4	4
	Light magenta	4	4	4
	Yellow	4-5	3-4	4

Wash fastness ratings: 5 for no color change/staining, 4 for slight color change/staining, 3 for noticeable color change/staining, 2 for considerable change/staining and 1 for excessive color change/staining

Table 4.15: K/S of the printed silk fabrics before and after washing

Pretreated fabrics	K/S of the printed silk											
	Black		**Cyan**		**Light cyan**		**Magenta**		**Light magenta**		**Yellow**	
	Before washing	**After washing**	**Before washing**	**After washing**	**Before washing**	**After washing**	**Before washing**	**After washing**	**Before washing**	**After washing**	**Before washing**	**After washing**
Untreated	6.84	6.43	2.81	2.79	2.59	2.00	3.06	2.46	2.26	2.05	4.26	4.05
0.1% w v^{-1} chitosan	6.28	6.21	3.53	3.13	3.23	2.84	4.09	3.59	3.23	3.20	4.62	4.31
1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine	8.70	8.25	5.06	4.83	4.41	4.11	3.95	3.84	3.56	3.30	6.91	6.23
0.1% w v^{-1} HTACC	7.69	7.19	3.11	3.03	2.31	2.3	4.00	3.82	3.58	2.93	5.47	5.24

Table 4.16: Degree of fixation of the printed silk fabrics before and after washing

Pretreated fabrics	Degree of fixation (%)					
	Black	**Cyan**	**Light cyan**	**Magenta**	**Light magenta**	**Yellow**
Untreated	93.25±1.25	95.74±3.21	78.07±0.97	82.74±2.58	89.39±4.22	95.61±0.84
0.1% w v^{-1} chitosan	94.19±5.98	91.38±2.88	88.96±0.75	89.92±2.75	95.42±4.11	90.93±2.13
1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine	94.88±2.59	94.01±1.46	91.91±2.18	96.78±1.59	95.59±2.59	91.50±1.40
0.1% w v^{-1} HTACC	94.06±0.60	96.88±0.33	97.30±2.32	96.75±2.16	85.80±3.64	95.82±1.61

The number of replication is three and three readings for each replication.

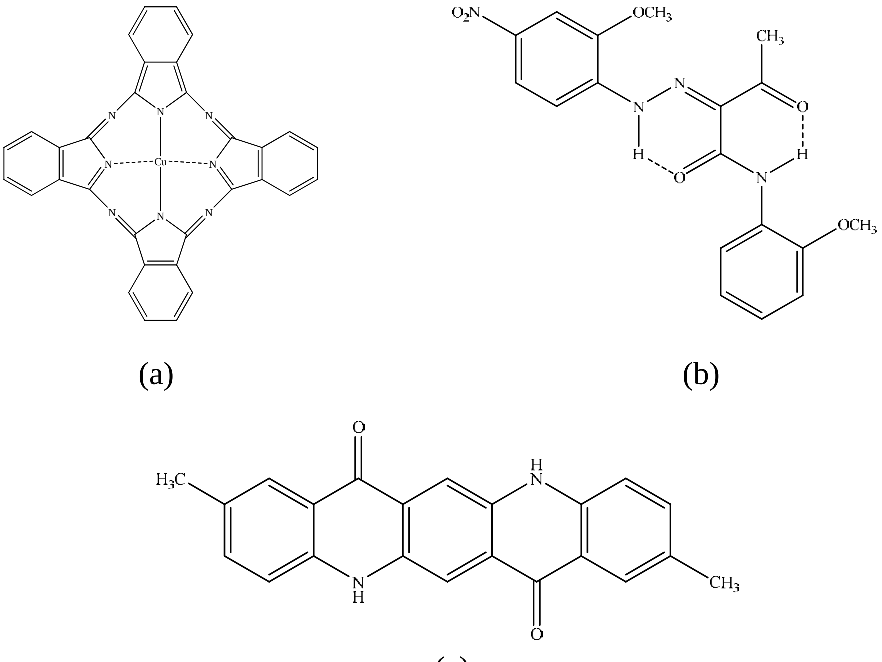
4.5 The interactions between the pretreatment solution and pigment by spectroscopic methods

4.5.1 Confirmation of functional groups of the dispersed pigment and the pretreatment reagent by FT-IR

The molecular structures of the pigmented inkjet inks as shown in Figure 4.21 are confirmed by FT-IR Spectroscopic method, suggesting the complicated spectra (Figure 4.22 and Table C1). The band of the cyan pigment (Figure 4.22 (a)) at 1609 and 1506 cm^{-1} are attributed to C=C stretching of aromatic moiety, and the band at 1506 cm^{-1} is due to C=N stretching.

The IR spectrum of the magenta pigment (Figure 4.22 (b)) shows the band at 1606 and 1504 cm^{-1} are attributed to the C=C stretching of aromatic moiety. Also, the NH stretching of the amino group is found at 3266 cm^{-1}.

Figure 4.22 (c) illustrates the IR spectrum of the yellow pigment in which the bands at 1594 and 1519 cm^{-1} are due to the C=C stretching of aromatic moiety and the band at 1552 cm^{-1} is the N=N stretching. These spectra support the band of S=O stretching of the -SO_3^- (sulfonic acid) group at around 1300, 1100 cm^{-1} by the pigment manufacturer (Cabot Company) and modified with the sulfonic acid group before ink preparation.



(a) (b)

(c)

Figure 4.21: Chemical structures of (a) the cyan pigment, C.I. pigment blue 15:4; (b) the magenta pigment, C.I. pigment red 122; and (c) the yellow pigment, C.I. pigment yellow 74

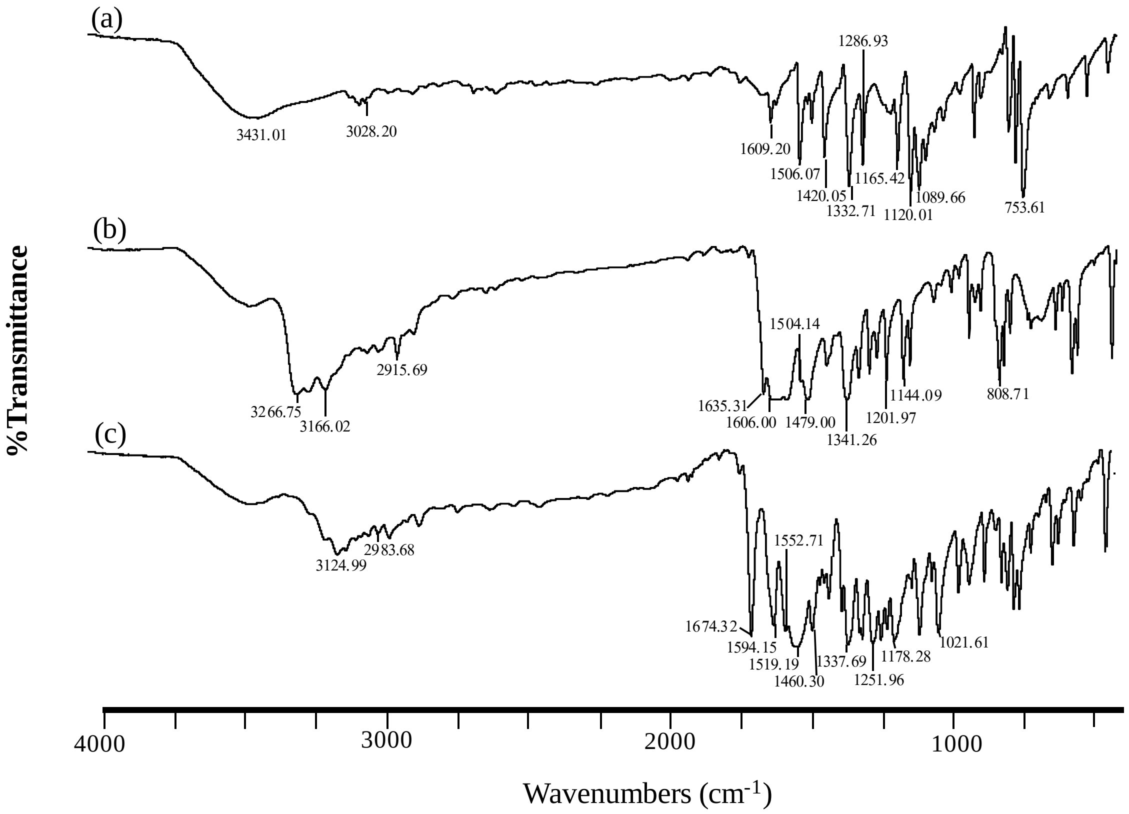


Figure 4.22: Infrared spectra of (a) cyan pigment, C.I. pigment blue 15:4, (b) magenta pigment, C.I. pigment red 122, (c) yellow pigment, C.I. pigment yellow 74

Chemical structures of (a) glycine, (b) chitosan, (c) *N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan chloride (HTACC) have been illustrated in Figure 4.14 and Table C2. The IR spectra of chitosan and HTACC are given in Figure 4.23. From spectrum (a) of Figure 4.23, chitosan shows the overlapped peak of N-H stretching and O-H stretching at 3436 cm^{-1}, and O-H bending at 1421 cm^{-1}. The strong characteristic peaks of chitosan at 1655, 1594, 1378 and 1250 cm^{-1} are assigned to the C=O stretching of amide I, N-H bending of amine in amide II, -NHCO stretching of amide and C-N stretching for amide III, respectively. In addition, the weak characteristic peaks at 1151, 1082, and 1027 cm^{-1} are ascribed to the C-O (bridge) stretching, C_3-OH and C_6-OH stretching, respectively. The IR spectrum (b) of HTACC in Figure 4.23 also shows that the peak of N-H bending of the amine group of chitosan at 1594 cm^{-1} disappears suggesting that the amino group of chitosan had reacted with glycidyltrimethylammonium chloride and the quaternary ammonium groups of $N^{+}(CH_3)_3$ were incorporated. In addition, it also shows the presence of the peak of C-H bending of trimethylammonium groups at 1478 cm^{-1}.The IR spectra (c) of glycine in Figure 4.23 shows that the peaks of N-H stretching of NH_3^{+} and N-H bending at around 3100 cm^{-1} and 1600, 1500 cm^{-1}, respectively. Moreover, the band of amino acid at around 1400 cm^{-1} is due to the carboxylate anion. From the IR spectra, it is found that glycine is possibly dissociated to the $-COO^{-}$ and $-NH_3^{+}$ groups. The result suggests that the cationic charge of the amino group on the silk surface can react with the negative charges of the sulfonic acid group ($-SO_3^{-}$) present on the pigment surface which is a weaker hydrogen bonding and it is expected to have a less effect on color absorption.

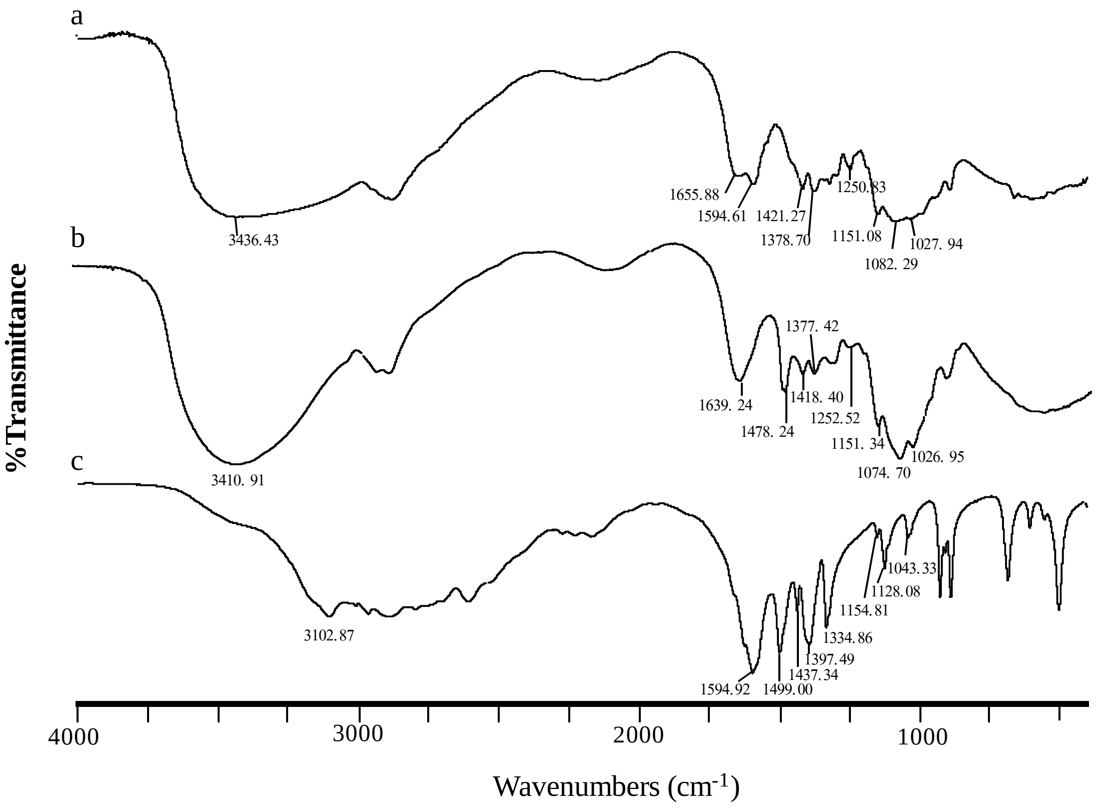
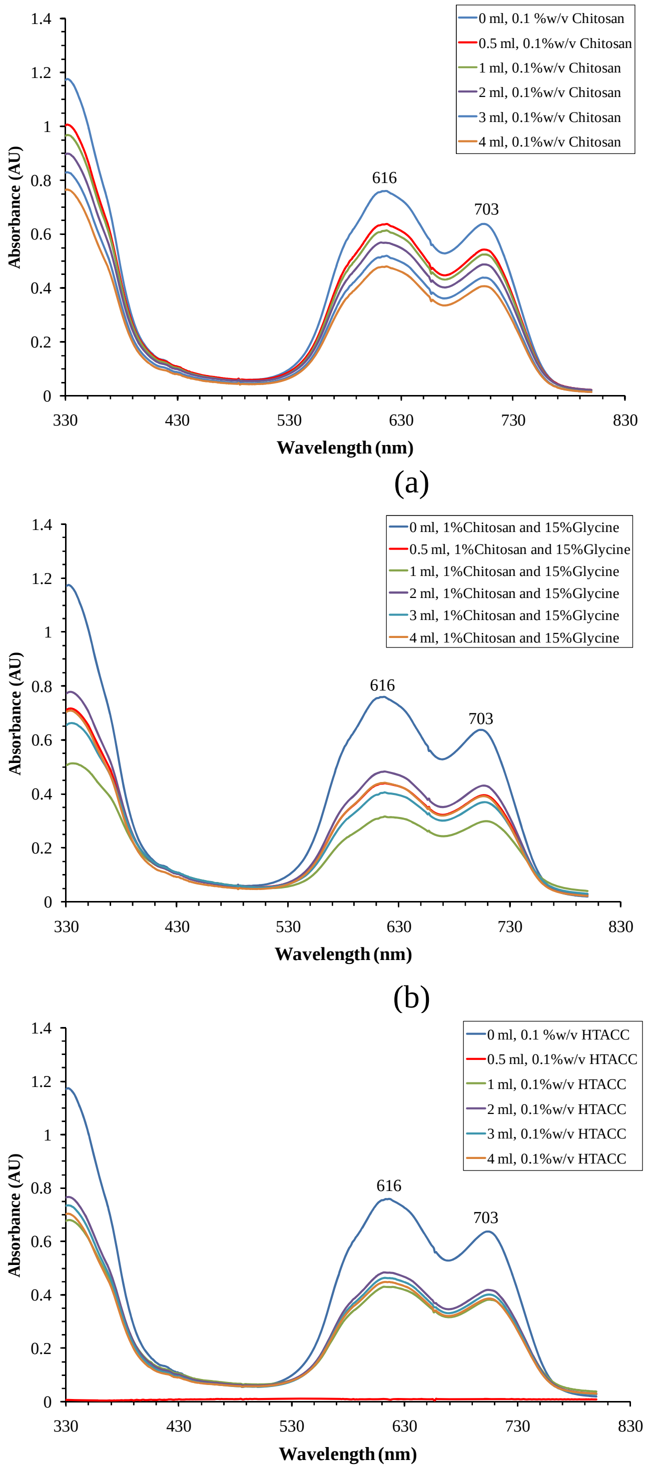


Figure 4.23: Infrared spectra of (a) chitosan, (b) HTACC, (c) glycine

4.5.2 Interaction of the pretreatment reagent and the pigmented inkjet inks

Pigment particle coagulation is an important step in the formation of an inkjet image. The size of the formed colorant flocs determines how deeply the colorant penetrates into the substrate and hence has a significant impact on image quality namely optical density, gloss, chroma, etc. (Yu and Gottberg, 2004). In this research, the interaction of the pretreatment reagents and the sulfonic acid containing pigments of the inks are expressed in the difference of absorbance at its maximum wavelength after the mixing as shown in Figures 4.24-4.26 and summarized in Tables 4.17-4.19. The sulfonic acid containing pigments are found in C.I. pigment blue 15:4, C.I. pigment red 122 and C.I. pigment yellow 74. The chemical structures are shown in Figure 4.21.

Two λ_{max} peaks in the UV/vis absorption spectra of both the cyan ink and the mixture of cyan ink and pretreatment agents are found at 616 and 703 nm as shown in Figure 4.24 and Table 4.17. The absorbance of the filtrate after filtration decreased with increasing amounts of the pretreatment reagent for the case of 0.1% w v^{-1} chitosan. Normally, the plot of aggregation efficiency is the direct way to express the interaction between the anionically modified pigments and cationic pretreatment. On the other hand, the untreated pigment concentration in a dispersion form after the complete coagulation can be used as an alternative and indirect method to assess the mentioned interaction. Both methods can correlate to the extent of color fixation and color yield. In the case of 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine, and 0.1% w v^{-1} HTACC, the marked difference in the absorbance was observed to decrease to the lowest readings with 1 ml of chitosan mixed with glycine solution, and the zero value with 0.5 ml of HTACC solution. One can summarize that HTACC is probably the best pretreatment reagent among the three investigated here.



(a)

(b)

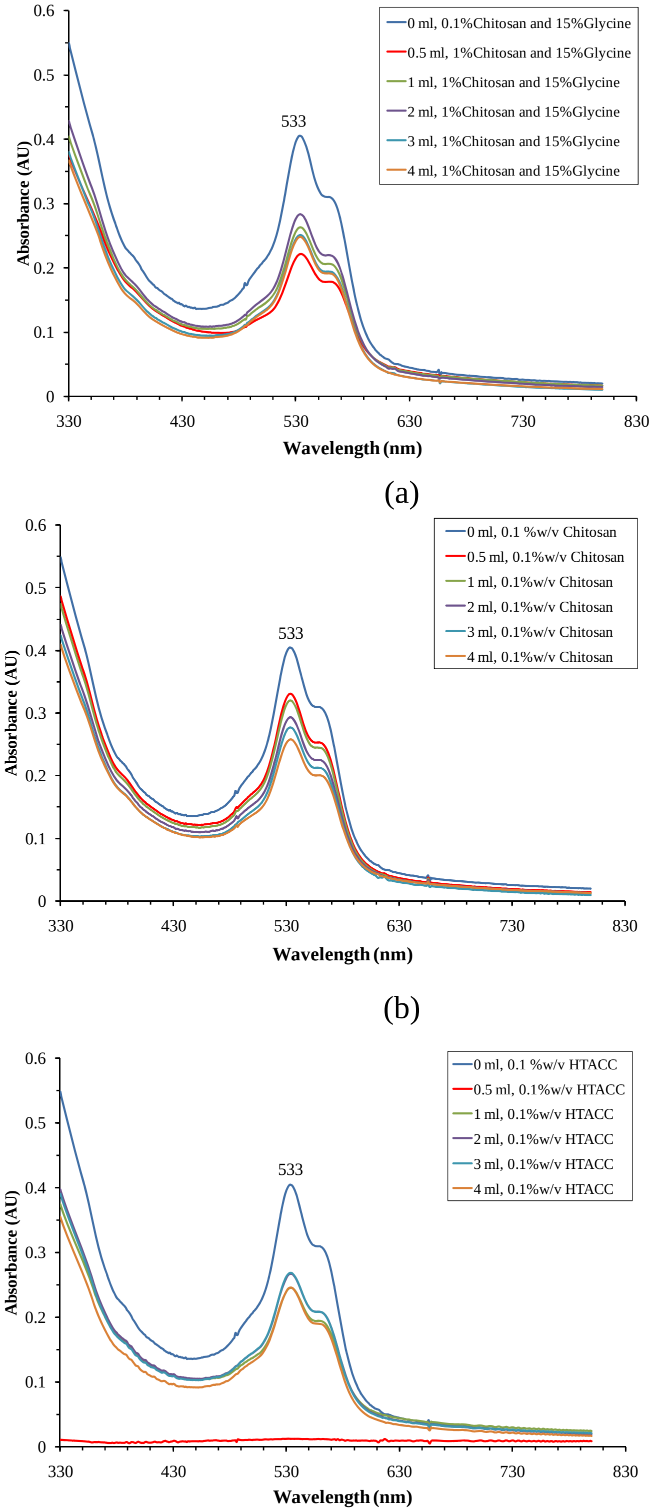
(c)

Figure 4.24: UV-Visible absorption spectra of the cyan ink in 0.5, 1, 2, 3 and 4 ml of the pretreatment solutions: (a) 0.1% w v^{-1} chitosan, (b) 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine, (c) 0.1% w v^{-1} HTACC

Table 4.17: The absorbance (λ_{max}) value of diluted cyan inks and pretreatment solutions

Pretreatment solution	Volume of pretreatment solution (ml)	Absorbance reading at λ_{max} after 24-h mixing	
		616 nm	703 nm
1% w v^{-1} chitosan and 15% w v^{-1} glycine	0	0.7593	0.6371
	0.5	0.4382	0.3929
	1	0.3144	0.2946
	2	0.4822	0.4285
	3	0.4059	0.3680
	4	0.4403	0.3895
0.1% w v^{-1} chitosan	0.5	0.6369	0.5428
	1	0.6130	0.5246
	2	0.5685	0.4878
	3	0.5196	0.4395
	4	0.4799	0.4076
0.1% w v^{-1} HTACC	0.5	0.0097	0.0114
	1	0.4308	0.3822
	2	0.4833	0.4182
	3	0.4640	0.4019
	4	0.4484	0.3864

The λ_{max} absorptions of the magenta ink and the mixture of this ink and the pretreatments are observed at 533 nm (Figure 4.25 and Table 4.18). The absorbance decreased with increasing amounts of the pretreatment reagent in the case of 0.1% w v^{-1} chitosan. In the cases of 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine, and 0.1% w v^{-1} HTACC, the marked difference in the absorbance value was observed to decrease to the lowest readings (the zero reading) with 0.5 ml of chitosan mixed with glycine solution and with 0.5 ml of HTACC solution.



(a)

(b)

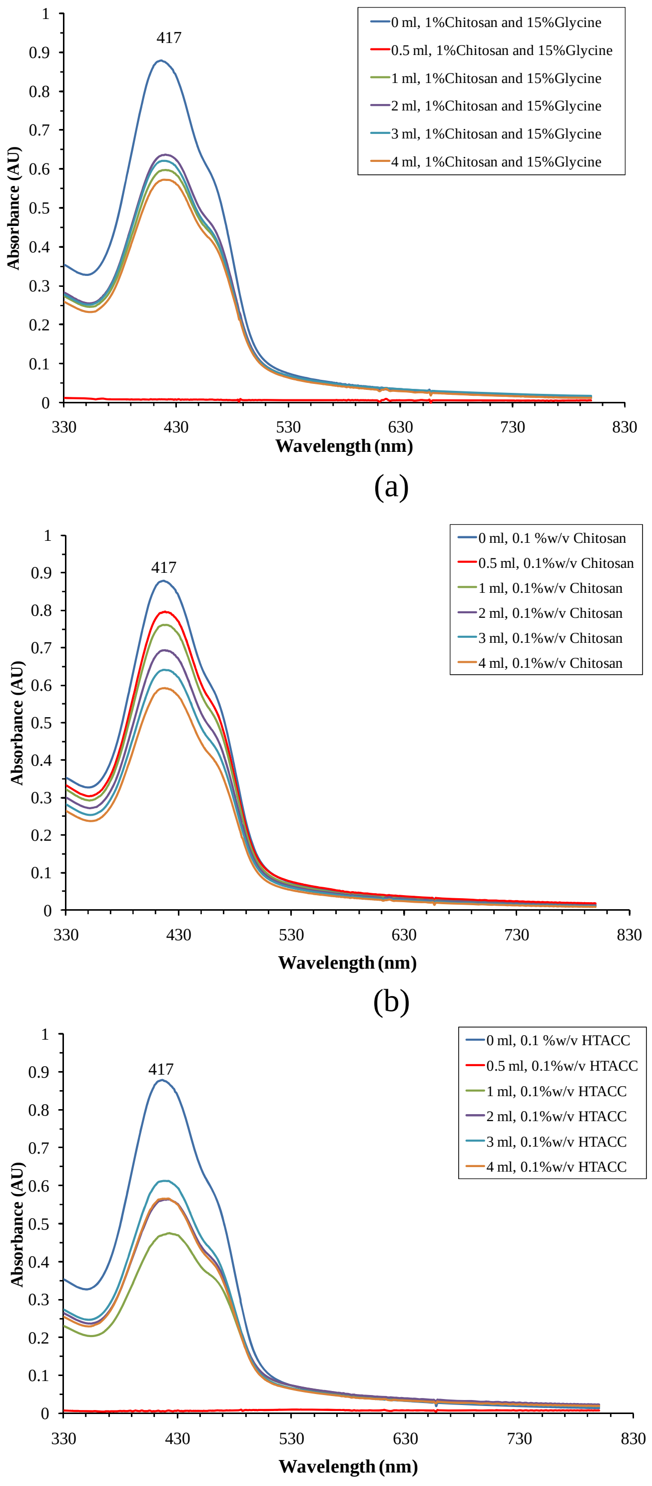
(c)

Figure 4.25: UV-Visible absorption spectra of the magenta ink in 0.5, 1, 2, 3 and 4 ml of the pretreatment solutions: (a) 1% w v^{-1} chitosan and 15% w v^{-1} glycine, (b) 0.1% w v^{-1} chitosan, (c) 0.1% w v^{-1} HTACC

Table 4.18: The absorbance (λ_{max}) value of diluted magenta inks and pretreatment solutions

Pretreatment solution	Volume of pretreatment solution (ml)	Absorbance reading at λ_{max}=533 nm after 24-h mixing
1% w v^{-1} chitosan and 15% w v^{-1} glycine	0	0.4050
	0.5	0.2205
	1	0.2626
	2	0.2828
	3	0.2501
	4	0.2477
0.1% w v^{-1}, chitosan	0.5	0.3309
	1	0.3200
	2	0.2932
	3	0.2772
	4	0.2577
0.1% w v^{-1} HTACC	0.5	0.0123
	1	0.2451
	2	0.2667
	3	0.2687
	4	0.2455

The λ_{max} absorptions of the yellow ink and the mixture of this ink and the pretreatments are observed at 417 nm (Figure 4.26 and Table 4.19). The absorbance decreased with increasing amounts of the pretreatment reagent in the case of 0.1% w v^{-1} chitosan. In the cases of 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine, 0.1% w v^{-1} HTACC, the marked difference in the absorbance value was observed to decrease to the lowest readings with 0.5 ml of chitosan mixed with glycine solution, and a zero reading with 0.5 ml of HTACC solution.



(a)

(b)

(c)

Figure 4.26: UV-Visible absorption spectra of the yellow ink in 0.5, 1, 2, 3 and 4 ml of the pretreatment solutions: (a) 1% w v^{-1} chitosan and 15% w v^{-1} glycine, (b) 0.1% w v^{-1} chitosan, (c) 0.1% w v^{-1} HTACC

Table 4.19: The absorbance (λ_{max}) value of diluted yellow inks and pretreatment solutions

Pretreatment solution	Volume of pretreatment solution (ml)	Absorbance reading at λ_{max}=417 nm after 24-h mixing
1% w v^{-1} chitosan and 15% w v^{-1} glycine	0	0.8785
	0.5	0.0084
	1	0.5971
	2	0.6349
	3	0.6203
	4	0.5712
0.1% w v^{-1}, chitosan	0.5	0.7941
	1	0.7609
	2	0.6925
	3	0.6419
	4	0.5927
0.1% w v^{-1} HTACC	0.5	0.0063
	1	0.4708
	2	0.5631
	3	0.6126
	4	0.5666

The interaction mechanism of the pigment and the pretreatment reagent can probably be explained by adopting the interaction mechanism of dye and chitosan. Chitosan has been extensively studied as an adsorbent for dye removal. Wong *et al.* (2003) suggests that the possible mechanisms of the adsorption process of chitosan and acid dye are likely to be ionic interactions of the colored dye ions with the amino groups on the chitosan. In aqueous solution, the acid dye is first dissolved and the sulfonic acid groups of acid dye ($D\text{-}SO_3Na$) are then dissociated and are converted to anionic dye ions as shown in Eq. (4.1).

$$D{-}SO_3Na \xrightarrow{H_2O} D{-}SO_3^- + Na^+ \quad (4.1)$$

Also, in the presence of H^+, the amino groups of chitosan ($R\text{-}NH_2$) became protonated as shown in Eq. (4.2).

$$R{-}NH_2 + H^+ \rightleftharpoons R{-}NH_3^+ \quad (4.2)$$

The adsorption process then proceeds due to the electrostatic attraction between these two counterions, as shown in Eq. (4.3).

$$R{-}NH_3^+ + D{-}SO_3^- \rightleftharpoons R{-}NH_3 \,\text{''''''''''}\, O_3S{-}D \quad (4.3)$$

Therefore, the difference in the degree of adsorption may mainly be attributed to the chemical structure of each dye. They found the different capacities of dye adsorption that may be due to the differences in the particle size of the dye molecules and the number of sulfonate groups on each dye. The results have demonstrated that monovalent and smaller dye molecular sizes have superior capacities due to the increase in dye/chitosan ratio in the system, enabling a deeper penetration of dye molecules to the internal pore structure of chitosan. In addition to ionic bonding, there seems to be a strong possibility that some of the dye atoms or molecular components such as N, S, O and benzene rings are hydrogen bonding with amino, acetyl and hydroxyl groups in the chitosan molecule. We can put pigment at the position of dye from which the pigments have the surface active functional group of sulfonic acid or its salt. Similar interaction mechanism can thus be presumed by the mechanism of the acid dye.

Colloidally stable pigment particles can be made to coagulate by modulating the repulsive stabilizing forces. The triggering mechanisms can come from the pretreatment reagent, for example, pH, ionic strength (salt from the substrate) or trigger solutions (Yu and Gottberg, 2002). The HTACC (the chitosan derivative) shows strong adsorption than that of chitosan which can be explained by the chemical groups on its molecule. The HTACC molecule has 2 chemical groups of the trimethylammonium group ($-N^+(CH_3)_3$) and hydroxyl group (-OH). HTACC becomes fully soluble with the neutral pH. Thus the interaction between the pigment and HTACC cannot be limited only by the pH. Commonly, the interaction between chitosan/pigment with electrostatic force depends on pH. The amino group ($-NH_2$) of chitosan are fully protonated to be positively charged ammonium ion ($-NH_3^+$) with acid having a pH lower than 5. When the chitosan solution and diluted ink were mixed, the pH of chitosan solution was changed to limit the adsorption of the pigment to the chitosan.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The inkjet textile printing system comprises three important production processes namely: ink preparation, textile design, and textile pretreatment. In the present work, the two main production processes for the inkjet textile printing were investigated. For the first purpose, the six colored, pigmented inks composed of black, cyan, light cyan, magenta, light magenta and yellow color inks were prepared by controlling the ink ingredients to exhibit the most important issues of rheological property and jet ability. For the second purpose, the influences of pretreatment reagents on color properties of the printed silk fabric, the image performance and the fabric performance, and their usage were evaluated.

5.1.1 Formulation of Pigmented inkjet inks and their properties

The six color inks were formulated with a constant pigment-to-binder ratio of 1/2. Various concentrations of diethylene glycol and glycerol used to fine tune the ink viscosity, surface tension and jettability patterns were compared with those generated by Epson original ink as shown in the test pattern images. The complete jetting patterns of the inks are the decision key point to select the proper ink formulation which was found to be the ink formulation 5.

Ink formulation 5 exhibits the Newtonian fluid property in each ink color. The black ink viscosity and surface tension are in the range of 3.00 to 3.27 mPa s and 38.7 - 40.6 mN m^{-1}, respectively. The cyan ink viscosity and surface tension are in the range of 2.85 to 3.33 mPa s and 43.1 - 44.4 mN m^{-1}, respectively. The light cyan ink viscosity and surface tension are in a range of 2.81 to 3.01 mPa s and 39.9 - 42.3 mN m^{-1}, respectively. The magenta ink viscosity = 3.44 mPa s and surface tension = 42.1 mN m^{-1}. The light magenta ink viscosity = 2.78 mPa s and surface tension = 41.3 mN m^{-1}. The yellow ink viscosity = 3.1 mPa s and surface tension = 45.5 mN m^{-1}.

The average particle size and the zeta-potential of the formulated inks are in the range of 100-300 nm and (-35) to (-50) mV, respectively. The ink data mentioned above confirm the acceptable property appropriate for the inkjet inks in digital textile printing technique.

5.1.2 Influence of pretreatment reagent on the color properties of the printed silk fabrics

Color gamut and color gamut volume are the main parameters to investigate the efficiency of the pretreatment reagents. The pretreated fabrics provided a wider color gamut and gamut volume than those on the untreated fabrics. The L* vs. C* (chroma) plot of the printed silk fabrics confirmed the results obtained by color gamut and gamut volume. The fabric pretreatments by 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine, and HTACC improved the chroma significantly while the color strength of the fabrics with HTACC pretreatments was the most improved, i.e., the highest value. The pre-treated fabrics with 1% w v^{-1} chitosan mixed with 15% w v^{-1} glycine solution, and HTACC solution increase its individual gamut volume by 24.9% and 46.9%, respectively. In addition, the HTACC pretreatment gave much better legibility with the sharp edges, evenly printed color densities, and higher contrast between the letter and the background than the other printed fabrics.

5.1.3 Influence of pretreatment reagents on the fabric performance and usage

The light and wash fastness of the formulated ink colors printed on the pretreated fabrics for all printed fabrics were acceptable with the commercial standards of evaluation. All the pretreatment reagents did not affect the light fastness of the fabrics at all. In addition, the results did not indicate the effect of pigment concentration on light fastness property in comparison with the commercial inks. The color change ratings, after washing, of all pretreatments were improved based on the grey scale assessment and the degree of color fixation retained at 90% for the process colors with the pretreatment with 1% w v^{-1} of chitosan mixed with 15% w v^{-1} glycine solution, and 0.1% w v^{-1} HTACC solution. Among the fabric pretreatment reagents, HTACC, and mixed chitosan and glycine can improve most of the printed qualities for the fabric with the following plausible reasons: The HTACC molecule contains the quaternary ammonium group from the conjugation of glycidyltrimethylammonium chloride to chitosan molecule whereupon it can interact with the anionic pigments in the inks. The chitosan and glycine pretreatment reagent can improve the color gamut of the printing ink because both of pretreatment molecules contain the amino groups (NH_2) which is protonated to NH_3^+ groups in acetic acidic solution that increase the active sites on the fabric surface by reacting with the sulfonic acid groups on the pigment surface to hold more pigmented inks on the printed areas.

5.2 Suggestions

5.2.1 Apart from the present work on the surface tension property, we have anticipated that the fine tune of the formulated ink surface tension with the surfactant (surfynol 104) or other surfactants can provide a higher level of ink quality, namely, jetting patterns, color appearance, and color reproduction.

5.2.2 The new pretreatment reagent, HTACC can be used at a very low concentration (0.1% w v^{-1}) which indicates that the good color property and usage performance. This pretreatment reagent can certainly be used for pretreatment for other textiles, such as polyester fabric, wool and nylon. Other possible method to use HTACC more effectively and economically is to mix or blend HTACC with polymer fiber and to spin the textile fiber for producing the ready-made textile to achieve good color reproduction besides the well recognized antibacterial property.

REFERENCES

Abou-Okeil, A. and Hakeim, O.A. (2005). Effect of metal ion binding of chitosan on the printability of pretreated wool fabric. *Coloration Technology* 121(1): 41-44.

Ali, M.K. (2008). Chemistry of textile inkjet inks. *Proceedings of IS&Ts NIP24 and Digital Fabrication*: 542-545.

Bahmani, S.A., East, G.C. and Holme, I. (2000). The application of chitosan in pigment printing. *Journal of the Society of Dyers and Colourists* 116: 94-101.

Bajaj, P. (2002). Finishing of textile materials. *Journal of Polymer Science* 83: 631-659.

Choi, P.S.R., Yuen, C.W.M., Ku, S.K.A. and Kan, C.W. (2005). Digital inkjet printing for chitosan-treated cotton fabric. *Fibers and Polymers* 6(3): 229-234.

Crutzen, A.M. (1995). Study of the ditallowdimethylammonium chloride interaction with cellulose. *Journal of the American Oil Chemists' Society* 72: 137–143.

Daplyn, S. and Lin, L. (2003). Evaluation of pigmented ink formulations for jet printing onto textile fabrics. *Pigment & Resin Technology* 32(5): 307-318.

Diamond, A.S. and Weiss, D.S. (2002). *Handbook of Imaging Materials*. 2nd ed. Basel. Marcel Dekker: 531-536.

Fang, K.J., Wang, S.H., Wang, C.X., Tian, A.L., Fu, S.H., Jiang, X. and Zhang, X. (2007). Effect of surface treatment of silk fabric with plasma on inkjet printing. *IS&T's NIP23: International Conference on Digital Printing Technologies and Digital Fabrication*: 526-530.

Freire, E.M. (2006). Inkjet printing technology (CIJ/DOD). In H. Ujiie (ed.), *Digital printing of textiles*, pp. 218-226. Cambridge: Woodhead Publishing.

Fu, Z. (2006). Pigmented ink formulation. In H. Ujiie (ed.), *Digital printing of textiles,* pp. 218-226. Cambridge: Woodhead Publishing.

Galea, B., Xing J.H., Gaglione, R., Attane, P. and Soucemarianadin, A. (1999). Formulation and Characterization of Textile Inks for InkJet Printing. In I. Rezanka and R. Eschbach (eds.), *Recent progress in inkjet technologies,* pp. 280-284. Springfield: Society for Imaging Science and Technology.

Hauser, H. and Buehler, N. (1998). Fine particle pigment concentrates in inkjet printing inks. *Proceedings of IS&Ts NIP14: International Conference on Digital Printing Technologies*: 92-94.

Hees, U., Frenche, M., Klunge, M., Provost, J. and Weiser, J. (2002). Development in textile inkjet printing with pigment inks. *Proceedings of IS&Ts NIP 18: International Conference on Digital Printing Technologies*: 242-245.

Hees, U., Frenche, M., Klunge, M., Provost, J. and Weiser, J. (2003). Textile inkjet printing with low viscosity pigment inks. *Proceedings of IS&Ts NIP 19: International Conference on Digital Printing Technologies*: 626-629.

Hudd, A. (2009). Inkjet printing technologies. In S. Magdassi (ed.), *The chemistry of inkjet inks,* pp. 6-9. New Jersey: World Scientific Publishing.

Janasak, A., Koopipat, C. and Kiatkamjornwong, S. (2007). Modulation transfer function measurement for inkjet printed silk fabrics. *Journal of Imaging Science and Technology* 51(2): 127-147.

Jocic, D., Vilchez, S., Topalovic, T., Navarro, A., Jovancic, P., Julia, M.R. and Erra, P. (2005). Chitosan/acid dye interactions in wool dyeing system. *Carbohydrate Polymers* 60(1): 51-59.

Kiatkamjornwong, S., Putthimai, P. and Noguchi, H. (2003). Comparison of textile print quality between inkjet and screen printings. *Proceedings of IS&Ts NIP 19: International Conference on Digital Printing Technologies*: 638-642.

Kiatkamjornwong, S. and Leelajariyakul, S. (2004). Pigmented Inkjet Ink Dispersion for Silk Fabric Printing. *IS&Ts NIP 20 International Conference on Digital Printing Technologies*: 605-609.

Kiatkamjornwong, S., Putthimai, P. and Noguchi, H. (2005). Comparison of textile print quality between inkjet and screen printings. *Surface Coatings International. Part B, Coatings Transactions* 88(1): 25-34.

Kiatkamjornwong, S., Noppakundilograte, S., Preudtiphap, M., Saengsuk, P., Wongwittkorn, P., Kiatticharuenwithaya. (2007). *Fabric pretreatment solution from chitosan and glycine for inkjet printing*, Petty Patent, application number 0803000082, application date: January 23, 2007. 6 pages.

Kobayashi, H. (2006). Industrial production printers-Mimaki's tx series. In H. Ujiie (ed.), *Digital printing of textiles*, pp. 218-226. Cambridge: Woodhead Publishing.

Le, H.P. (1999). Progress and trends in ink-jet printing technology. In E. Hanson (ed.), *Recent progress in inkjet technologies II*, pp. 5-6. Springfield: Society of Imaging Science and Technology.

Leelajariyakul, S., Noguchi H. and Kiatkamjornwong, S. (2008). Surface-modified and micro-encapsulated pigmented inks for inkjet printing on textile fabrics**.** *Progress in Organic Coatings* 62(2):145-161**.**

Li, H. B., Du, Y.M., Xu, X. J. and Zhan, H.Y. (2004). Effect of molecular weight and degree of substitution of quaternary chitosan on its adsorption and flocculation properties for potential retention-aids in alkaline papermaking. *Colloids and Surfaces A-Physicochemical Engineering Aspects* 242(1-3): 1-8.

Lim, S-H. and Hudson, S.M. (2004). Application of a fibre-reactive chitosan derivative to cotton fabric as an antimicrobial textile finish, *Carbohydrate Polymers* 56(2): 227-234.

Lim, S-H. and Hudson, S.M. (2004). Application of a fibre-reactive chitosan derivative to cotton fabric as a zero-salt dyeing auxiliary. *Coloration Technology* 120: 108-113.

Lin, L. and He, W. (2008). A Novel method for the evaluation of jettability. *IS&T's NIP24: International Conference on Digital Printing Technologies and Digital Fabrication*: 129.

Nam, C-W., Kim, Y-H. and Ko, S-W. (1999). Modification of polyacrylonitrile (PAN) fiber by blending with *N*-(2-Hydroxy)propyl-3-trimethyl-ammonium chitosan chloride. *Journal of Applied Polymer Science* 74: 2258-2265.

Needles, H.L. (1986). *Textile fibers, dyes, finishes, and processes*. New Jersey. Noyes publications: 64-67.

Phattanarudee, S., Chakvattanatham, K. and Kiatkamjornwong, S. (2009). Pretreatment of silk fabric surface with amino compounds for inkjet printing. *Progress in Organic Coatings* 64: 405-418.

Putthimai, P. (2003). *Print qualities of screen and inkjet printings on cotton fabrics*. Master's Thesis. Department of Photographic Science and Imaging Technology, Faculty of Science, Chulalongkorn University: p. 105.

Sapchookul, L., Shirota, K., Noguchi, H. and Kiatkamjornwong, S. (2003). Preparation of pigmented inkjet inks and their characterization regarding print quality of pretreated cotton fabric. *Surface Coatings International Part A: Coatings Journal* 86(A10): 403-410.

Shahidi, F., Arachachi, J.K.V. and Jeon, Y. J. (1999). Food applications of chitin and chitosans. *Trends in Food Science & Technology* 10: 37-51.

Stiffness Method A (45° cantilever method). (1999). *JIS L 1096: 1999 Testing methods for woven fabrics*. Tokyo: Japanese Standards Association.

Szafran, M., Rokicki, G. and Wiśniewski, P. (2001). New water thinnable polymeric binders in die pressing of alumina powders. In M-I. Baraton and I. Uvarova (eds.), *Functional gradient materials and surface layers prepared by fine particles technology*, pp. 75-80. Dordrencht: Kluwer Academic Publishers.

Thanapongjongruay, P., Hoven, V.P., Noguchi, H. and Kiatkamjornwong, S. (2009). Pretreatment of silk fabric surface with chitosan, glycine, and chitosan derivative for inkjet printing. *Proceedings of the 2nd Polymer Graduate Conference of Thailand*: 141-145.

Tielemans, M. and Roose, P. (2008). Study of the rheology of aqueous radiation curable polyurethane dispersions modified with associative thickeners. *Progress in Organic Coatings* 63: 182-188.

Tincher, W.C. and Yang, R. (1999). Inkjet resin-pigment printing of silk fabrics. *IS&Ts NIP15 International Conference on Digital Printing Technologies*: 200-202.

Tuladhar, T., Harvey, R. Tatum, J. and Drury, P. (2009). Understanding inkjet inks and factors influencing the jetting behavior. *IS&T's NIP25: International Conference on Digital Printing Technologies and Digital Fabrication*: 423-426.

Urban, D. and Takamura, K. (2002). *Polymer dispersion and their industrial application*. Weinheim. Wiley-VCH Verlag GmbH: 88-89.

Wong, Y.C., Szeto, Y.S., Cheung, W.H. and McKay, G. (2003). Equilibrium studies for acid dye adsorption onto chitosan. *Langmuir* 19(19): 7888-7894.

Xue, C-H., Shi, M-M., Chen, H-Z., Wu, G. and Wang, M. (2006). Preparation and application of nanoscale microemulsion as binder for fabric inkjet printing. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 287: 147-152.

Yu, Y. and Gottberg, F.V. (2000). Surface modified color pigments for inkjet ink application. *IS&Ts NIP 16 International Conference on Digital Printing Technologies*: 512-515.

Yu, Y. and Gottberg, F.V. (2002). Coagulation kinetics of surface modified pigment particles. *IS&Ts NIP 18 International Conference on Digital Printing Technologies*: 383-387.

Yu, Y. and Gottberg, F.V. (2004) Titration of Surface Modified Pigment Particles. *IS&Ts NIP 20 International Conference on Digital Printing Technologies*: 769-772.

Yuen, C.W.M., Ku, S.K.A., Kan, C.W. and Choi, P.S.R. (2007). Enhancing textile ink-jet printing with chitosan. *Coloration Technology* 123: 267-270.

Vigo, T.L. (1997). *Textile processing and properties: Preparation, dyeing, finishing and performance*. 2nd ed. Amsterdam. Elsevier Science B.V.: pp. 364-365.

Zhang, C. and Fang, K. (2009). Surface modification of polyester fabrics for inkjet printing with atmospheric-pressure air/Ar plasma. *Surface & Coating Technology* 203: 2058-2063.

APPENDICES

APPENDIX A

GRETAG MACBETH TEST CHARTS

(294 COLOR BATCHES)

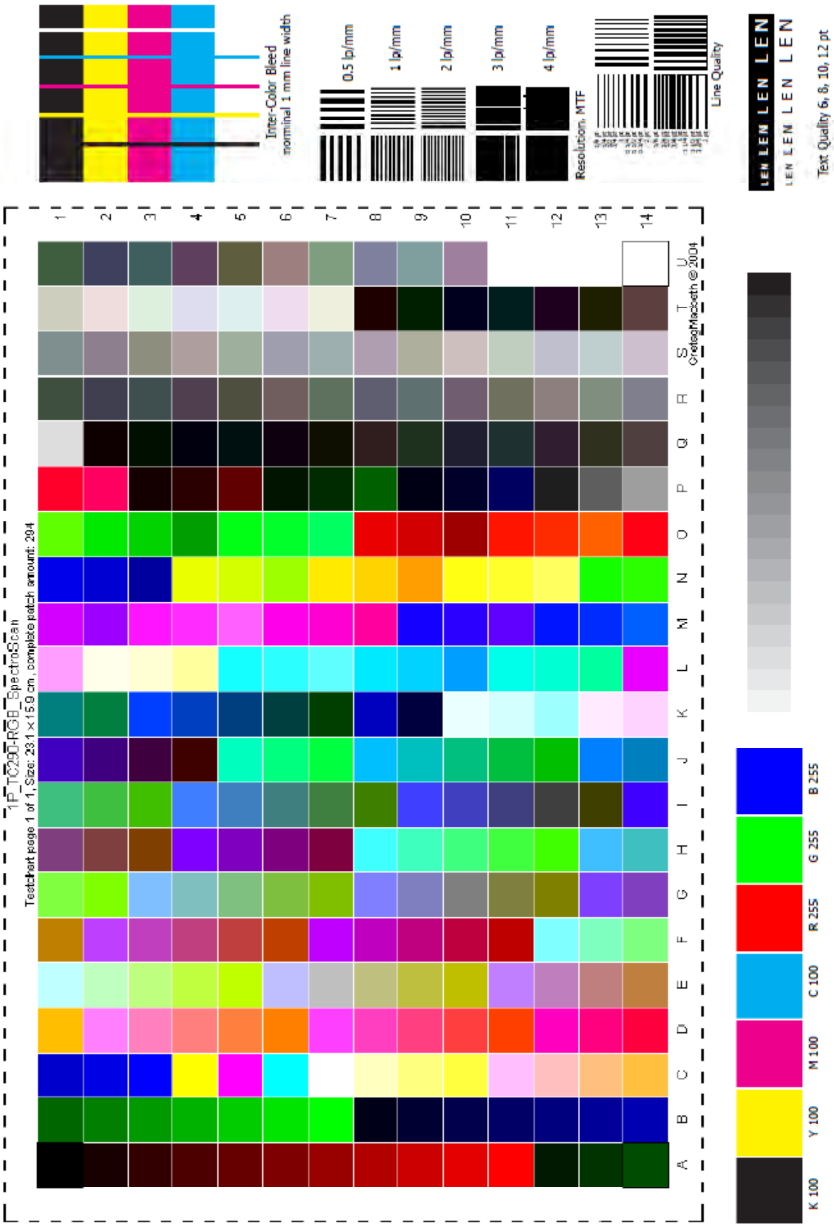


Figure A1: Gretag Macbeth test charts (294 color batches)

APPENDIX B

THE METHOD OF CALCULATION OF COLOR GAMUT VOLUME

■第４章　画像データの統計量■

SHIPP 画像の客観的評価の参考として、次に示す３種類の項目について評価を行った。

（１）画像の統計量(最小・最大値、平均値、分散・共分散、１次元ヒストグラム)

（２）主成分分析(principal component analysis)による色情報量の解析

（３）画像の空間周波数特性(自己相関関数)

また、画像データの正当性を検査するためのチェック・サムも求めた。

4.1　画像の統計量

各プレーンの画素の平均値及び分散・共分散行列は、全画素数をＮとすると次の式で与えられる。

[画素の平均値]

$$\begin{pmatrix} \overline{P}_1 \\ \overline{P}_2 \\ \overline{P}_3 \end{pmatrix} = \frac{1}{N} \begin{pmatrix} \sum P_1 \\ \sum P_2 \\ \sum P_3 \end{pmatrix} \tag{4-1}$$

[分散・共分散行列]

$$\begin{pmatrix} V_{P_{11}} & V_{P_{12}} & V_{P_{13}} \\ V_{P_{21}} & V_{P_{22}} & V_{P_{23}} \\ V_{P_{31}} & V_{P_{32}} & V_{P_{33}} \end{pmatrix} = \frac{1}{N} \begin{pmatrix} \sum\left(P_1-\overline{P}_1\right)^2 & \sum\left(P_1-\overline{P}_1\right)\left(P_2-\overline{P}_2\right) & \sum\left(P_1-\overline{P}_1\right)\left(P_3-\overline{P}_3\right) \\ \sum\left(P_2-\overline{P}_2\right)\left(P_1-\overline{P}_1\right) & \sum\left(P_2-\overline{P}_2\right)^2 & \sum\left(P_2-\overline{P}_2\right)\left(P_3-\overline{P}_3\right) \\ \sum\left(P_3-\overline{P}_3\right)\left(P_1-\overline{P}_1\right) & \sum\left(P_3-\overline{P}_3\right)\left(P_2-\overline{P}_2\right) & \sum\left(P_3-\overline{P}_3\right)^2 \end{pmatrix} \tag{4-2}$$

分散・共分散行列の対角要素 V_{11}, V_{22}, V_{33} は各プレーンの画素値の分散であり、非対角要素は対応するプレーン同士の共分散を表している．プレーン同士の相関は、

$$\begin{pmatrix} R_{P_{11}} & R_{P_{12}} & R_{P_{13}} \\ R_{P_{21}} & R_{P_{22}} & R_{P_{23}} \\ R_{P_{31}} & R_{P_{32}} & R_{P_{33}} \end{pmatrix} = \begin{pmatrix} 1 & \dfrac{V_{P_{12}}}{\sqrt{V_{P_{11}}}\cdot\sqrt{V_{P_{22}}}} & \dfrac{V_{P_{13}}}{\sqrt{V_{P_{11}}}\cdot\sqrt{V_{P_{33}}}} \\ \dfrac{V_{P_{21}}}{\sqrt{V_{P_{22}}}\cdot\sqrt{V_{P_{11}}}} & 1 & \dfrac{V_{P_{23}}}{\sqrt{V_{P_{22}}}\cdot\sqrt{V_{P_{33}}}} \\ \dfrac{V_{P_{31}}}{\sqrt{V_{P_{33}}}\cdot\sqrt{V_{P_{11}}}} & \dfrac{V_{P_{32}}}{\sqrt{V_{P_{33}}}\cdot\sqrt{V_{P_{22}}}} & 1 \end{pmatrix} \tag{4-3}$$

で与えられる。一般的に RGB 系の画像では各プレーン間の相関が高いため、各プレーンの分散を調べただけでは色彩分布の広がりを判定することは困難である。そこで主成分分析の手法を用いて画像の色彩分布の広がりを客観的に求めることを考える。

画像に関する統計を取る際に注意しなければならないのは、各自然画像中に、その色空間に応じて

" SHIPP RGB"、" SHIPP LAB"、" SHIPP XYZ" の識別文字が含まれていることである。文字の部分は、" SHIPP RGB" と" SHIPP LAB" の場合には0か255、" SHIPP XYZ" の場合には0か基準白色D65に対応するデータを有するので、画像の性質を知るための統計量の計算をこの文字領域を含んで行うのは不都合である。この理由から、文字領域を除いた画像領域のみで計算を行った。文字領域の位置は図4.1に示すA及びBの座標値で表し、表4.1にこの座標値を示す。

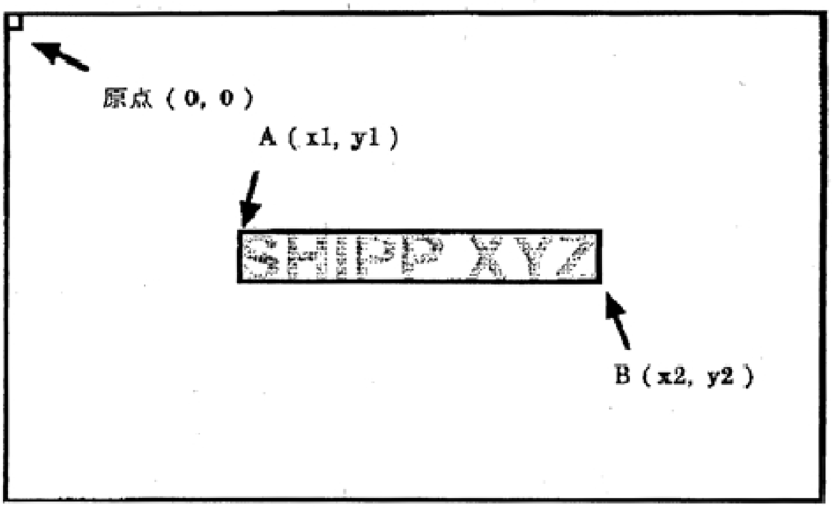


図4.1　文字領域を表す座標

表4.1　文字領域の位置と大きさ

画　像	A（x1, y1）	B（x2, y2）	Size
BrideRGB	（2770,　35）	（3035,　71）	266 × 37
HarborRGB	（　34,　35）	（　299,　71）	266 × 37
WoolRGB	（3794,　35）	（4059,　71）	266 × 37
BottlesRGB	（2770,　35）	（3035,　71）	266 × 37
BrideLAB	（2770,　36）	（3021,　72）	252 × 37
HarborLAB	（　34,　36）	（　285,　72）	252 × 37
WoolLAB	（3794,　36）	（4045,　72）	252 × 37
BottlesLAB	（2770,　36）	（3021,　72）	252 × 37
BrideXYZ	（2770,　36）	（3016,　72）	247 × 37
HarborXYZ	（　34,　36）	（　280,　72）	247 × 37
WoolXYZ	（3794,　36）	（4040,　72）	247 × 37
BottlesXYZ	（2770,　36）	（3016,　72）	247 × 37

4.2　主成分分析

主成分分析は、ある多変量の空間に対して各々の変量の相関が最小となるような直交変換を施すことによって、より少ない変量で元の空間の情報を効果的に表す手法である。この主成分を求めるには分散・共分散行列の固有値問題を解けばよいことが知られている。

Vを３行３列の分散・共分散行列、xを長さ３の列ベクトル、λをスカラーとすると、次の方程式の一般解を求めればよい。

$$V \cdot x = \lambda \cdot x \tag{4-4}$$

この方程式を満たす３つの値λを固有値、xを固有ベクトルと呼ぶ。主成分は分散・共分散行列の固有ベクトルそのものであり、主成分の分散が固有値に等しい。また、各主成分の寄与率は、

第n主成分の寄与率 ＝ 第n主成分の固有値 ÷ 固有値の合計　　(4-5)

で与えられ、この値によってその主成分が元の情報をどの程度反映しているかを表している。

このようにして求められた３つの主成分は互いに直交しているので、各々の主成分の標準偏差 (固有値の平方根)を掛け合わせたものは、色彩分布の３次元的な広がり、すなわち体積を表す。そこで、３次元体積V_{3D}を

$$V_{3D} = \sqrt{\lambda_1} \cdot \sqrt{\lambda_2} \cdot \sqrt{\lambda_3} \tag{4-6}$$

として定義する。

各画像の統計量及び主成分分析結果を表4.2から表4.13に、１次元ヒストグラムを図4.2から図4.13に示す。

APPENDIX C

FT-IR ANALYSES OF THE CYAN, MAGENTA AND YELLOW PIGMENT DISPERSIONS

Table C1: FT-IR analyses of the cyan, magenta and yellow pigment dispersions

Cyan pigment C.I. pigment blue 15:4		**Magenta pigment C.I. pigment red 122**		**Yellow pigment C.I. pigment yellow 74**	
Wave number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment
3431	N-H stretching	3266	N-H stretching	1674	N-H bending
1609	N-H bending	1635	N-H bending	2983	-C-H stretching
3028	=C-H stretching	2915	-C-H stretching	3124	=C-H stretching
1609 and 1506	C=C stretching (aromatic)	3166	=C-H stretching	1594 and 1519	C=C stretching (aromatic)
1089	C-N stretching	1606 and 1504	C=C stretching (aromatic)	1251	C-N stretching (2˚)
1506	C=N stretching	1341	C-N stretching (2˚)	1021	O-C-O stretching
1420	C-H bending for CH_2, CH_3	1479	C-H bending for CH_2, CH_3	1519 and 1337	N=O stretching
753	C-H bending (ortho)	1341, 1144	*S=O stretching of $–SO_3^-$	1552	N=N stretching
1332,1165	S=O stretching of $–SO_3^-$			1460	C-H bending for CH_2, CH_3
				1337, 1178	S=O stretching of $–SO_3^-$

Table C2: FT-IR analyses of chitosan, HTACC and glycine

Chitosan		**HTACC**		**Glycine**	
Wave number (cm^{-1})	Assignment	Wave Number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment
3436	O-H stretching, N-H stretching of $-NH_3^+$	3410	O-H stretching, N-H stretching of $-NH_3^+$	3102	N-H stretching of $-NH_3^+$
1655	C=O stretching amide I	1639	C=O stretching amide I	1638	C=O stretching amide I
1594	N-H stretching amine	1478	C-H bending (trimethyl ammonium gr.)	1594, 1499	N-H bending
1421	O-H bending	1418	O-H bending	1397	Carboxylate anion
1378	-NHCO stretching amide	1377	-NHCO stretching amide	1128	C-O stretching
1250	C-N stretching	1252	C-N stretching	1043	C-N stretching
1151	C-O (bridge) stretching amide	1151	C-O (bridge) stretching amide		
1082	C_3-OH stretching	1074	C_3-OH stretching		
1027	C_6-OH stretching	1026	C_6-OH stretching		

APPENDIX D

UV-VISIBLE ABSORPTION SPECTRA OF THE INK IN 0.5 ML OF EACH PRETREATMENT SOLUTION

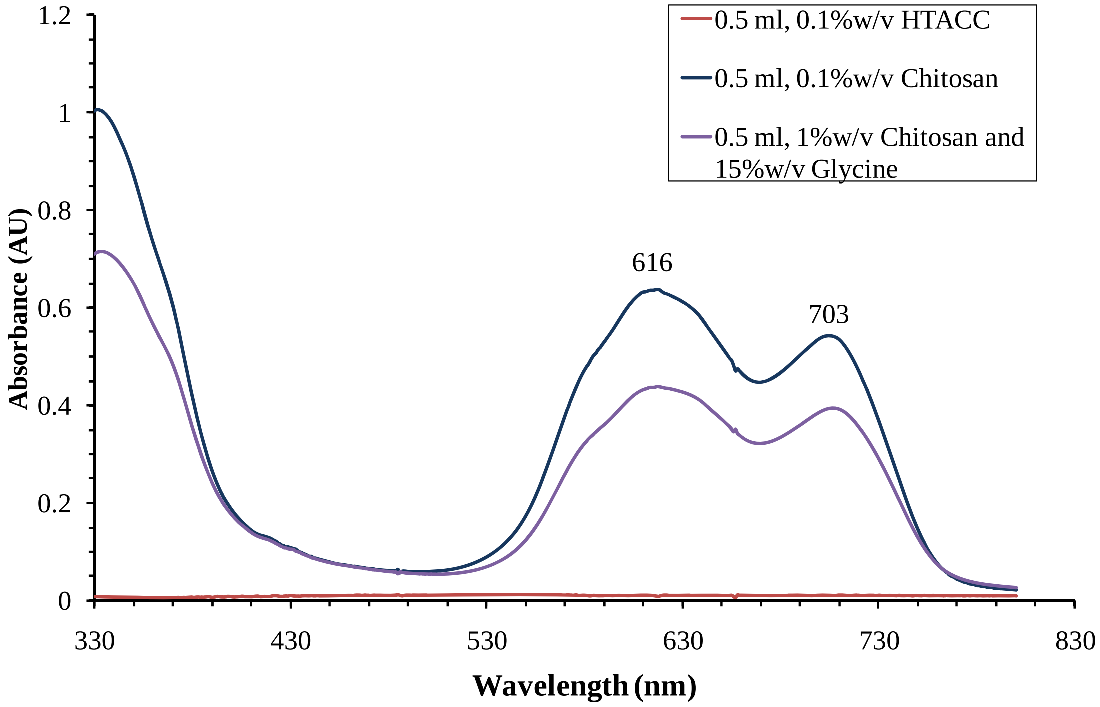


Figure D1: UV-Visible absorption spectra of the cyan ink in 0.5 ml of each pretreatment solution

Table D1: The absorbance (λ_{max}) value of diluted cyan inks in 0.5 ml of each pretreatment solution

Pretreatment solution	Volume of pretreatment solution (ml)	Absorbance reading at λ_{max} after 24-h mixing	
		616 nm	703 nm
1% w v^{-1} chitosan	0	0.7593	0.6371
and 15% w v^{-1}			
glycine	0.5	0.4382	0.3929
0.1% w v^{-1} chitosan	0.5	0.6369	0.5428
0.1% w v^{-1} HTACC	0.5	0.0097	0.0114

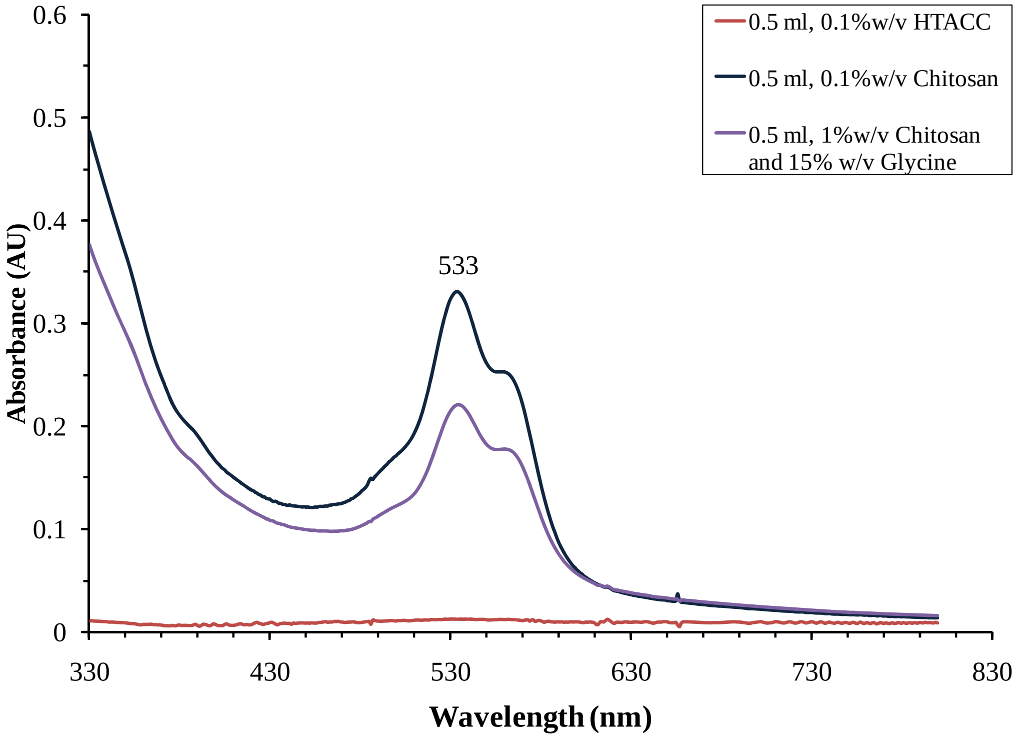


Figure D2: UV-Visible absorption spectra of the magenta ink in 0.5 ml of each pretreatment solution

Table D2: The absorbance (λ_{max}) value of diluted magenta inks in 0.5 ml of each pretreatment solution

Pretreatment solution	Volume of pretreatment solution (ml)	Absorbance reading at λ_{max}=533 nm after 24-h mixing
1% w v^{-1} chitosan	0	0.4050
and 15% w v^{-1} glycine	0.5	0.2205
0.1% w v^{-1}, chitosan	0.5	0.3309
0.1% w v^{-1} HTACC	0.5	0.0123

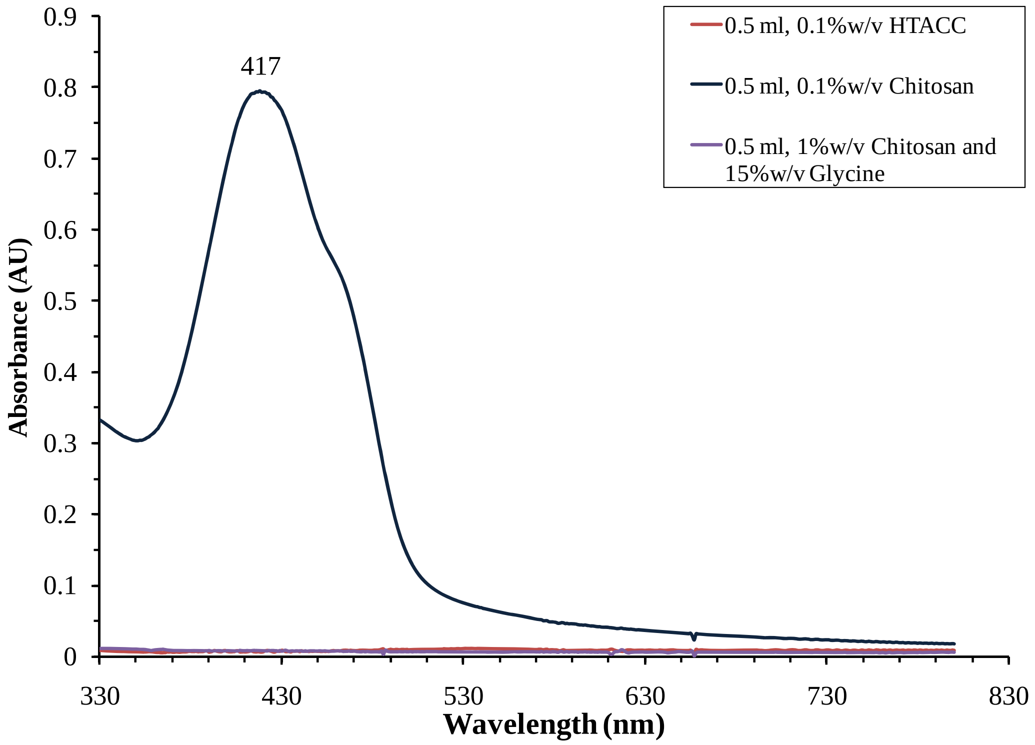


Figure D3: UV-Visible absorption spectra of the yellow ink in 0.5 ml of the pretreatment solutions

Table D3: The absorbance (λ_{max}) value of diluted yellow inks in 0.5 ml of each pretreatment solution

Pretreatment solution	Volume of pretreatment solution (ml)	Absorbance reading at
		λ_{max}=417 nm after 24-h mixing
1% w v^{-1} chitosan	0	0.8785
and 15% w v^{-1} glycine	0.5	0.0084
0.1% w v^{-1}, chitosan	0.5	0.7941
0.1% w v^{-1} HTACC	0.5	0.0063

VITA

Mr. Pichet Thanapongjongruay was born on February 1, 1981 in Nakhon Pathom, Thailand. He graduated with a Bachelor’s Degree in Chemistry from the Faculty of Science, Silpakorn University on March 9, 2005. Since then, he has been working as a researcher in the Research Centre for Art and Design Materials, Silpakorn University. He has been a graduate student in the Program of Imaging Technology, Faculty of Science, Chulalongkorn University since 2006 and finished his Master’s degree in Science in April 2010.