# Investigation into the Application of Polymer Finishes on Textiles by Inkjet Printing

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### ABSTRACT

Digital finishing of textiles involves the application of polymer finishes onto the textile substrates in controllable quantities and at prescribed locations that gives the substrate multiple functionalities and performance characteristics. In this study, piezoelectric Drop-on-Demand inkjet printing of shrink resist finishes onto textiles was investigated with a view to imparting dimensional stability and potentially could produce sculptured textural effects with subsequent laundering felting of untreated areas. Therefore, a range of formulations containing Synthappret BAP was applied onto wool and cotton fabrics using traditional finishing method, pad-dry-cure, and the shrink resist performance was evaluated. Based on the shrink resist performances, a suitable formulation containing 40 g/L Synthappret BAP was identified for digital ink development for shrink resisting, and the viscosity and surface tension of this initial formulation was optimised to formulate inkjet inks to be tested in piezoelectric DMP to evaluate jettability performances. "Chaotic" spraying of drops was observed for the inks containing lower concentrations of rheology modifiers, and the whole surface of the printhead facing the substrate was wetted after a few cleaning cycles. In contrast the inks containing higher concentrations of modifiers jetted well initially however became unstable after few minutes of operation. The formulation containing 45% glycerol as the viscosity modifier performed best out of all the inks tested, however even it also became unstable after printing for few minutes.

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### THE AUTHOR

Md. Nazmul Karim has graduated as a Textile Engineer from Bangladesh University of Textiles, previously College of Textile Technology under University of Dhaka, in 2008. After that he joined the Textile Division (EVX/T) of BASF Bangladesh Limited as Assistant Manager for technical services. At the beginning of his career in BASF, he had an intensive industrial training for almost eight months on two of the largest continuous textile ranges in Bangladesh, involving pre-treatment to finishing of the fabrics. After industrial training, he took over the responsibilities of technical services in the fabric continuous pre-treatment and finishing segment of the Textile Division in BASF Bangladesh. During his career in BASF, he successfully conducted many trials, solved technical problems, optimised pre-treatment and finishing formulations, and participated in many industrial projects jointly with retailers such as WalMart, H&M, M&S, IKEA, C&A. He actively participated in BASF-IKEA global project of "Ecosoft Pigment Printing". In 2010, he was selected for Manchester University Equity and Merit Scholarships 2010, and left BASF in September 2010. After leaving BASF, he started the MSc by Research Textile Science and Technology programme at the University of Manchester, and as part of this program, he conducted the research project on inkjet/digital finishing of functional fluids on textiles under supervision of Prof Chris Carr, Prof Stephen Yeates, and Dr Muriel Rigout. During his project, he gained hands on experiences on physical testing of textile finishes, Kawabata Evaluation System (KES-F), Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS) method for particle size measurement in Malvern Zeta Nanosizer, Anton Parr Viscometer, and formulation of inkiet inks. He also achieved the skills of operating a piezoelectric Dimatix Material Printer (DMP), and optimising the parameters of DMP to achieve improved jetting performance of functional fluids.

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## **ABBREVIATIONS**

- A/W After Wash
- **B/W** Before Wash
- CAD Computer Aided Design
- CAV Critical Application Value
- **CCD** Charge Coupled Device
- CIJ Continuous Inkjet
- CMC Carboxy Methyl Cellulose
- cmc critical micelle concentration
- **CRA** Crease Recovery Angle
- CSIRO Commonwealth Scientific and Industrial Research Organisation
- **DLS** Dynamic Light Scattering
- DMP Dimatix Material Printer
- **DOD** Drop-on-Demand
- HLB Hydrophilic-Lipophilic Balance
- KES-F Kawabata Evaluation System for Fabrics
- LED Light Emitting Diode
- MEMS Micro Electro Mechanical System
- Oh Ohnesorge Number
- **o.w.f.** on the weight of fabric
- PEG200 Polyethylene Glycol of Molecular Weight 200
- PEO Polyethylene Oxide
- PIJ Piezoelectric Inkjet
- POD Print-on-Demand
- **PSD** Particle Size Distribution
- R&D Research & Development

- **Re** Reynolds Number
- **SDC** Society of Dyers and Colourists
- **SEM** Scanning Electron Microscopy
- **THV** Total Hand Value
- TIJ Thermal Inkjet
- UV Ultra Violet
- We Weber Number

## **THESIS OVERVIEW**

This project between the Schools of Materials and Chemistry was conducted mainly in two phases. In the first phase, the shrink resist finishes were applied by a typical textile finishing method, and the performance of the finishes were evaluated to select an initial formulation for inkjet ink development; thereafter in the second phase a range of inks were prepared to investigate the jettability performances in a piezoelectric DMP. Therefore, these two stages are covered in all the four chapters of this thesis with a list of references at the end of each chapter.

The main body of the thesis starts with the introduction to textile printing followed by literature reviews of inkjet technologies, textile finishing, and inkjet/digital finishing of textiles in *Chapter 1*.

*Chapter 2* includes a list of materials used in this investigation, and the experimental approaches used to apply and evaluate the performance of shrink resist finishes, to design inkjet inks, and to test the jettability performances of formulated inks.

The results of this study are illustrated in *Chapter 3* followed by discussions in each section. In addition, a detail objective of this study, textile fibres, and the principle material of this study Synthappret BAP are discussed at the beginning of this chapter. Moreover, the analysis of the results obtained in this study, and the general observations are included in the discussion of each section followed by the comparison with previous studies.

Finally, conclusions are drawn, and future work is suggested at the end of this thesis in *Chapter* 5.

## CHAPTER 1 LITERATURE REVIEW

Chapter 1 Literature Review

#### 1.1 Textile Printing

#### 1.1.1 Historical Background

Evidence of artistic human nature has been reflected from our natural quest to produce garments or other artefacts from the early days of human history where colours were applied to different substrates by their finger tips and sticks. Then production of patterns on fabrics by applying beeswax as a resist to the dyes extracted from plant or by tying threads tightly around the areas to be resisted provided a new dimension in colouration. Afterwards, the discovery of mordants to fix some of the plant dyes and to produce different colours with the same dye suggested a style of printing that was to become of prime importance [1].

An early example of textile printing was found on a block printed tunic dated sometime between the 4<sup>th</sup> and 7<sup>th</sup> century [2]. Evidence suggests that wooden blocks were used to print textiles and then used to reproduce short Buddhist religious texts that believers carried as charms [2, 3]. In an empirical decree of 593 BC, Sui emperor ordered the printing of Buddhist images and scriptures which was the first reference to block printing [3]. A thin piece of paper, containing the written texts, was glued face down onto a wooden plate and then characters were carved out to make wood-block printing plate, which was then used to print the texts. In the twelfth century, block printing of textiles started to expand in Surat in Gujrat (India), mainly for wall hangings, canopies and floor spreads [4], and textile printing spread around the world through spice trade.



Figure 1.1 Carved Wood-block Printing Plate Dated from Fifth Century [3]

#### 1.1.2 Definition of Textile Printing

Celanese Acetate [5] defined textile printing as the process for producing patterns on yarns, warp, fabric, or carpet by depositing colour or other treating material, usually in the form of a paste, which is then treated with steam, heat, or chemicals for fixation. L. W. C. Miles [1] considered textile printing as the process of bringing together a design idea, one or more colourants, and a textile substrate. Therefore, localised application of colourants or non-colourants on any textile substrate, to achieve pattern of colours or textures on textile surface, can be referred as textile printing.

#### 1.1.3 Classification of Textile Printing

Textile printing can be classified depending on: (A) styles of printing and (B) methods or equipment used to print on textile surface, which are discussed below:

#### (A) On the Basis of Styles of Printing

Considering the styles of printing, traditional textile printing can broadly be classified into three methods: Direct printing, Resist printing & Discharge printing.

Styles of Printing	Features			
Direct printing	Printing paste containing colourants, thickener and other additives are printed by means of direct contact of mediums like blocks, screens, and stencil etc. on textile substrates [6].			
Resist printing	Textile substrate is printed with chemicals (Known as <i>chemical resist</i> ) or wax (known as <i>physical resist</i> ) [6] and subsequently over dyed or overprinted to resist the fixation of applied colour in the printed area [7].			
Discharge printing	During steaming, the ground shade coloured with a dye is destroyed in the areas to which print paste containing a discharging agent has been applied. A discharging agent is usually a reducing agent and often contains an illuminating dye, for example, vat dyes [7].			

Table 1.1 Overview of Different Styles of Textile Printing [6-7]

Although these printing styles differ in the mechanistic action of the dyes and chemicals used, but can be conducted by any of the standard printing methods i.e. block, screens, rollers and either by automatic or semi-automatic machines [6].

#### (B) On the Basis of Printing Techniques and Equipment Used

On the basis of techniques and equipment used to print the substrates, most well-known textile printing methods are: block printing, roller printing, screen printing (flat bed and rotary), transfer printing and digital printing. These techniques except digital printing are briefly discussed below and digital printing is discussed in detail in section 1.1.6.

#### **Block Printing**

Block printing is the oldest printing method, which is carried out by using blocks with raised printing surfaces; blocks are inked and then pressed on to the fabric [2].

#### **Engraved Roller Printing**

Another conventional printing technique declining steadily in importance is roller printing, which was invented in Europe (Bell, 1875, Lancashire) unlike other manual printing methods in Asia and Far East [6].

#### **Screen Printing**

Screen printing was developed from stencilling. The French used woven silk fabric, which was stretched across a frame, to provide continuous support for the paper stencil in 19<sup>th</sup> century and the combination was known as a screen. Due to the better control on the amount print paste applied, soon after the paper stencil was replaced by durable paint on fabric [2]. There are two main types of screen printing techniques depending on the types of screen used: rotary screen printing and flatbed screen printing; of which rotary screen printing is most widely used. In spite of the dominance of rotary screen printing and improved print definition, there has been continued interest in flat screen technologies due to the increasing trend towards very short runs [7]. The relative cost of flatbed and rotary screen printing, Figure 1.2, highlights the benefits of the use of flatbed techniques for short production runs [8].

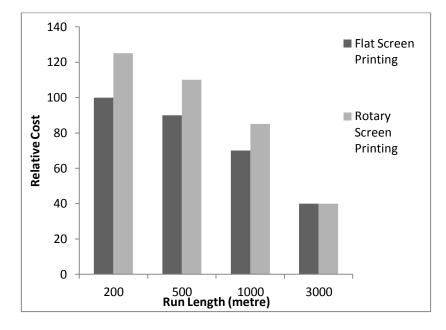


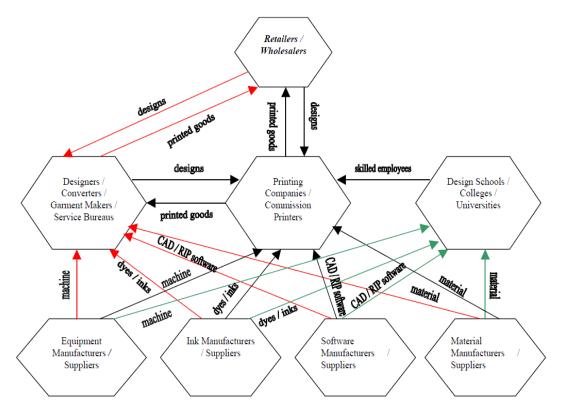
Figure 1.2 Relative Cost (approximate) of Rotary and Flat Screen Printing [8]

#### **Transfer Printing**

In Transfer Printing, the design is first printed on a flexible non-textile substrate, typically paper, and then transferred onto textiles by a separate process [2]. Although commercialisation of sublimation transfer printing in 1960's and early 1970's provided a major breakthrough with simple processing, low investment and no effluents, because of the present trend towards fast response and the increasing importance of short runs per colour way, the process economics may not favour this technique [7].

#### 1.1.4 Textile Industry and Printing Methods

The textile and clothing trade, which accounts for 6% of total world exports, has been playing a vital role in the world economy with many of the small and least developed countries hugely dependent on this sector for foreign exchange earnings, and employment generation, and often accounts for more than 90% of total industrial export and 50% of the total employment generation in these countries [9]. Textile printing is often the mainstream activity positioned at the centre of the supply chain networks of mature textile industries, Figure 1.3 [10].



# Figure 1.3 Key Stakeholders in the Textile Printing Supply Chain and their Major Interactions [10]

The black arrows show the physical interactions with the printing company/ commission printers (full-scale production) whereas the red arrows show the physical interactions with the designers/ converters/ garment makers (short or medium run production). The green arrow indicates the physical interactions between the equipment/ inks and dyes/ software/ materials manufacturers and suppliers and the design schools/ colleges and universities.

Most of the textile fabrics produced in the world are either dyed (almost 70%), 20% are printed, 5% are yarn dyed and the remaining 5% are white [10]. Without any doubt the screen printing method is the most widely used printing technology (approximately 80% of total printing), followed by roller printing (14%) and transfer printing (5%), and finally printing technology with the least market share is inkjet printing (currently less than 1%), Figure 1.4 [11].

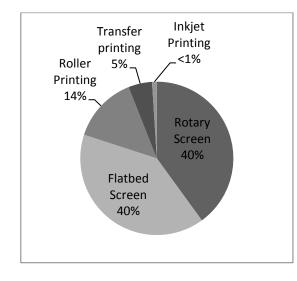


Figure 1.4 Market Share (%) of Different Textile Printing Techniques [11]

Roller printing had its highest market share in the 1970's and since then its usage has diminished and it has been replaced by rotary screen printing which reached to 60% market share in the 1990's. Rotary screen printing has been dominating the market over the years because of its flexibility to print on different surfaces, ability to print sharp outlines, tonal effects, and textured effects. Moreover, Rotary printing can be used to print small quantities to mass production. Due to the printing industry shifting from the West to the Far East and an associated reduction of running length, there has been an increase in Flatbed printing which is predominantly used in the Far East [10]. Figure 1.5 illustrates the printing production technology trends.

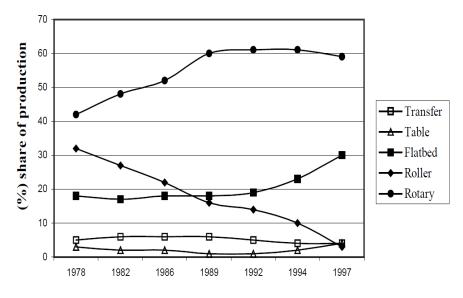


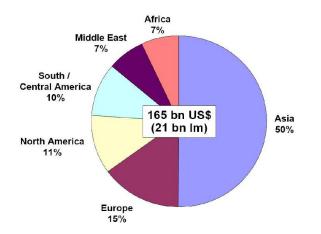
Figure 1.5 Printing Production Technology Trends [10]

#### 1.1.5 Global Textile Printing Market Trends

A Global Strategic Business Report on "Textile Printing" projected a global textile printing production of 32 billion metres by 2015 [9]. In addition over the last few years, the global textile printing market trend have indicated the technical improvement and only small changes in the existing technologies rather introducing a totally new concept of printing is prevailing [7].

#### 1.1.5.1 Geographical Relocation

In the 1980's the textile printing market was stable in Western European countries and USA, but due to simplifications of screen printing, low labour costs and less environmental restriction, it has shifted to Asian and other developing countries [12]. Hudd [11] has shown from Gherzi research 2008 that, out of the 21 billion linear metres or the 165 billion US\$ textile printing market, almost 50% of global printed fabrics were produced in Asia, 15% in Europe, 11% in North America and the rest was produced in other parts of world, Figure 1.6.



#### Figure 1.6 Worldwide Textile Printing Production by Region [11]

#### 1.1.5.2 Fibre Usage Trends

Aizenshtein [13] established the trends of textile fibre consumption with the usage of cotton and other cellulosic or natural fibres decreasing over the years; whereas the demand for polyester fibre has been increasing, Figure 1.7. It is predicted that there will be a slight increase of cotton fibre usage from 2010 to 2020, but consumption of other cellulosic fibres will remain same. However in contrast there will be a rapid growth of polyester usage.

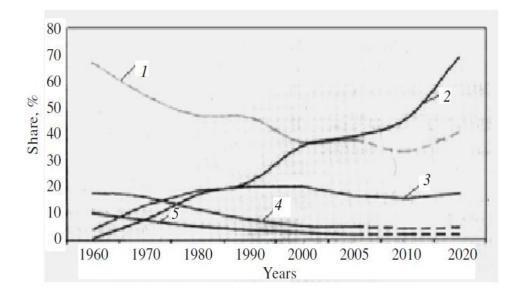


Figure 1.7 Change in the Market Share of Fibres in the World Textile Raw Material Balance Sheet: 1) Cotton; 2) Polyester Fibres; 3) Other Synthetic Fibres; 4) Cellulose fibres; 5) Other Natural Fibres [13].

#### 1.1.5.3 Colourant Usage Trends

The textile printing market is dominated by pigment printing because of its simplicity, economical, environment friendly and can be printed on any type of fibres [12]. In 2002, of the 25 billion square metres worldwide production, 48% was by pigment printing and in some markets the figure was well over 90%. In contrast reactive colourants contributed approximately half of the pigment (approximately 24%) printing market share [14]. According to BASF AG, the market share will remain constant for pigments up to 2012 and there will be a slight decrease for Reactive dyes [14], Figure 1.8.

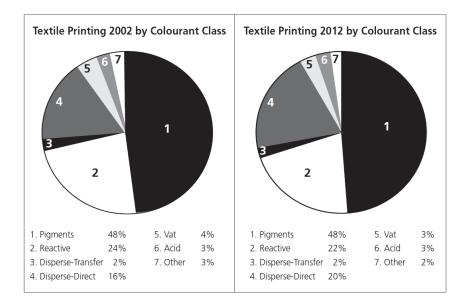


Figure 1.8 Textile Printing by Colourant Class 2002-2012 (BASF AG Data) [14]

#### 1.1.5.4 Reduction in Run Sizes

Over the past few years, there has been a reduction in production run sizes and repeated orders of printed fabric, and surveys have indicated a worldwide print run average of 2,250 yards only and in Western Europe, the figure is as low as 700 yards only [15].

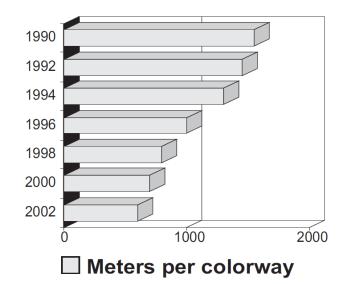


Figure 1.9 Reduction in Colour Way Run Lengths (BASF AG Data) [14]

One of the possible reasons behind the reduction in run length may be the change in consumer behaviour. Moreover, the fashion styles/seasons for printed textiles has increased to over 5/6 times in a year and the demand for greater variety of colour and design has increased. In addition, the customer wants quick response and quick order turnaround [16].

#### 1.1.5.5 Changes in Business Model

The traditional textile business model involved creating profit through mass production and selling of surplus items at discounted price. That model restricted customer choice and decreased manufacturing profits [17]. However, nowadays the retailer prefers to keep less stock and place frequent order in order to replenish the stock [18].

#### 1.1.5.6 Ecological Considerations

Increasing ecological awareness, environmental legislation, and scarcity of water and energy has driven R&D efforts in search for alternatives [9]. The sources of pollutants have been identified and ways of minimising their associated problems developed [19]. Moreover, automation in print paste preparation has reduced manual handling, hence ensuring a safer working environment [20]. However, the textile industry has been facing new environmental constraints continuously, and both printers and suppliers are under huge pressure to minimize waste disposal and reduce environmental discharge [7].

Therefore, the rapid changes in trends of global textile printing market have intensified the manufacturer's quest for alternative printing methods that will meet current market demands and digital printing has that potentiality to become the new generation printing method.

#### 1.1.6 Digital Printing

Digital Printing or Inkjet printing is known as non-impact printing method in which only the liquid inks makes contact with the substrate. Lord Rayleigh developed much of the fundamental theory for inkjet printing method at the end of nineteenth century [21] but the industrial development mainly started in the late 1950s and 1960s [22].

#### 1.1.6.1 Advantages of Digital Printing

#### **Mass Customisation**

A new theory of production is mass customisation, specializing in short runs, which allows customers to specify what they exactly want. Moreover, mass customisation offers almost unlimited design and multiple colour ways, and in addition it is very much customer oriented. Digital printing offers mass customisation of textile printing production by acting both as sampling and production tool. It saves time and money in sampling by providing immediate results, flexibility in design and colouration but is able to minimize inventory by acting as production tool [12].

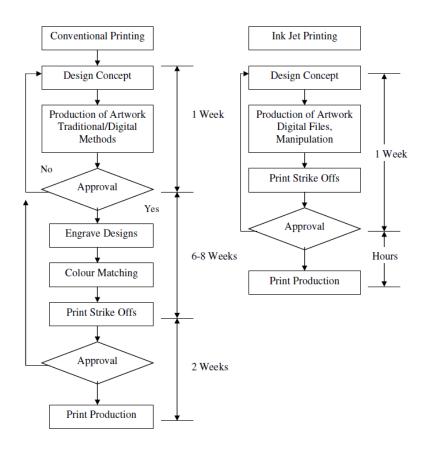
Mass customisation can be regarded as similar to Print on Demand (POD) which is defined as "delivering what was needed, when it was needed and in the exact quantity required" by InfoTrends in 1992 [23]. The basic principles POD according to InfoTrends are shown in Figure 1.10.



Figure 1.10 Basic Principles of Print on Demand (POD) According to InfoTrends [23]

#### **Reduction in Downtime & Sampling Cost**

Digital Printing reduces production down time, because it doesn't require any lengthy setup and clean up time between patterns and can in principle print without any interruption. Moreover, it doesn't require any screen; thus reduces costs in sampling and eliminates registration problem[12]. Whereas for conventional printing, sampling can take 2-8 weeks' and for bulk production, the time scale is 3-12 weeks [24].



# Figure 1.11 Comparison of Production Routes of Conventional and Digital Textile Printing [25, 26]

In addition, conventional methods involve long downtimes, high engraving and labour costs, lengthy set-up and registration problems [27]. Therefore, conventional methods are not suitable for short run productions. In conventional printing such as screen printing, printing cost per meter square reduces with the increase of run lengths, whereas that of inkjet printing costs remain the same regardless of run length [14].

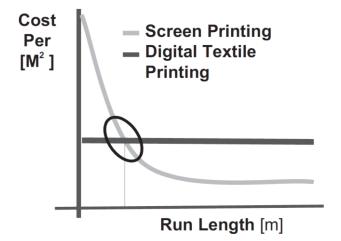


Figure 1.12 Cost per Metre Square: Conventional Printing Vs Inkjet Printing [14]

#### **Non-Impact Printing**

Most of the digital technologies do not require "aggressive" stabilising/holding down methods for substrates which may impair the quality of the fabric. As the technology involves noncontact printing of substrates, so it allows printing without image distortion which may occur in traditional printing methods such as screen printing [28].

#### **Ecological Advantages**

The environmental performance profile of digital printing is much better than other conventional textile printing methods, although there is not much published research to support the environmental advantages of digital printing, but few general conclusions can be drawn from the literature analysed by Viluksela et al. [29]. As there is less consumption of chemicals in digital printing, accordingly there is less waste output and lower usage of water and chemicals. However, they suggested some areas related to environmental performances such as less consumption of inks and energy need to be improved.

In addition to the above factors there are also other advantages of digital technology such as less or no overlapping of colour, can vary every print "On-the-fly", more accurate colour matching, easy to modify the images etc. [28].

#### 1.1.6.2 Limitations of Digital Printing

Since the development of digital textile printing technology, it has mainly been used for sampling or short run productions. There are some limiting factors which restricted the development of digital printing for textile industries; one of the most important is the speed. Due to the low drop ejection frequencies, the speed of digital printing is lower than traditional textile printing methods. Moreover, fabric pre-treatment is necessary to achieve good print quality, high material cost and lack of proper ink chemistry has made conservative textile

manufacturers reluctant to adopt this new technology [12]. Furthermore, although digital printing can produce sharp outlines, because of low drop volume of Cyan (C), Magenta (M), Yellow (Y) and Black (K), uneven printing may occur and it becomes difficult to produce deep shades [30, 31]. The comparisons between rotary screen printing and inkjet printing are illustrated in Table 1.2.

Features	Rotary Screen Printing	Inkjet Printing	
Print speed	Up to 30-70 m/min	Up to 1-4 m/min	
Resolution	Usually 100 dpi with maximum of 255-300 dpi	Up to 1440 is possible	
Screen cost	Screens required for printing; additional costs for engraving, washing and storage	No screen required for printing; so savings in additional costs	
Effluent	More	Less	
Inks	Aqueous colour pastes in large batches	Pre-formulated in small containers supplied by manufacturers	
Special pre- treatment	No special pre-treatment required	Special pre-treatment required	
Strike-offs	Strike-offs on proof may differ from bulk	Strike-offs on bulk machine	
Half-tones	Difficult	Not a problem	
Repeat distance	Restricted	No restriction	
Registration Usually design mis-regist set-up		Instant registration	

Table 1.2 Comparison between Rotary Screen Printing and InkjetPrinting of Textiles [25, 26]

Considering set up and cleaning up, screen preparation and down time, Tippet [32] found that although the speed of rotary screen printing is 6-12 times higher than that of digital printing system, it was suggested the gap between digital and screen printing would continue to narrow. However, developments in the chemical system for colouration, digital integration of cutting and printing, colour management are still required to improve for successful adaptation of digital technology in textile printing [33].

#### 1.1.6.3 Classification of Inkjet Technologies

Inkjet printing techniques are broadly classified into two main classes: Continuous Ink Jet (CIJ) and Drop-on-Demand (DOD). Inks are fired through nozzles all the times at a constant speed and pressure in CIJ techniques and unstable jet of inks are broken into droplets after leaving the nozzle. It allows the drops to go to substrate or deflected on to a gutter by charging the drops electrically. On the other hand, in DOD, inks are ejected when required to form images [22].

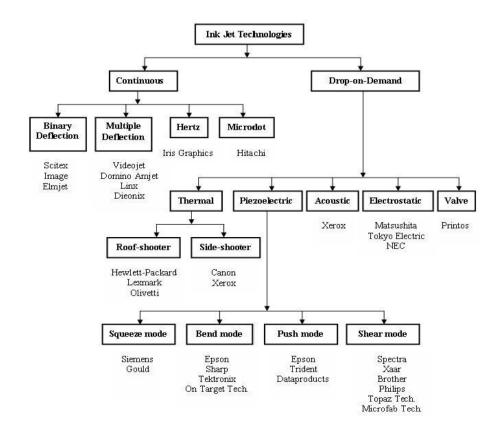


Figure 1.13 Inkjet Technologies Map [34]

There are mainly two main drop ejector mechanisms for inkjet printing: piezoelectric inkjet (PIJ) and thermal inkjet (TIJ). A piezoelectric actuator squeezes the ink droplets out of nozzle in PIJ, whereas in TIJ, an electric heater raises the temperature of the ink to bubble nucleation point; thus ink is propelled outside the nozzle due to the explosive expansion of the vapour bubble. Figure 1.13 shows inkjet technologies map [34].

#### (A) Continuous Inkjet Technology

In CIJ, the jet of ink generated by each nozzle breaks up randomly into droplets of variable sizes which are corrected by providing a periodic excitation. The size of the droplets depends on jet velocity and frequency of the excitations and can be maintained to high accuracy. The periodic excitation is provided in traditional CIJ by coupling a piezoelectric transducer to the

print head. Depending on the image to be formed the drops are electrically charged, after leaving the nozzle, and pass through an electrical field to cause them to deflect [22].

There are two types of deflection methods in Piezoelectric-driven CIJ: Binary and multiple deflections. In Binary deflection, the drops are addressed to either single pixel location or to the circulating gutter, whereas in multiple deflections the drops can be directed to several pixels with variable deflections. These two methods are illustrated in Figure 1.14 (A) & (B).

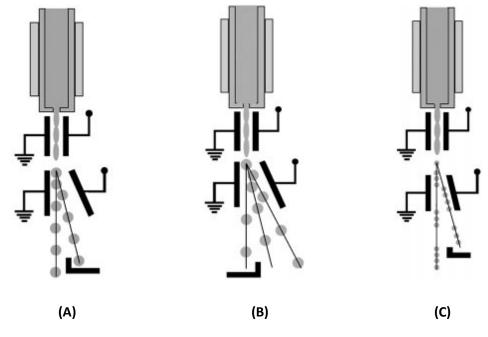


Figure 1.14 Binary Deflections (A), Multiple Deflections (B), & Hertz Method (C) [22]

There is another method of CIJ, Figure 1.14 (C), invented by Dr Carl H. Hertz , in which the amount of ink deposited per pixel is variable, and is known as the Hertz method [35]. In this method small drops (of the order of 3 pL) are generated at speed of 40 m/s with excitation frequencies of over 1 MHz & the drops not intended to substrate are deflected to a gutter. A smaller charge is given to the printing drops to prevent them from merging in flight. Irish graphics, which is now part of Kodak, has commercialized this technology on digital colour proofers.

Kodak introduced thermal CIJ system [36, 37] where in this system, each nozzle contains an annular electrical heater that generated heat which raises the temperature of the jet of the inks in the vicinity of nozzle and lowers the viscosity of the inks. The drops resulting from the jet are of equal size because of constant jet velocity and periodic heating pulse.

#### (B) Drop-on-Demand Inkjet

Drop-on-demand inkjet technology is the most widely used method in inkjet printing market and they can be classified into four major methods: thermal, piezoelectric, electrostatic and acoustic inkjet. Most of the Drop-on-demand printers use either thermal or piezoelectric principle, whereas other two methods are still in the development stage [34].

#### Thermal or Bubble Jet Drop-on-Demand

In TIJ, a current pulse is allowed to flow through an electric heater, which is built inside the nozzle by microelectronic device fabrication techniques, to raise the temperature of the ink in its vicinity to over 300°C. This rise in temperature causes ejection of an ink droplet through the nozzle orifice because of violent nucleation and expansion of a vapour bubble. Water is preferred to other solvents due to their ability to form more explosive bubble growth [22].

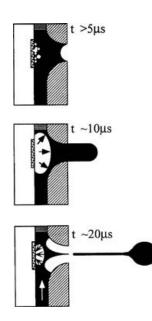


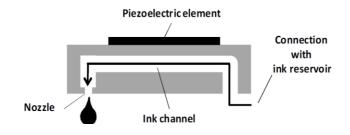
Figure 1.15 Drop Formation Process of a Thermal Inkjet (Where t= time in  $\mu$ s) [34]

Among several configuration of TIJ drop ejectors, the most common being the 'roof-shooter' (print heads from Hewlett-Packard, Lexmark, and Olivetti) and 'side shooter' (Canon and Xerox print heads) [34].

#### Piezoelectric Drop-on-Demand Inkjet

A piezoelectric element, typically made of Lead Zirconate Titanate (PZT), is used to generate droplets in piezoelectric DOD inkjet printing. Application of voltage to the electrodes of the piezoelectric element causes a volume reduction in the ink chamber and droplets of inks are forced out of nozzle [38]. There are different types of PIJ print heads depending on the geometry of the drop ejector and/or operation of the piezoelectric elements: Shear mode,

bend mode, push mode, squeeze mode, nozzle excitation and porous layer feed [39]. The print head that will be used to investigate jetting of polymer finishes on textiles in this study is a shear mode type and is manufactured and marketed by Fujifilm as a Dimatix Material Printer (DMP).



# Figure 1.16 Cross-section of a Single Piezoelectric Drop-on-Demand Ejector [40]

A comparison between Piezoelectric DOD and Thermal DOD Inkjet is listed in Table 1.3.

Features	Thermal DOD	Piezoelectric DOD
Drop volume	23 pL	2-25 pL
Drop diameter	35 µm	15-30 μm
Drop frequencies	5-8 KHz	2-20 KHz
Native resolution	Lower	Higher
Compactness &	More compact & less Costly	Less compact & more costly
cost		
Air management	Superior	Inferior
Ink path	Simple	Complex
Ink type	Mainly fire aqueous inks	Can easily fire any fluid
Drop volume	Pre-pulsing techniques can	Up to an order of magnitude
variation	be used to produce modest	of drop volume variation is
	changes in drop volume	possible through the shape
		of wave form

# Table 1.3 Comparison between Piezoelectric Drop-on-Demand andThermal Drop-on-Demand Inkjet Technologies [22, 41]

#### 1.1.6.4 Physical Consideration of Drop-on-Demand Droplet Formation

Yeates et al. [42] stated three distinct stages in printing with DOD printhead: drop generation, drop flight, and drop impact, that are discussed below:

#### **Drop Generation**

In the DOD printhead a piezoelectric actuator or a thermal pulse generates a pressure pulse to form droplets and if this pressure pulse exceeds the critical value, a liquid column is protruded from the orifice and the drop separates due to the surface tension leading to unstable neck formation. The time scale for the whole process is in the range of 5-250  $\mu$ s and is illustrated in Figure 1.17.

The three important physical properties of a fluid forming droplets are density,  $\rho$ , surface tension,  $\gamma$ , and Viscosity,  $\eta$  that are represented by Weber Number,  $We = v^2 d\rho/\gamma$ , and Reynolds number,  $Re= vd\gamma/\eta$ , where v and d are the fluid velocity and a characteristics length. The Weber Number plays an important role at early stage of drop generation where interplay of inertia over surface tension is important (I), whereas the Reynolds number is important in the middle to latter stages where interplay with the viscoelasticity of ligament is important.

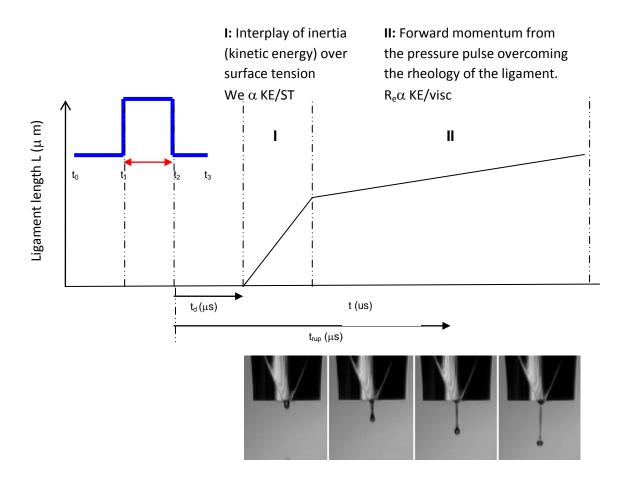


Figure 1.17 Schematic Representation of Pressure Pulse Generation and Droplet Ejection for DOD Inkjet Printing From [44]

The dimensionless Ohnesorge number,  $Oh = We^{1/2}/Re$  is used by Fromm [43] to eliminate the velocity dependence and he calculated that if Oh<0.5, DOD printing is possible then. Derby and Reis [44] defined a range of 0.1<Oh<1, after investigating a range of different fluids, within

which DOD printing is possible. If *Oh>1*, then drop will not form because of viscosity deposition within the liquid and when *Oh<0.1*, a series of satellite drops will form rather than a single drop as desired.

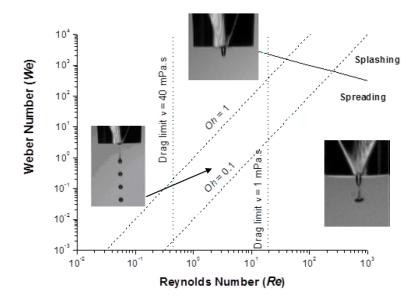


Figure 1.18 Diagram Illustrating Region Bounded by Ohnesorges Number and Defines the Limiting Region for Drop generation in a DOD Inkjet Printhead [45].

#### **Drop Flight**

An aerodynamic drag on the droplet in flight can lower the drop's velocity and may cause drop deflection by random fluctuation in the surrounding atmosphere. Derby [45] demonstrated the critical value for *Re* will vary from 19.5 for liquid of viscosity 1 cP to 0.48 for a liquid of viscosity 40 cP.

#### **Drop Impact**

This is the last step of DOD printing process in which the drop loses its kinetic energy because of viscosity dissipation and surface extension. However, there is a limiting value for drop velocity which depends on roughness and porosity of the surface. If drop velocity is too high, there is a possibility of drop splashing.

After considering the above stages of printing, the optimal range of static values for DOD inkjet printing are suggested as a viscosity ( $\eta$ ) lying in the range 2-20 cP and the surface tension ( $\gamma$ ) in the range 20-50 mN.m<sup>-1</sup>.

#### 1.1.6.5 Inkjet Technologies for Textile Application

King [46] discussed currently available printheads and inkjet technology trends for textile application, and addressed the issues of improved speed and performance in terms of reliability and resolution, and current printhead design and selection. The speed of most of print heads for textile applications are quoted in the range of less than 20 m<sup>2</sup>/h to 30 linear metere/minute, where there are number of printhead that offer the speed in the range of 70 m<sup>2</sup>/h or more.

The printhead machines, based on Epson's micro piezo DOD technology, are capable of fabric transport and supporting bulk ink supply. These features, in combination with modest pricing, have made this technology lucrative to the industrial printers, and is being used by vendors like Mimaki (TX series), Mutoh (ViperTX series), Stork (Ruby 5), Robustelli (Mona Lisa series), La Meccanica (Qualijet), DigiFab (StampaJet), ATP Color (T series), MS Macchine (MS series), Hollanders (ColorBooster), Yuhan Kimberly (UJET MC3 series), and Splash of Color (Heatwave DFP model). However, these system developers are currently shifting towards newer Epson technology that offers an increased number of nozzles per printheads and increased productivity. For example, the Mimaki JV5 and a number of models from Mutoh are engineered with eight rows of 180 nozzles each, whereas earlier generation Mimaki's TX2 model has two rows of 180 nozzles each. In spite of the popularity of Epson-based technology, system developers have also used other technology like Nassenger 7TX which is engineered with 24 Konica Minolta printheads with print rates up to 250  $m^2/h$ . Regianni's DReAM printer based on HP-Scitex Vision's Aprion printheads can also print up to 250 m<sup>2</sup>/h. Moreover, a significant increase in print speed has resulted from banking print heads together to form arrays. This technology has been used in the case of Osiris' ISIS machine the continuous inkjet printhead developed by Markem-Imaje S.A.( USA/France) that cover the entire width of the print design as the printhead traverses back and forth across the width of the machine [46]. Table 1.4 represents manufacturer name, type of printheads, number of nozzles, drop frequencies, drop volumes, vendors of piezoelectric printheads for textile applications.

35

Manu-	Print	No. of	Frequency	Drop	Digital Textile Printers
facturer	Head	Nozzle		Volumes	
Epson	DX4	2×180	Typical	3.5 to 10	Mimaki "TX2"
			8 KHz	pL	
Epson	DX5	8×180	Typical	3.5 to 10	Mimaki "JV5",
			8 KHz	pL	Stork "Saphire",
					Robustelli "Monna Lisa"
Fuji Dimatix	Spectra	256	Max 20 Khz	70-85 pL	Kornit "93 series",
	Nova				Axexco "Vega"
	256				
Konica	KM 256	256	15-18 KHz	15 pL	"Nassenger V"
Minolta					
Konica	KM 512	2×256	12.8 KHz	14 pL	"Nassenger VII"
Minolta					
Konica	KM	2×512	12.8 KHz	14 pL	No printers known as
Minolta	1024				yet
Kyocera	KJ4	2656	20 KHz	4pL to 21	Mimaki TX400
				pL	
Ricoh	Gen 4	2×194	Max 30	5-25 pL	Mimaki TX400
			KHz		
Seiko Printek	Jet	508	6-40 KHz	Typical 42	MS srl "XR" Series
	508GS			pL	

Table 1.4 Piezoelectric Print Heads for Textile Applications [39]

#### 1.1.6.6 Inkjet Inks

Inkjet inks are the most important component in inkjet printing. The formulation and chemistry of inks determine the printing image quality as well as jetting characteristics of inks and reliability of printing.

#### (A) Classification of Inks

Figure 1.19 illustrates the classification of inkjet inks and different types of inks are discussed briefly in the following:

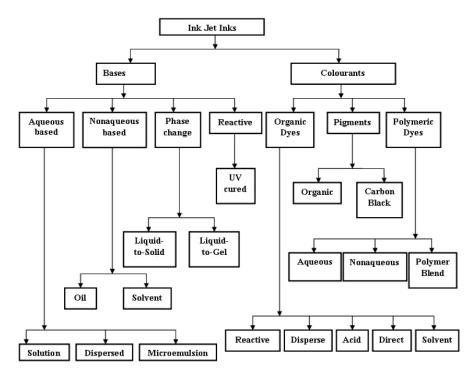


Figure 1.19 Classification of Inkjet Inks [34]

## **Aqueous-Based Inks**

Water-based inks, which have been developed over the 30 years for both thermal and piezoelectric inkjet applications, have the main advantage over solvent based inks in that they contain little or no volatile organic components [42]. It has been commonly used in home and small office inkjet printers like the Hewlett-Packard Desk Jet series, Canon BJC series, and Epson Colour Stylus series. Because of the basic bubble formation process, water seems to be the material of choice for thermal inkjet [34] and due to the requirements of print heads, nearly all the inks used for textile printing are water-based [26]. A typical composition of water based inkjet inks is listed in Table 1.5.

Component	Function	Concentration(%)
Deionised water	Aqueous carrier medium	60-90
Water soluble solvent	Humectant, viscosity controller	5-30
Dye or pigment	Provide colour	1-10
Surfactant	Wetting agent, penetrating agent	0.1-10
Biocide	Prevents biological growth	0.05-1
Buffer	Controls the pH of ink	0.1-0.5
Other additives	Chelating agent, binder,	>1
	defoamer etc.	

Table 1.5 Typical Composition of Water-Based Inkjet Inks [34]

#### **Oil-Based Pigment Inks**

This type of ink contains dispersed pigments in a low viscosity, non-volatile oil with pigment particle sizes of less than one micron. The viscosities of this type of ink are approximately 10 cP and have surface tensions below 30 mN.m<sup>-1</sup>. These types of inks have produced images with excellent light and water fastness, and there are no issues of cockle when printing on paper, as the inks do not contain any water. These inks are used in wide format applications such as receipts and lottery tickets [42].

#### **Phase Change Inks**

Phase change inks are solid at room temperature and consist of mainly transparent mixtures of synthetic waxes, are known as hot melt or solid inks. These inks are jetted as a molten liquid which solidifies immediately upon hitting the recording surface, thus preventing spreading or penetrating of inks on or into the printed media. The quick solidification process ensures good image quality on wide variety of recording media [34].

#### 100% Solid UV Cure Inks

UV curable inks, which can be either clear or pigmented, contain a blend of monomeric and oligomer acrylates or epoxies that are polymerised by using UV light in the presence of a photo-initiator [47, 48]. Upon exposure to irradiation, all the ink components are chemically cross-linked; thus the printed film is instantly hardened on the substrate. These types of inks give good quality printing across a range of non-porous substrates like plastics and metals, and can be used for printing of beverage can labels and credit cards. To achieve good printing performance, ink viscosity should be around 10 cP at operating temperature and the surface tension is required to be in the region of 23-29 mN.m<sup>-1</sup> with a pigment particle size is typically below 1  $\mu$ m [42].

#### **Solvent- Based Inks**

As there is no absorption or penetration occurring with solvent based inks, the printed image depends on quick evaporation of ink solvent to be fixed onto the substrates. These type of inks are mainly used in industrial marking or coating applications where printing is done on non-porous substrates like plastics, metals or glass [34]. The use of aggressive solvents such as toluene, anisole, tetralin and other substituted aromatics has been increasing because of utilising inkjet printing as a fabrication tool [49].

## (B) Drying Mechanism of Inks

Upon the jetting onto the substrates, depending on the ink type, drying occurs by different mechanisms such as absorption, evaporation or penetration. Drying mechanisms of different inkjet inks are identified in Table 1.6.

Ink	Print head Drying Mechanis	
Aqueous	Thermal/Piezoelectric	Continuous absorption/
		Penetration evaporation
Oil	Piezoelectric	Absorption/penetration
	continuous	
Solvent	Continuous	Evaporation
	piezoelectric	
Hot melt	Piezoelectric	Solidification
UV curable-based	Piezoelectric	Polymerization
	continuous	
Reactive-based	Piezoelectric	Oxidation polymerization
	continuous	

## Table 1.6 Drying Mechanism for Different Inkjet Inks [34]

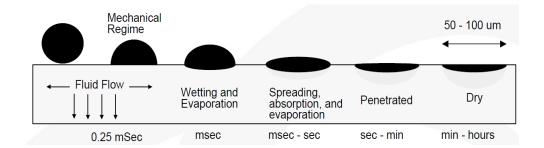
## (C) Physics of Inks

Ink design is influenced by jetting performance, operation reliability and stability in use and storage. These are usually prepared according to various parameters determined by the head design [26]. The general requirements for inks, according to Blank et al. [50], are listed as:

- Purity (to avoid blockage);
- Particle size;
- Viscosity;
- Surface tension;
- Conductivity (Continuous flow application);
- Stability;
- pH Value;
- Foaming properties.

Blank et al. also lists [50] the substrate and end use requirements:

- Substrate orientation;
- Fastness Properties;
- Wash stability;
- Handle;
- Compatibility with conventional textile printing.



# Figure 1.20 Ideal Ink Containing Colloidally Stable Black Pigment [51]

Tyler [26] cited one particular study by Schulz [52] and mentioned some general requirements of inks which are briefly discussed below.

## **Control of Viscosity**

Viscosities must be adjusted in such a way to produce a flow that is high enough to avoid starvation at the nozzle as well as not so high that it flows out on the nozzle plate. Viscosities also affect the size of the droplet and drop speed. If drop speed is too low, then there is a possibility of drop deflection on its way to drop formation on the substrate by air currents; thus affect the print quality.

## **Control of Surface Tension**

Surface tension of the inks must be in the range so that it wets the capillary channels, flows through the nozzle and forms the droplets correctly.

#### **Electrical Properties of Droplets**

Electrical properties are of great importance for continuous inkjet heads especially for electrostatic deflection of drops. It will not be possible to control the droplets during jetting without charging.

#### **Droplet Formations**

The tail or ligament that comes up with the ink drops during droplet formation is required to be absorbed by the head during its fall, otherwise several drops may formed and land in different places on the substrate which may impair print quality. There is still a possibility of spatter as the drop jets on to the substrate even if heads and tail merge; so ink developers are required to keep a balance between controlled dot gains and overspreading. Viscosity, surface tension and drop size are key variables to maintain this balance. Moreover, the pressure and molecular weight of the gas through which the drop falls play a vital role in addition to the viscosity [53]. Indicative inkjet inks requirements are listed in Table 1.7.

Ink properties	CIJ	CIJ Multi-	DOD	Valve-jet	Office	Office
	binary	deflection	piezo		pieezo	ТIJ
Vicosity (cP)	1.5	1-10	5-30	100	1.5	1-3
Surface tension	>35	25-40	>32	>24	>35	>35
(dyne/cm)						
Maximum particle	1	3	1	5	1	0.2
Size (Microns)						
Conductivity	Yes	Yes	No	No	No	No
(Micro Siemens)	>500	>1000				

Table 1.7 Indicative Inkjet Ink Requirements [54]

# 1.2 Textile Finishing

Textile finishing is considered to be the last manufacturing step of textile fabrics where fabric properties and performance are developed. It may be an integral part of wet processing but not restricted to wet processing only. After leaving the loom or knitting machine, any operations or process carried out to improve the performance or usefulness of fabric can be considered as finishing [55]. Therefore the processes such as heat-setting, napping, embossing, pressing, calendering etc. and the application of chemicals that changes the character of the fabric are included in textile finishing [5].

## 1.2.1 Types of Textile finishing

There are mainly two types of textile finishing: chemical finishing and mechanical finishing. Chemical finishing uses water as a media to apply chemicals on to the fabric, whereas mechanical finishing is considered as a dry operation, although applied chemicals are often required in this operation to successfully process the fabric. Although mechanical devices are used in both types, a major distinction can be made by determining whether the chemical or machine plays a vital role in changing fabric properties [55]. The commonly used textile finishing techniques are listed in the Table 1.8.

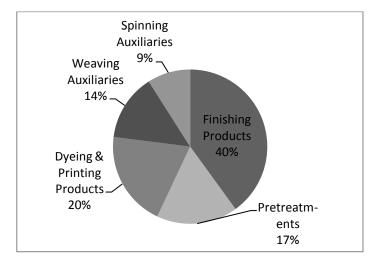
Chemical Finishing	Mechanical Finishing
Water-repellency and waterproofing	Calendering
Flame-retardant finishing	Emerising
Chemical softening	Raising
Antistatic and soil-release finishes	Compressive shrinkage
Easy care finishing	
Anti-microbial, rot proofing and hygiene finishes	
Shrink proof finishing	
Coating, laminating, bonding, flocking and prepregging	

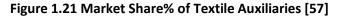
Table 1.8 Most Commonly Used Textile Finishing Techniques [56]

Chemical finishing especially shrink resist finishing of wool and cotton is discussed in this chapter.

# **1.2.2** Significance of Chemical Finishing

Chemical finishing has been a vital part of textile processing over the years. As the demand for high performance textiles has grown, the trend to use high tech finishing products that provide the required fabric properties has also increased accordingly. Surveys showed that amount of textile chemical auxiliaries sold and used globally in a year is one-tenth of the world's fibre production. Figure 1.21 illustrates the percentage of market share of textile chemical auxiliaries & Figure 1.22 represents the distribution of finishing products by amount and value. The largest percentage of textile chemicals are used in finishing (approximately 40%) followed by dyeing and printing and softeners are most important individual finishing product group [57].





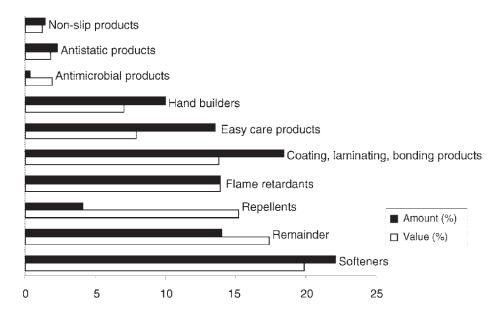


Figure 1.22 Distribution of Finishing Product Groups by Amount and Value [57]

## 1.2.3 Application of Chemical Finishes

The application of finishing chemicals depends on the particular type of chemical used, fabrics involved and machinery type used. Chemicals such as softeners, ultraviolet protection agents and some soil release agents that have strong affinity to textile fibres can be applied by exhaustion, whereas the chemicals that do not have an affinity for fibres are applied by a suitable continuous processes that involve either immersing the textile in a solution of the finishing chemical or applying the finishing solution to the fabric by some mechanical means. The fabric must be dried after application of finishing chemicals and then fixed by a method called 'curing' (high temperature treatment) if required [57]. A typical pad-dry- cure unit is illustrated in the Figure 1.23.

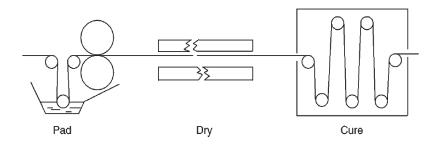


Figure 1.23 Schematic Diagram of Typical Pad-Dry-Cure Process [58]

Different methods of finishing application, drying and curing have been identified by Schindler, W.D. and Hauser, P.J. [57] and are discussed in this section.

#### 1.2.3.1 Application Methods

#### Wet on Dry Application

The pad application of chemicals on dry fabric involves passing of dyed or printed fabric after drying through a solution containing finishing chemicals. The wet pick up of chemical solution depends on fabric characteristics, machine parameter and solution properties [59]. For consistent chemical application on to the fabric, nip pressure across the width of fabric should be constant, solution level and temperature should not change, and fabric speed should remain the same throughout the application [60].

#### Wet on Wet Application

To save the cost of drying of dyed fabric, wet fabric is padded with the chemical finishing solution. In wet on wet application, the wet pickup of the fabric leaving the pad must be 15-20% higher than that of the fabric entering the pad. Another problem required to be addressed in this method is that the water entering into the pad with incoming fabric may interchange with the finishing solution, thus diluting the original solution which may cause tailing effect. Therefore, a chemical feed more concentrated than the pad solution must be employed to overcome this problem.

#### Low Wet Pick Application

Typical pad applications range between 70-100% wet pick up which requires large amounts of water to be removed during drying. Moreover, migration of finishing chemicals may occur due to the evaporation of this water, which leads to uneven finish distribution along the fabric [61]. Therefore, this problem of migration can be solved by reducing the amount water in the finishing solution. However, too low a wet pick up may lead to uneven distribution of finishing chemicals because of a discontinuous liquid phase [62]. So it is necessary to find out the minimum amount of finish liquid that can be applied to a given fabric without producing any

non-uniform distribution of finish after drying and curing, and this minimum amount of finish is known as the 'critical application value' (CAV) [63]. The value of CAV values depends on fibre types, fabric construction and absorbency. Hydrophilic fibres like cellulosic fibres have CAV in the range of 35-40%, whereas that for hydrophobic fibres like polyester is less than 5% [57].

#### 1.2.3.2 Drying of Wet Textiles

Wet textiles contain water in three different areas: on the surface, interstices and in yarn capillaries. The water in the first two areas is most loosely bound and can be removed by squeezing, centrifugation or vacuum extraction. The remaining water in the yarn capillaries are absorbed internally by fibre must be removed by thermal vaporisation.

There are three heat transfer methods to dry the fabric: conduction, convection and radiation method. Conduction is the most efficient method which involves direct contact of heating surfaces with the fabric such as cylinder cans. However, the only drawback is that it cannot control the width of the fabric. In contrast, convection drying is the most common method which allows the control of fabric dimensions as well as high processing speed. Moreover, it involves the direct contact of fabric with hot air that is heated to the desired temperature by gas- or oil-fired burners or steam heat exchangers and passed over the fabric by high velocity blowers. The third method is radiation which includes infra-red and radio frequency dryers, and often used as pre-dryers to minimise much of the moisture; thus reducing the finish migration and increase dryer efficiency.

Figure 1.24 illustrates a schematic of a Tenter frame (pad dry cure unit) utilising convection heat transfer to dry textiles.

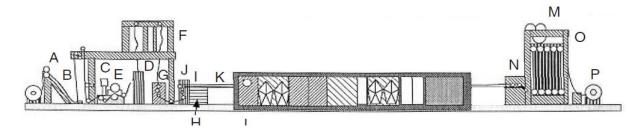


Figure 1.24 Tenter Frame [58]

#### 1.2.3.3 Curing of Chemical Finishes

The heating equipment that is used for drying can be used for curing of finishing chemicals on the fabric. However, the fabric temperature cannot be increased above 100°C before removing all the water from the fabric, Figure 1.25. Curing and drying can be combined as well as in separate in two steps.

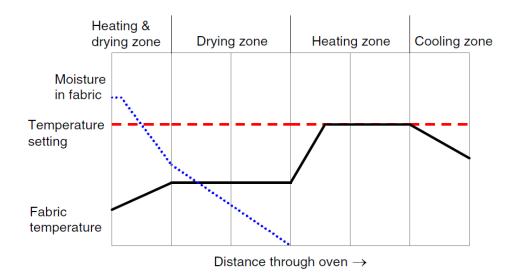


Figure 1.25 Temperature and Moisture Profile in Tenter [57]

# 1.3 Shrink Resist Finishes

The term shrinkage is used to define the contraction in length, breadth, volume of the fabric on washing [64]. Shrinkage can be further defined as "a dimensional change in a fabric or garment caused by an application of a force, energy, or a change in environment that either allows the goods to relax or forces the fabric to move in a given direction"[65]. Therefore, the finishes that are applied to textile substrates to achieve anti-shrinkage properties, thus prevent or control shrinkage on washing, are called shrink resist or anti-shrink or anti-felt finishes. Shrinkage of wool and cotton fabrics will be discussed in this section.

## 1.3.1 Wool Felting Shrinkage

Wool fabric tends to felt and shrink severely on washing; even more than 50% is not unusual for untreated fabric [56]. It is an animal fibre composed of an outer layer of overlapping scales (called the cuticle) surrounding an internal core (the cortex), Figure 1.26. The cortical cells are mainly composed of Keratin, a protein containing high sulphur content related to the

disulphide bond crosslink amino acid. These species play a vital role in many shrink resist systems as well as give wet strength, low lateral swelling and insolubility [66].

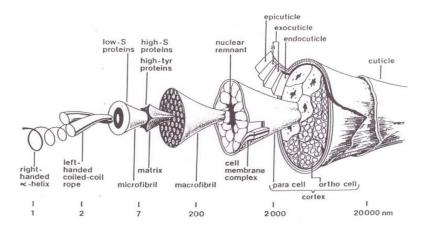


Figure 1.26 Structure of Wool Fibre (from Division of Protein Chemistry, CSIRO, Australia)

Cotton and other synthetic fibres are smooth, whereas wool fibres are more or less wrinkled, or crimped in appearance depending on the breed of sheep from which the wool is taken and it's diet [67].

## 1.3.1.1 Causes of Wool Shrinkage

Heywood [56] mentioned two distinct reasons for shrinkage of wool during washing: felting and relaxation; and are discussed below:

## **Felting Shrinkage**

In felting shrinkage, fibres become entangled with one another which causes overall contraction of the wool textile fabric structure [68]. This type of shrinkage arises from the ratchet-like nature of the fibre scales. There will be low resistance to sliding during movement of the fibres against any surfaces in the root-to-tip direction, whereas for movement in opposite direction causes contact with edges of the scales and strongly resists movement. Therefore, this preferential uni-directional friction is responsible for wool fibre felting.

There are three main factors which influence the felting; these are moisture, mechanical agitation and heat. Moisture causes wool fibre to swell and it can absorb up to 30-38% of its own weight in water. The greater the mechanical agitation, the more the fabric felts. In addition, heating has some effect on felting and felting reaches its maximum level in the temperature range of 50-60°C after which it does not increase further.

#### **Relaxation Shrinkage**

The stress and strain introduced into the structure of the fabric by different handling and manufacturing process are released during washing of garments in the water. This change causes shrinkage which is known as relaxation shrinkage. These stress and strains are sometimes deliberately given to fabric or garments in drying or pressing processing, where manufacturers make undersized garments so that it comes back to its original after washing. However, if garments or fabrics are not washed subsequently, then there will be problem of dimensional change during first laundering of garments.

#### 1.3.1.2 Wool Shrinkage Control Options

Heywood [56] identified the available options for controlling wool shrinkage which are discussed below:

#### (A) Physical Considerations

The objective of all shrinkage control system is to prevent selective fibre movement during washing that can be achieved by reducing the frictional difference between with-scale and against-scale directions.

#### **Friction Control**

This is most widely used method to control felting, which is carried out by raising the coefficient of friction in the with-scale direction, reducing friction in against-scale direction, or modifying the fibre geometry. The coefficient of friction in against scale direction can be modified by modifying scale behaviour or by applying a friction reducing agent. Modification of scale behaviour is mostly used in commercially available shrink resist treatment which involves aggressive chemical treatment to attack the protein structure and make it more flexible when wet.

#### The 'Spot Welding' Concept

The concept of spot welding is to create linkages between adjacent fibres by the application of a suitable polymer, which can be cross-linked. The linkages must be of sufficient number and have sufficient strength to prevent fibre movement. The major concern of this technique is depositing the polymer onto the fibre surface in such a way to form linkages between the adjacent fibres.

#### (B) Chemical Considerations

There are two chemical areas to consider; scale modification and fibre coating. Most of the commercially available shrink resist finishing techniques involved both of these factors, whereas for all successful applications, at least one is considered.

## **Scale Modification**

Scale modification involves usage of some chemical means to modify the nature of the scales of the wool fibre by degrading the protein structure, which makes the fibre surface more flexible and swollen on immersion in water. The most important way of degrading the keratin structure of cuticle cells is by cleavage of the cystine disulphide bond between two protein chains [66]. The choice of oxidant is also important in order to achieve maximum felting control; the most common of these is chlorine which rapidly attacks wool proteins and oxidises cystine crosslinks to cysteic acid.

## **Fibre Coating**

Fibre coating is an essential component of scale masking and spot welding. However, certain requirements for fibre coating are necessary such as the coating must be fixed to fibre surface even under extreme conditions such as dyeing, or reductive bleaching; the polymer must spread evenly over the fibre surface and polymers must crosslink after application to provide sufficient mechanical strength.

#### 1.3.1.3 Commercial Process Routes for Shrinkage Control of Wool Fabric

Fabric is usually treated by a pad-dry-cure method using a standard padding equipment, which is preferably adjacent to the dryer to be used in order to avoid premature dry patches and incorrect curing. Alternatively, fabric can be treated in dyeing machines by the exhaustion method, but special care is required to avoid relaxation shrinkage. However before application of the polymer, all the contaminants are required to be removed and the pH needs to be adjusted.

There are two types of resins which are used in single step padding process to control wool shrinkages; one is the isocyanate-based polymer systems typified by Synthappret BAP (Bayer), Braxan WF (Ciba) and Protolan 367 (Rotta), and another is the siloxanes typified by Ultratex ESB (Ciba) [56]. The isocyanate-based polymers are mainly applied at a slightly alkaline pH and heat-cured at high temperature (150-160°C), whereas the siloxanes are applied at slightly acidic pH. The main problem in finishing with siloxanes is that, the garment may develop pronounced cuff edge felting at the creases and folds [56]. The isocyanate type systems are

better able to control this type problem and therefore preferred, although they have poorer handle. However, this handle property can be improved by using a polyurethane dispersion with the isocyanates.

Parameters	Isocyanates	Siloxanes
Fabric pH	6-8	7-8
Dosage	1-2% on the weight of wool	9-16% on the weight of wool of
	of both Synthappret BAP	Ultratex ESB 130, plus Ultratex
	and Impranil DLH, and	EW in the ratio of 1 part EW to
	3-5 g/l Sodium Bicarbonate	80 parts ESB 130
Curing	150-160°C fabric	120-140 °C plus batch in
	temperature at the end of	crease-free state for 7 days
	drying	

Table 1.9 Typical Requirements for One-Step Padding Process ofFabric (Adapted from [56])

## 1.3.2 Cotton Shrinkage

The primary wall of cotton fibre consists of a network of cellulose fibrils and is covered with an outer cuticle of pectin, fats and waxes, which makes the fibre impermeable to water, Figure 1.27. The secondary wall consists of concentric layers of cellulose fibres in a spiral arrangement around the fibre axis. The lumen is what remains of the central canal [69].

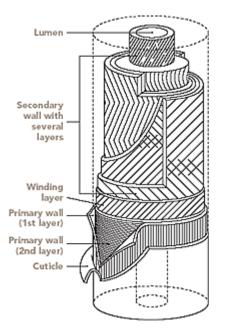


Figure 1.27 Structure of a Cotton Fibre [69]

The structure of cotton, and the way it's spun, woven and finished are mainly responsible for shrinkage. Berkley [64] determined that the nature of the cotton fabric shrinkage was due to the fibre structure and found that cotton does not regain its original shape after drying. Parker [70] mentioned the influence of this shrinkage when fibres are spun into yarn and yarns are woven into fabric. There are mainly two types of shrinkage which occurred in cotton fabric: relaxation shrinkage and swelling shrinkage. Relaxation shrinkage occurred on wetting out the fabric, where it releases distortions and tensions that were introduced in looms or knitting machines; whereas swelling shrinkage occurred due to swelling of the fibre in water. When fibres are immersed in water, warp yarns follow a long curvature around the swollen weft yarn; thus the fabric shrinks irreversibly due to the presence of warp crimp after drying. Figure 1.28 represents mechanism of swelling shrinkage.

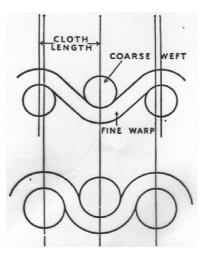


Figure 1.28 Mechanism of Swelling Shrinkage in Cotton Fabric [71]

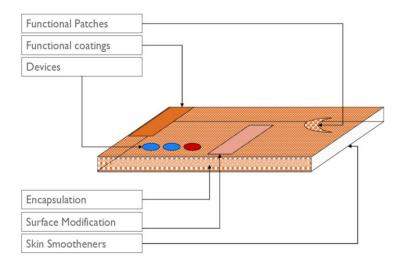
Cotton shrinkage can be controlled by either mechanical or chemical finishing, or a combination of both. Chemical finishing or crosslinking by suitable chemicals, typically formaldehyde-based reagents such as Dimethylol Dihydroxy Ethylene Urea (DMDHEU), has been the most commonly used method to control cotton shrinkage, and easy care or durable press finishing is one of the most favoured methods available to manufacturers. The chemical cross-linking alters the swelling shrinking phenomena and thus reducing shrinkage by altering the relaxed dimension. This type of finishing not only improves the dimensional stability i.e. shrinkage control, but also provides smooth appearance as related to better crease recovery angle, anti-pilling properties and good retention of some dyestuff. However, the major problems with this cross-linking system is risk of losing strength in the fabric [72], and the formaldehyde release [73].

# **1.4 Digital Finishing of Textiles**

Digital finishing may be defined as a type of inkjet printing by which different chemicals are applied on to the textile substrates in controllable quantities and at prescribed locations that gives the substrate multiple functionalities and performance characteristics [74]. Therefore, digital finishing produces functional properties on the selected areas of the fabric by depositing the finishing composition from the nozzles in a series of droplets to deposit a predetermined pattern of droplets on selected area of the substrates [75].

## 1.4.1 Scopes of Digital finishing

Digital finishing gives exact localisation and patterning of functionalities in and onto the 3D matrix of textile substrates that is represented in Figure 1.29. Moreover, it provides integration of present and future technologies like advance thermo- and hydro-regulation, sensors, actuating and controlled release function, but provides also approaches towards to existing functionalities [74].



#### Figure 1.29 Digital Functionality of Textile Substrates [76]

Craamer et al. [75] cited an unexamined patent application No. JP61-152874 assigned to Toray industry, which suggested impregnating a textile substrate with a functional composition in the form of dots of mean diameter 30 to 500 microns and occupied area ratio is 3 to 95%. It also suggested a number of functional compositions that can be applied in the form of dots, such as antibiotics, moisture absorbents, water repellents, antistatic agents, ultraviolet ray absorbents, infrared ray absorbents, optical whitening agents, swelling agents, solvents, saponifiers, embrittlement agents, inorganic granules, metal granules, magnetic material, flame retardants, oxidants, reducing agents, perfumes etc. A suggested typical textile digital finishing unit is illustrated in Figure 1.30.

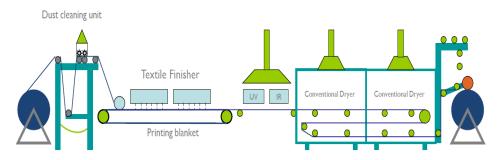


Figure 1.30 Schematic Diagram of a Typical Textile Digital Finishing Unit [77]

## 1.4.2 Benefits of Digital Finishing of Textiles

Digital finishing provides the option of applying chemical substances with exact dosage and in concentrated form that sometimes make interim drying unnecessary. It also increased efficiency per process run by reducing the number of cycles of operation and moreover allows very uniform layers to be formed on to the fabrics due to precision of dosage and nozzle control [74]. Furthermore, a digital finishing technique is cleaner and efficient process in terms of material and energy consumption with higher levels of process automation and digital data sharing. In addition, there are economic advantages like lower production costs, savings in terms of process water, energy and wet chemistry, enabling new business models with high added value, shorter production runs, higher productivity, higher flexibility, better inventory management, and enabling (mass) customization [74].

## 1.4.3 Current Research and Future of Digital Finishing

The Digitex (Digital Programmed Jetting of Fluids for Multifunctional Protective Textiles) project of European (high tech) textiles and clothing industries has developed the technology of digital finishing on textile substrates. There are three types of results which were obtained from Digitex projects: product related, process application, computer aided modelling and tools. Firstly, a number of digital finishing were developed in that projects such as antimicrobial, chromic functionalities, controlled release functions, single-sided hydrophobic functions, functional and conceptual garments. Secondly, process related innovations are digital dyeing, digital UV coatings, substrate instability and deformation monitoring, substrate intake quality monitoring and print head monitoring. In addition there were improvements in computer aided modelling and tools such as drop substrate interaction tool, drying and curing tools and substrate simulation [74]. Figure 1.31 represents single sided hydrophobic finished textile substrate by inkjet printing.

Craamer et al. [75] suggested a composition for flame retardant and antistatic finishing by continuous inkjet printing. Ali et al. [78] have formulated inks incorporating fluorocarbon,

based on C8 and C6 chemistry and applied it on both sides of the fabric and measured contact angles and spray rating to evaluate the results. Rybicki et al. [79] has developed the method of anti-bacterial finishing of flat textiles by an industrial inkjet printer with the Xaar 128-360 printing head.

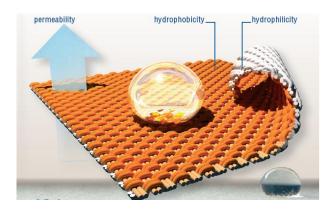


Figure 1.31 Single Sided Hydrophobic Finishing of Textile Substrates [74]

A report by NanoMarkets [80] suggested that worldwide functional ink demand will grow up to 205 million litres by 2016 from 12 million litres in 2009. As the cost of solvents and aqueous based inks are lower than that of other inks, accordingly they will be used most. In addition NanoMarkets expects the revenue of worldwide functional inks will reach to approximately \$5.5 billion by the end of 2016 from \$329 Million in 2009, Figure 1.32.

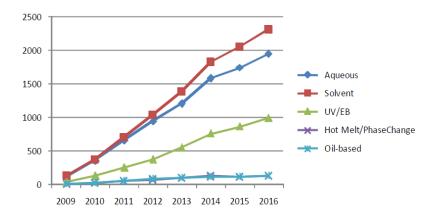


Figure 1.32 Worldwide Functional Ink Revenue by Ink Types 2009-2016 (\$ Millions) [80]

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CHAPTER 2 MATERIALS AND METHODS

# 2.1 Materials

## 2.1.1 Textile Fabrics

In this investigation 100% cotton, scoured-bleached,  $20 \times 20/60 \times 60$  sheeting woven fabric, and scoured set 100% wool Botany Serge, 300 g/m<sup>2</sup>, supplied by Whaley's, Bradford, UK were used to investigate shrink resist performance of the fabrics.

## 2.1.2 Textile Finishing Chemicals

#### Synthappret BAP

Synthappret BAP is a bisulphite adduct of a polyisocyanate polyurethane and mainly suitable for anti-felting of wool and wool blends without any necessity for pre-chlorination of the wool [1]. The chemical was supplied by TANATEX Chemicals B V Netherlands.

#### **Kieralon Jet B Conc**

Kieralon Jet B Conc is a mixture of non-ionic surfactants and was supplied by BASF AG. The major component of Kieralon Jet B Conc is isotridecanolethoxylate (approximately 70-80%) [2]. This product has high wetting power and suitable for the washing processes where there is very high liquor turbulence. It is recommended to use in finishing liquor solution to increase chemical pick up of the fabric [3].

## Sodium Bicarbonate

The shrink resist finishes that are applied on the fabrics are required to be cross-linked at weakly alkaline pH. This pH should be below the range at which fabric yellows and loses strength because of alkali damage to the fibre. Therefore, the finishing bath pH was adjusted to 7-7.5 by the addition of sodium bicarbonate [1]. Laboratory grade sodium bicarbonate was bought from Tennants Ltd, UK.

## 2.1.3 Chemicals for Ink Formulation

## 2.1.3.1 Viscosity Modifiers

Viscosity modifiers play a very important role in increasing the reliability and quality by controlling the drop formation and break-up process. If the molecular weights of viscosity modifiers are very high, then jet break-up become difficult because of their elasticity [4]. There are several viscosity modifier available, of which glycerol, Polyethylene Glycol of molecular weight 200 (PEG200) and Carboxymethyl Cellulose (CMC) were used in this study.

#### Glycerol

Glycerol, which has molecular formula of HOCH<sub>2</sub>CHOHCH<sub>2</sub>OH, is a colourless viscous solution belonging to the alcohol family of organic compounds [5]. Natural or native glycerol can be

obtained as a by-product in the conversion of fats and oils to soaps, whereas synthetic glycerol can be produced from propylene. The fastest growing method of producing glycerol is from the conversion of fatty acid methyl esters for biodiesel, where 100 kg of glycerol is formed in 1000 kg of biodiesel [6]. The glycerol that was used in this experiment had molecular weight of 92.09 and surface tension of 63.4 mN/m at 20 °C [7] and was purchased from Sigma-Aldrich.

## Polyethylene Glycol (PEG 200)

Polyethylene glycol (PEG) is a synthetic polyether, which is available in a range of molecular weights. Low molecular weight PEG is a clear, viscous liquid, and the products with molecular weight lower than 10,000 is known as polyethylene glycol, whereas polyether with molecular weight higher than 10,000 is known as polyethylene oxide (PEO) [8]. PEG 200 was purchased from Sigma-Aldrich. Figure 2.1 illustrates the molecular formula of PEG 200.

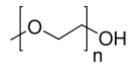
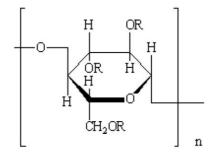


Figure 2.1 Molecular formula of PEG 200 [8]

## **Carboxymethyl Cellulose**

Carboxymethyl Cellulose (CMC) was used as a viscosity modifier, and is the sodium salt of the carboxymethyl ether of cellulose. It is prepared from cellulose by treatment with alkali and monochloro-acetic acid or its sodium salt [9]. CMC was purchased from BDH Chemicals. Figure 2.2 illustrates the structural formula of CMC.



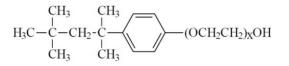
where R = H or CH<sub>2</sub>COONa

## Figure 2.2 Structural Formula of CMC [9]

#### 2.1.3.2 Surfactants

## Triton X-100

Triton X-100 is an Octylphenol ethylene oxide condensate that is produced from octylphenol polymerised with ethylene oxide, Figure 2.3. It is a viscous (viscosity approximately 240 cP at 25°C) non-ionic surfactant with critical micelle concentration of 0.22 to 0.24 mM [10]. Triton X-100 was purchased from Sigma-Aldrich.



#### x = 9-10

#### Figure 2.3 Molecular Formula of Triton X-100 [10]

Another surfactant used in this experiment is Kieralon Jet B Conc which was discussed earlier in section 2.1.2.

#### 2.1.3.3 Humectants

Humectants are mainly used to control or limit the evaporation of the inks. Humectants such as glycols and alcohols act as hygroscopic agents to remove moisture from the air during printing or in the idle position of printer, thus preventing clogging of print heads [11]. In this study, glycerol was used as both a humectant and a viscosity modifier.

## 2.2 Experimental Approach

## 2.2.1 Characterisation of Synthappret BAP

#### 2.2.1.1 Solid Content (%) of Synthappret BAP

The solid content of Synthappret BAP was measured by drying a known amount of the chemical solution on a plate in a vacuum oven at 100°C. The Synthappret BAP was left in the oven until the water and other solvents were evaporated completely. Solid content, usually expressed as a percentage (%), was measured from the weight of the chemicals before evaporation and weight of the solids that was left after evaporation, by using following equation.

Weight of the chemical (before evaporation – after evaporation)

Solid Content % =

Weight of the chemical before evaporation

— X 100%

#### 2.2.1.2 Surface Tension

Surface tension was measured by using torsion balance (model OS) for surface and interfacial tension measurement. Xennia technology test method (XenTM No. 0003) [12] was used to

determine the surface tension of Synthappret BAP and the ink formulations. The machine was calibrated by measuring known surface tension of water several times at a certain temperature of testing environment.

#### 2.2.1.3 Viscosity

For viscosity measurements, a Brookfield DV-II+PRO Programmable Digital Viscometer was used. The DV-II+PRO programmable digital viscometer combines accuracy, reliability, and versatility of traditional viscometer with the advantages of electronic sensing, indication, and output. Viscosity (cP), temperature (°C) and % torque can be obtained from this viscometer [13]. Depending on the viscosity of the solution, there were a range of spindles available. As the viscosity of Synthappret BAP was identified as "high" in TANATEX product information [1] sheet, spindle S00 was used to determine the viscosity of BAP. The spindle S61 was used for the solutions of low viscosity.

#### 2.2.1.4 Measurement of pH

A Hanna pH 210 (Microprocessor pH metre) meter was used to measure the pH of Synthappret BAP and solutions containing chemicals for shrink resist finishing.

#### 2.2.1.5 Particle Size Measurement

Particle size of Synthappret BAP was measured by using a Malvern Nano series Zetasizer using a process called Dynamic Light Scattering (DLS). DLS measures the Brownian motion of the particles and relates this to the size of the particles by illuminating the particle with a laser and analysing the intensity fluctuations in the scattered light [14].

## 2.2.2 Shrink Proof Finishing of Wool and Cotton

A range of formulations containing increasing amount of Synthappret BAP from 10g/l to 60 g/l (recommended by chemical supplier) with 1g/L of Kieralon Jet B Conc were prepared and their pH was adjusted to 7.0 to 7.5 by the addition of NaHCO<sub>3</sub>. A typical pad-dry-cure method was used to apply the shrink resist finish onto the textiles. The effects of the chemical pick up on cotton and wool was investigated and adjusted by varying the padder pressure and speed. The wet pick-up% on wool and cotton was found to be 70% & 80%, respectively, at 1 bar pressure of padder. Both wool and cotton fabric were padded with the shrink resist chemical solution, then dried at 108°C for 4 minutes and cured at 150°C for 3 minutes. For wool, before padding, the fabric samples were dipped into finishing solutions for few minutes to ensure sufficient chemical pick-up. The recipes used for shrink proof finishing of wool and cotton is illustrated in Table 2.1.

Chemicals &	1	2	3	4	5	6
Parameters						
Synthappret BAP (g/L)	10	20	30	40	50	60
Kieralon Jet B Conc						
(g/L)	1					
NaHCO₃ (g/L)	4					
Water (g/L)	rest to make total 1 L solution					
рН	7-7.5					
Pick-Up%	70% for wool and 80% for cotton					
Drying	at 108°C for 4 minutes					
Curing	at 150°C for 3 minutes					

Table 2.1 Formulation Composition and Application Parameters forShrink Resist Finishing on Wool and Cotton.

## 2.2.3 Performance Evaluation of Finished Fabric

The performances of treated fabrics were evaluated by investigating the wash stability of the finishes, dry crease recovery angle before and after finishing, and by the Kawabata Evaluation system. The surface morphology of the finished and unfinished samples was investigated by using Scanning Electron Microscopy (SEM).

## 2.2.3.1 Wash Stability Test

The wash stability of the shrink resist finishes was investigated by following the British standard (BS EN ISO 5077:2008) for textiles – determination of dimensional change in washing and drying [15]. The specimen was conditioned in a standard atmosphere and measurements were taken before subjected to the appropriate washing and drying procedure. Then the samples were washed in a Wascator by following the Woolmark 5x5a programme for home laundry wash and SDC ECE Phosphate reference detergent B was used as standard reference detergent. After drying, conditioning and re-measuring the specimen, the changes in dimensions (area shrinkage %) were calculated.

## 2.2.3.2 Crease Recovery Angle Measurement

The total dry crease recovery angle of finished fabric before and after five washes was measured by using British Standard (BS EN 22313:1992/ISO 2313:1972). The rectangular specimens of prescribed dimensions were cut in both warp and weft directions, folded them by means of a suitable device and maintained in this state for a specified short time under a

specified load. After the specified time, the creasing load was removed, the specimen allowed to recover for a specified time, and the crease recovery angle then measured [16].

## 2.2.3.3 Kawabata Evaluation System (KES)

The Kawabata Evaluation System for fabrics (KES-F) was used to determine the mechanical properties of untreated and Synthappret BAP treated fabric (before and after 5 washing cycles). The samples (20 × 20 cm) were conditioned for 24 hours at 20 °C and 65% relative humidity prior to analysis. Primary hand values (stiffness, smoothness and softness) and Total Hand value was measured using: the women's summer thin dress (203 LDY) and men's winter suit (101W) mathematical transformation equations for cotton and wool, respectively.

## 2.2.3.4 Scanning Electron Microscopy (SEM)

The surface morphology of untreated and finished fabric was analysed by using Philips XL 30 field emission scanning electron microscope. The samples were fixed horizontally on to stubs for gold plating in argon gas chamber in order to prevent accumulation of electric charging on the sample during analysis. The main SEM parameters were: working voltage: 5 kV, Spot size: 3, working distance: 15~30mm, magnification: 100~4000 times.

## 2.2.4 Ink Design Approach

The formulation that provided best quality in terms of shrink resist finishing in pad-dry-cure finishing of wool and cotton was chosen for the initial ink formulation. The surface tension, viscosity and particle size of this initial formulation were optimised, in order to make it suitable for the application in piezoelectric Dimatix Material Printer (DMP), by using different surfactants and viscosity modifiers.

#### 2.2.4.1 Surface Tension Optimisation

Kieralon Jet B Conc was used in finishing recipes of shrink resist finishing of wool and cotton to increase rapid wetting of the fabric by reducing the surface tension of the finishing solution; thus increased wet chemical pick up% of wool and cotton was achieved [3]. Therefore, Kieralon Jet B Conc was used to optimise the surface tension of the initial formulation chosen for ink formulation. In addition, Triton X-100, a non-ionic surfactant that was used by Di Risio [17] to formulate a bio-ink containing the horseradish peroxides enzyme, was also investigated to optimise the surface tension of initial formulation containing Synthappret BAP. The solutions were prepared with increasing concentration of surfactants and their surface tension was measured by the torsion balance (model OS) in order to observe the effect of the surfactants on the surface tension of the solutions, and minimise the surface tension.

#### 2.2.4.2 Control of Viscosity

To optimise the viscosity of the inks, increasing concentrations of glycerol, PEG200 and CMC were incorporated into the initial formulation and the optimised amount of surfactant.

#### 2.2.5 Inkjet Printing

#### 2.2.5.1 Inkjet Printer

A piezoelectric inkjet printer (Dimatix DMP 2800) was used to investigate the jettability of shrink resist finishing inks. A Dimatix DMP 2800 is a laboratory scale printer that allows the evaluation of inkjet inks used for new technologies. It has a MEMS-based cartridge-style disposable printhead with 16 21µm nozzles linearly spaced at 254µm and a typical drop size of 10pl. Each cartridge has the capacity of 1.5 ml. The main constraints for material requirements are the viscosity and surface tension [18]. The cartridge reservoirs were cleaned with deionised water before filling formulated inks. Figure 2.4 illustrates the printhead nozzles of DMP.



Figure 2.4 Printhead nozzles: 16 Nozzles, 254µm Spacing, 21.5µm Diameter [19].

The drop watcher system of Dimatix allows the observation and capture of the events during drop formation and the trajectory of drops after drop formations. The drop imaging system is based on bright background illumination with a stroboscopic LED array against a ground glass screen that is synchronized with a monochrome CCD high speed camera. This material deposition system also allows controlling of other jetting parameters like waveform, pulse width, individual nozzle voltage, meniscus vacuum, firing frequency, cartridge temperature, and cleaning cycles. Figure 2.5 illustrates FUJIFILM Dimatix Material Printer.



Figure 2.5 FUJIFILM Dimatix Material Printer (DMP) 2800 [20]

# 2.2.5.2 Piezoelectric Jetting Cycle

The stages of jetting cycle of a DMP are described in the DMP user manual [20]. The stages are: a) Equilibrium or standby, b) Phase 1 (drawing ink from reservoir), c) Phase 2 (ejection and drop formation), d) Phase 3 (drop break off and jet withdrawal), which are illustrated in Figure 2.6.

The equilibrium stage is mainly the standby position of the piezo as it is before the firing pulse begins and the fluid chamber is depressed in this stage. In phase 1, piezo backs to its neutral straight position as the voltage drops to zero, thus allowing the fluid to be pulled into the chamber through the inlet. In Phase 2, the chamber is compressed and the pressure generated to eject a drop. Finally in phase 3, known as the recovery phase, piezo voltage is brought back down and chamber decompresses partially to start refilling for the next pulse.

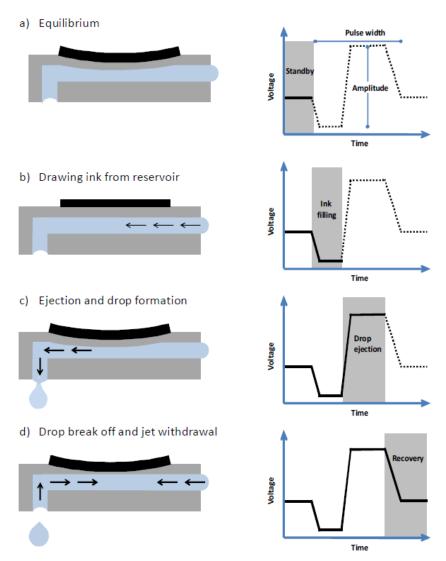


Figure 2.6 Generic Piezoelectric Jetting Cycle[19]

# 2.2.5.3 Control of Jetting Performance

The drop watcher of Dimatix 2800 makes it easier to control the jetting performance, because it monitors any problems in jetting and then allows the necessary corrective actions. For controlling the jetting performance, the strategy that was mentioned by Risio [19] in the control of jetting performance of bio-ink was followed in this experiment, and is illustrated in Figure 2.7.

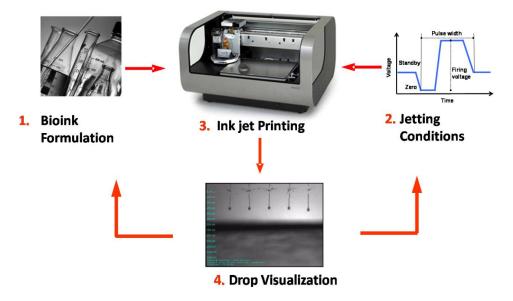


Figure 2.7 Jettability Control of Inkjet Inks [19]

## 2.2.5.4 Formulations for Printing

A range of inks containing Synthappret BAP, viscosity modifier (glycerol, PEG 200, CMC), NaHCO<sub>3</sub>, humectant (glycerol) or without humectant, surfactant or without surfactant were prepared to observe their jetting performance in the DMP. All the formulations of inks were filtered through 0.45µm pore size syringe filter to avoid clogging of nozzles. After filling the cartridge with ink, the fluid module and jetting module were attached together. Figure 2.8 illustrates this cartridge set containing fluid module and jetting module, which was left for 30 minutes with the nozzles facing down, after filling with inks, to allow the ink to settle down [20].

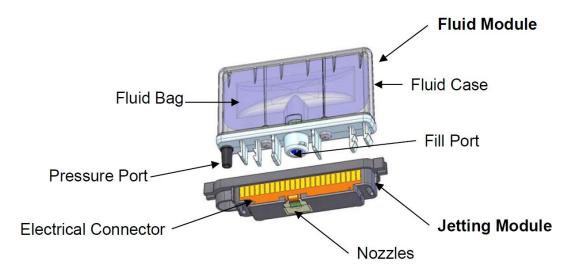


Figure 2.8 Fluid Module and Jetting Module of DMP [20]

## 2.2.5.5 Jettability Test

In all the experimental work, a drop watcher was used to view the jetting nozzles, face plates and the jetting of the fluids. The waveform used had a voltage range between 25 and 30V, duration of 7.424  $\mu$ s, with different pulse widths between 65 and 100  $\mu$ s and a frequency of 5 KHz. A suitable cleaning cycle with a 1.0 sec purge was used before jetting of each ink.

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CHAPTER 3 RESULTS AND DISCUSSION

# 3.1 Objectives

The main objective of this study was to develop a digital print method for the application of a shrink resist finish onto textiles that imparted dimensional stability and potentially could produce sculptured textural effects with subsequent laundering felting of untreated areas. Therefore, one of the most common methods of textile shrink resist finishing was investigated by applying Synthappret BAP onto cotton and wool fabrics, and a suitable formulation was selected for digital ink development, based on the performance of shrink resist finishes in terms of dimensional stability, crease recovery angles, and hand values. Thereafter, the viscosity and surface tension of the selected formulations were optimised, and a range of inkjet inks were prepared to observe the jettability performance in piezoelectric DMP.

# 3.2 Textile Fibres

The world textile industry has experienced the highest growth in twenty-five years in 2010. During this year, manufacturing volumes of natural and manmade fibres went upwards by 8.6%, or 6.4 million tons, to 80.8 million tonnes [1]. Moreover, Global Industry Analysts Inc. predicted the global textile fibre market would be 93 million tonnes in 2015 [2]. Aizenshtein [3] has also projected that the share of polyester fibres in the world market will grow continuously until 2020, whereas other fibres will lose their market share in future. Figure 3.1 represents the trends in cotton production from 1977/78 to 2009/10 indicating a decrease in cotton production over recent years with a decrease of 22.3 million tonnes in 2010/11 has been forecasted [4].

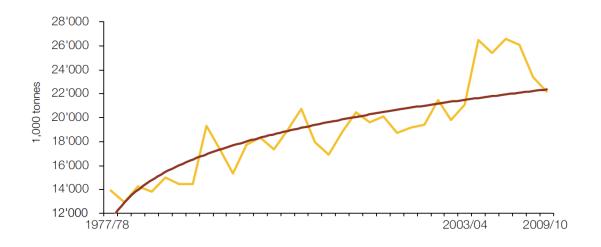


Figure 3.1 Global Cotton Production Trends 1977/78-2009/10 [4]

The global wool production was 1.1 million tonnes clean weight in 2009, which is 7.4% lower than the previous year and predicted to fall further in following years [4]. Figure 3.2 illustrates the global wool production trends by countries.

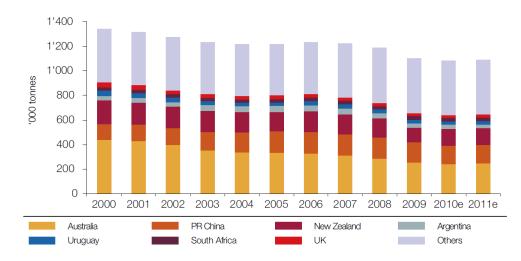


Figure 3.2 Global Wool Production Trends 2000-2011 [4]

### 3.3 Characterisation of Synthappret BAP

Synthappret BAP is a bisulphite adduct of a polyisocyanate polyurethane and mainly suitable for anti-felting of wool and wool blends without any chlorination [5]. Polyisocyanates are found to be the most effective among all the polymers available for shrink resist finishing of wool, but it does readily react with water, so inert solvents are required for its application medium [6, 7]. Guise and Jackson [8] cited Petersen [9] who found that isocyanates react with bisulphite to give water-soluble adducts that are stable in water at room temperature, but it gives reactions analogous to the parent isocyanates in the presence of nucleophiles.

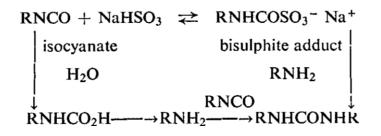


Figure 3.3 Reaction of Isocyanates with Sodium Bisulphite to Produce Bisulphite Adducts[8]

However, Guise and Jackson [8] could not produce bisulphite adduct by applying Petersen [9] methods to Synthaprett LKF and related polyisocyanates; and suggested another method, which used alcohols as solvents, to convert these polyisocyanates into their bisulphite adducts.

After investigating the properties mentioned in product information sheet , Synthappret BAP was found to have a solid content of 47.5 $\pm$ 0.6 wt.-%, a surface tension @ 20 °C of 33.5 $\pm$ 0.5 mN.m<sup>-1</sup>, a viscosity@ 21.5°C of 500.9 cP and a pH of 3.12.

By dynamic light scattering technique (DLS), the particle size distribution (PSD) profile of Synthappret BAP was measured, and the median particle size of Synthappret BAP was found approximately 10.1 nm. The particle size distribution (PSD) of Synthappret BAP by mean volume% is illustrated in Figure 3.4.

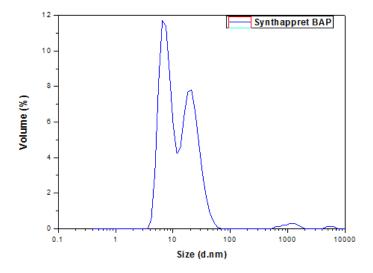


Figure 3.4 Particle Size Distribution of Synthappret BAP by Mean Volume %

### 3.4 Shrink Resist Finishing of Wool and Cotton

The wool and cotton fabrics were treated with the shrink resist formulations containing 10 g/L to 60 g/L Synthappret BAP, 1 g/L Kieralon Jet B Conc and 4 g/L NaHCO<sub>3</sub>. The wet chemical %pick up of the wool and cotton fabrics were measured as 70% and 80% o.w.f., respectively. The shrink resist effect of the polymer treatment of the fabrics were evaluated by investigating the effect of Synthappret BAP treatment on the laundering shrinkage and the fabric was also characterised by dry crease recovery angle, Kawabata evaluation system and SEM imaging of the untreated and treated fabrics.

# **3.4.1** Effect of Synthappret BAP on the Laundering Shrinkage of Wool and Cotton Fabrics

The effect of applying Synthappret BAP to wool and cotton fabrics on the area shrinkage due to laundering, typically expressed as percentage (%) area shrinkage, is illustrated in Figure 3.5.

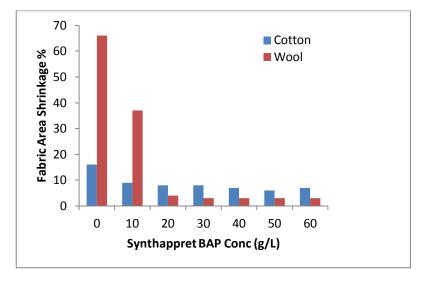


Figure 3.5 Area Shrinkage (%) of Untreated and Synthappret BAP Treated Cotton and Wool Fabrics after 5X5A Washing Cycles

As the wool fibre has the raised cuticular surface structure, it is susceptible to felting shrinkage during home laundering [10, 11], and accordingly the shrinkage of untreated wool was found to be much higher, ~65% area shrinkage, than that of the cotton fabric, which does experience felting shrinkage. It was observed that with increased application levels of the Synthappret BAP, the shrinkage of wool reduced significantly and dimensional stability was imparted. Ammayappan et al. [10] and others [12-14] also suggested the improvement of dimensional stability i.e. reduction of the %area shrinkage of wool fabrics and wool-cotton blends by depositing the Synthappret BAP polymer on cuticle layer and the masking of wool fibres scales, which reduces the differential friction effect of the fibres. In addition inter-fibre bonding by the polymer at fibre contact points is also likely to restrict fibre movement during laundering and prevent felting shrinkage. At an application level of 20-30 g/L, the Synthappret BAP imparted its best effect and further increase of the amount of Synthappret BAP to be applied was unnecessary. In contrast with the untreated cotton fabric there was a lower level of shrinkage, related to swelling shrinkage, but again the Synthappret BAP had a beneficial effect in imparting dimensional stability. The best effect was achieved at the 40-50g/L Synthappret BAP application level. The Synthappret BAP treatment generated inter-fibre and inter-yarns bonds in the cotton fabrics, which helps to impart dimensional stability [15].

SEM analysis of the treated fabrics indicates the presence of inter-fibre cross-links and is the likely mechanism for reducing felting shrinkage, Figure 3.8-3.10. Although evidence for scale smoothing is also evident.

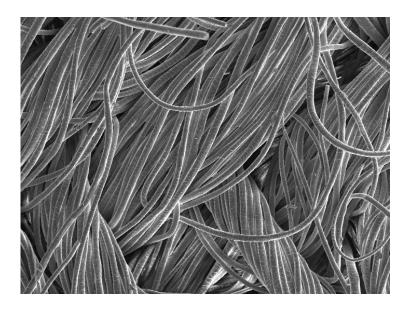


Figure 3.6 SEM Micrograph of Untreated Wool Fabric. Magnification x 100

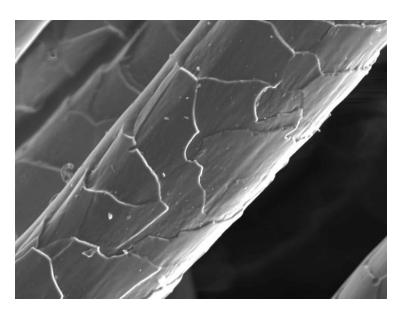


Figure 3.7 SEM Micrograph of Untreated Wool Fabric. Magnification x 2000

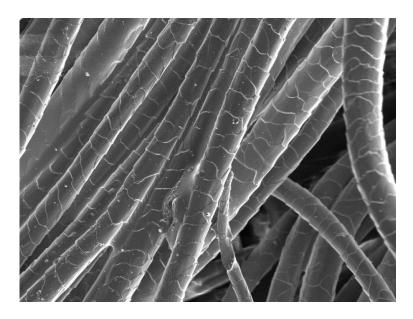


Figure 3.8 SEM Micrograph of 40g/L Synthappret BAP Treated Wool Fabric. Magnification x 500

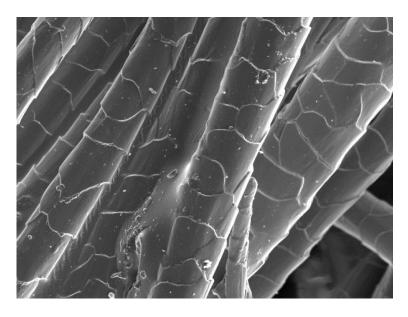


Figure 3.9 SEM Micrograph of 40g/L Synthappret BAP Treated Wool Fabric. Magnification x 1000

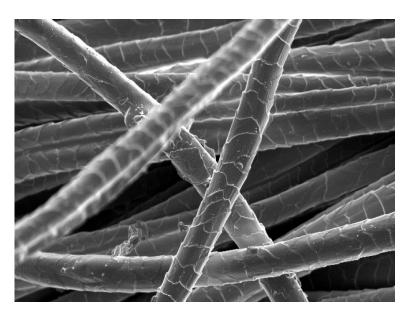


Figure 3.10 SEM Micrograph of 40g/L Synthappret BAP Treated Wool Fabric, After 5x5A Washing. Magnification x 500

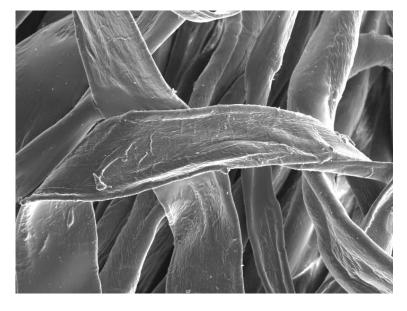


Figure 3.11 SEM Micrograph of Untreated Cotton Fabric. Magnification x 1000

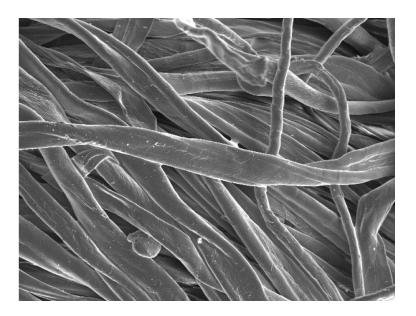


Figure 3.12 SEM Micrograph of 40g/L Synthappret BAP Treated Cotton Fabric. Magnification x 500

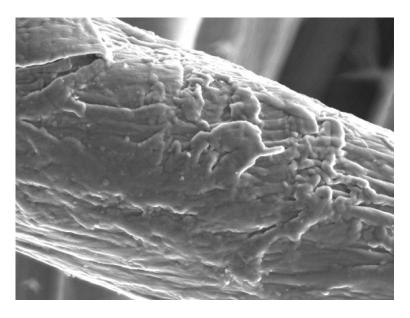


Figure 3.13 SEM Micrograph of 40g/L Synthappret BAP Treated Cotton Fabric. Magnification x 4000

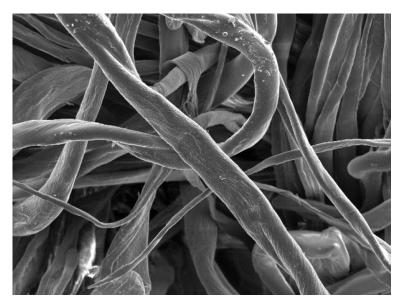


Figure 3.14 SEM Micrograph of 40g/L Synthappret BAP Treated Cotton Fabric, After 5x5A Washing. Magnification x 500.

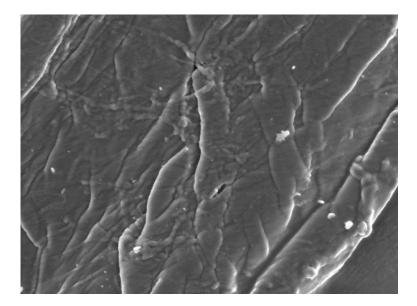


Figure 3.15 SEM Micrograph of 40g/L Synthappret BAP Treated Cotton Fabric, After 5x5A Washing. Magnification x 4000

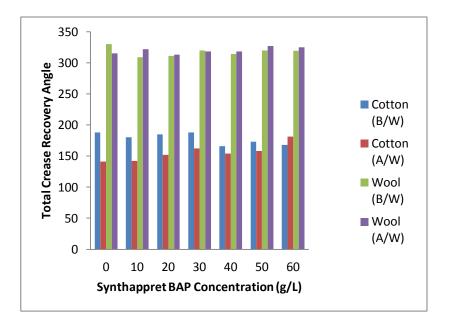
The SEM images of cotton and wool fabrics treated with 40 g/L of Synthappret BAP indicate the presence of surface polymer and inter-fibre bonding, Figures 3.12 to 3.15, and the failure of this bonding during washing [16]. With the wool fibres, anti-felting effect is achieved through spot welding preventing the fibres becoming entangled. After the 5x5A washing the inter-fibre bonding was still observed but some scale damage was also detected. Moreover, there was evidence of some polymer particles being present on the fibre surface.

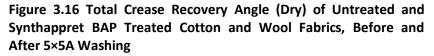
For the cotton fibres significant surface polymer deposition was observed and this was durable to the repeated washing process. In addition after the 5x5A washing fibrillation was observed

due to wet abrasion of the cotton fibres. It was observed to be higher for untreated, Figure 3.11, and 10-20 g/L Synthappret BAP treated cotton, however decreased with the increased concentration of Synthappret BAP.

### 3.4.2 Effect of Synthappret BAP on the Crease Recovery of Wool and Cotton Fabrics

The dry crease recovery angles (CRA) of the fabric samples (treated and untreated) in both warp and weft directions were measured before and after 5x5A washing cycles. The overall CRA was measured by averaging the CRA in both warp and weft directions, Figure 3.16.





### B/W- Before wash A/W- After 5×5A washing cycles

It is apparent that Synthappret BAP does not have any beneficial effect on the dry crease recovery of both the unlaundered treated cotton and wool fabrics, in fact surprisingly it has a negative effect and this may be due to the increased fabric rigidity of the polymer treated fabrics and their probable reduced resiliency to recovering from deformation. Jiang et al. [17] also mentioned the use of Synthappret BAP as durable press finishing agent performed up to certain level. Therefore, the combination of Dimethylol Dihydroxy Ethylene Urea (DMDHEU) and Synthappret BAP was suggested to have improved dry wrinkle or crease recovery angles of cotton fabrics. After the washing cycles the dry CRA has decreased for the cotton fabric and may be due to the fabric shrinkage reducing the fabric resiliency to deformation. However after the Synthappret BAP application to the cotton fabrics the crease recovery progressively improves particularly for the 60 g/L level. Likewise for the wool fabric at the 60 g/L level a small improvement in crease recovery was observed.

### 3.4.3 Kawabata Evaluation System (KES) Analysis of Wool and Cotton Fabrics

The Kawabata Evaluation System (KES) was used to determine the mechanical properties of the fabric samples before and after 5x5A washing cycles and establish the mechanistic action of the Synthappret BAP application on shrinkage, crease recovery and fabric handle. After 5x5A washing, the bending stiffness, and associated hand values, of untreated and 10 g/L Synthappret BAP treated wool fabric could not be measured because of the excessive felting shrinkage after laundering. The relevant bending stiffness, shear stiffness, and shear hysteresis values obtained from KES are collated Table 3.1.

Conc. of BAP	Bending Stiffness (g.cm <sup>2</sup> /cm)				Shear Stiffness (gf/cm.deg)				Shear Hysteresis 2HG5 (gf/cm)			
(g/L)	Cotton		Wool		Cotton		Wool		Cotton		Wool	
(8/ -/	B/W	A/W	B/W	A/W	B/W	A/W	B/W	A/W	B/W	A/W	B/W	A/W
0	0.06	0.07	0.10	-	0.71	1.35	0.37	1.88	2.28	5.73	0.57	5.29
10	0.06	0.06	0.12	-	1.01	1.17	0.41	0.55	3.14	5.02	0.64	1.09
20	0.07	0.07	0.15	0.10	1.17	1.08	0.44	0.33	3.07	4.49	0.65	0.46
30	0.14	0.07	0.18	0.11	2.03	1.43	0.56	0.30	3.76	4.18	0.85	0.38
40	0.15	0.06	0.24	0.13	2.19	1.11	0.81	0.32	4.07	4.24	1.16	0.43
50	0.18	0.07	0.28	0.15	2.59	1.41	0.88	0.36	4.55	3.75	1.33	0.44
60	0.19	0.07	0.33	0.17	2.80	1.39	0.88	0.38	4.60	3.59	1.28	0.51

Table 3.1 Effect of Polymer Application and Repeated Washing on the KES Bending Stiffness, Shear Stiffness, and Shear Hysteresis of Untreated and Treated Cotton and Wool Fabrics.

The bending stiffness of both the cotton and wool fabrics increased with higher levels of application of the Synthappret BAP polymer due to the inter-fibre bonding [18], reducing fabric flexibility. Similarly the shear stiffness of treated wool and cotton also increased with polymer addition, again reflecting the inter-fibre bonding. The shear hysteresis at 5<sup>0</sup>, 2HG5, has been identified as a sensitive indicator of fabric softness and is a measure of inter-yarn friction [19]. Therefore if a treatment lubricates the fibre/yarn surface, such as a fabric softener, the 2HG5 value decreases while if the treatment roughens/degrades the surface 2HG5 increases. In this case the polymer/fibre bonding harshens the fabric handle and this is reflected in the much higher 2HG5 values. The shear hysteresis increases with higher polymer add-ons as more inter-fibre bonding occurs.

The effect of repeated washing on the original untreated cotton and wool fabrics is to increase all three mechanical parameters, B, G and 2HG5. These increases are due to felting shrinkage of the wool fabric causing the fibres to become entangled and locking the structure. Similarly for the cotton fabric there is swelling shrinkage and wet fibrillation of the fibres resulting in greater fibre contact and rigidity. In contrast the effect of repeated laundering on the polymer treated fabrics is to reduce the mechanical rigidity of the fabric by breaking inter-fibre bonding and generally "relaxing" the fabrics. In many cases the stiffness of the fabrics after washing is less than the original unwashed untreated cotton and wool fabrics.

The primary hand value of the cotton and wool fabrics in terms of stiffness (KOSHI), smoothness (NUMERI) and softness (FUKURAMI), and total hand value (THV) were calculated using the women's summer thin dress and men's winter suiting standard model fabric equations, respectively, and are listed in Tables 3.2 and Table 3.3.

Synthappret BAP Conc. (g/L)	KOSHI (Stiffness)		NUMERI (Smoothness)		FUKURAMI (Fullness & Softness)		Total Hand Value (THV)	
	B/W	A/W	B/W	A/W	B/W	A/W	B/W	A/W
0	6.2	6.2	6.4	6.7	9.1	10.1	0.8	-0.7
10	6.2	6.0	7.1	6.4	10.2	9.9	-0.5	-0.5
20	6.5	6.1	6.5	7.4	9.8	10.7	-0.3	-1.1
30	7.6	6.4	5.8	7.0	9.6	10.2	-1.0	-0.7
40	7.7	6.1	5.6	6.9	9.4	10.3	-0.9	-0.8
50	7.8	6.5	5.5	6.6	9.3	10.1	-0.8	-0.7
60	7.9	6.6	5.6	6.3	9.3	10.0	-0.8	-1.0

 Table 3.2 Primary and Total Hand Values of Cotton Fabrics Before

 and After 5x5A Washing Cycles

It is evident from the results in Table 3.2 that the cotton fabrics get stiff, less smooth and less soft when the polymer is applied. Further the Total Hand Value as an indicator of fabric quality gets worse with increasing polymer addition. On washing the wet mechanical action improves the fabric smoothness, softness and stiffness however in general it is still above that observed for the original untreated fabric.

Table 3.3 Primary and Total Hand Values of Wool Fabrics Before andAfter 5x5A Washing Cycles

Synthappret BAP Conc. (g/L)	KOSHI (Stiffness)		NUMERI (Smoothness)		FUKURAMI (Softness & Fullness)		Total Hand Value (THV)	
	B/W	A/W	B/W	A/W	B/W	A/W	B/W	A/W
Untreated	3.3	-	7.0	-	5.6	-	3.9	-
10	3.7	-	7.5	-	7.0	-	4.3	-
20	4.1	2.3	7.3	8.8	7.0	8.8	4.3	4.5
30	5.1	3.1	7.1	8.6	7.3	8.3	4.3	4.7
40	6.4	3.7	6.6	8.0	7.6	7.7	4.1	4.5
50	7.0	4.2	4.9	7.7	6.0	7.6	3.4	4.5
60	7.0	4.4	4.8	7.1	6.7	7.5	3.3	4.2

Examination of the PHV and THV data, Table 3.3, for the wool fabric indicates the fabric stiffness and fabric softness/fullness both increase with polymer application. This apparent contradiction is due to the extra weight that is incorporated into the fabric with the polymer addition. The smoothness and THV for the treated fabrics both increase, and then decrease as the higher polymer additions increase rigidity and alter the frictional properties of the fibres and fabric. However washing again breaks inter-fibre bonding and removes surface polymer and improves the overall fabric quality.

### 3.5 Digital Ink Development

As one of the objectives of this study was to develop a digital print method for the application of a shrink resist finish onto wool that imparted dimensional stability. It was important to identify a base Synthappret BAP formulation from which to begin the optimisation of the inkjet delivery. Similarly for cotton the same starting point was selected where improved crease resistance and handle modification could be achieved with a view for improved dimensional stability and texturing effects. Therefore the following formulation in Table 3.4 was selected for formulating inks for inkjet printing.

Chemicals	Concentration (g/L)
Synthappret BAP	40
Kieralon Jet B Conc.	1
NaHCO <sub>3</sub>	4
Water	Add to make 1L solution

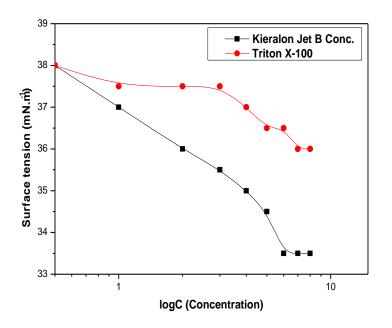
Table 3.4 Initial Formulation Selected for Formulating Inks for InkjetPrinting

The surface tension and viscosity of the above formulation was modified by using increased concentrations of surfactants and viscosity modifiers, respectively, and the inkjet inks with the "optimized" surface tension and viscosity were assessed for their jettability performance in a piezoelectric Drop-on-Demand DMP.

### 3.5.1 Effect of Surfactants on the Surface Tension of Initial Formulation

The surface tension of the initial formulation without any surfactant (Kieralon Jet B Conc) was 38 mN.m<sup>-1</sup>, and that for pure water was found to be 73 mN.m<sup>-1</sup> at 20°C. Therefore, the presence of Synthappret BAP in the formulation reduced the surface tension of the formulation significantly, and the surface active property of Synthappret BAP was observed.

Figure 3.17 illustrates that the surface tension of the formulations decreased progressively with increased surfactant concentration, and decreased to a baseline level of 33.5 mN.m<sup>-1</sup> and 36 mN.m<sup>-1</sup> with Kieralon Jet B Conc and Triton X-100, respectively, which are within the suitable application range of piezoelectric DMP. However, Hait and Moulik [20] found the critical micelle concentration (cmc) of Triton X-100 is 0.24 mM (0.15 g/L) in water that is in the range of 0.22 to 0.24 mM mentioned by Sigma-Aldrich [21], whereas Risio and Yan [22] found the cmc of Triton X-100 is 0.05 wt.-% (0.5 g/L) of surfactant concentration for Bioink. These are relatively lower concentrations in comparison to the application levels of Kieralon Jet B Conc (6 g/L) and Triton X-100 (7 g/L) required achieving optimum level with no further decrease in surface tension. Therefore, the competitive action of the surfactants and Synthappret BAP in the formulations resulted in reducing the changes in the surface tensions of the formulation.



## Figure 3.17 Effect of Surfactant Application on the Surface Tension of the Formulations

Kieralon Jet B Conc was found to be more efficient than Triton X-100 in terms of reducing the surface tension. However, the Kieralon Jet B Conc formed an opaque solution with higher dosing, whereas a transparent and homogenous solution was observed with same amount of Triton X-100 and accordingly in this inkjet application is preferred. Although the detailed chemical composition of Kieralon Jet B Conc was not disclosed, the technical information sheet [23] suggested its possible use as a detergent as well as a wetting agent in any pre-scouring process for the textiles. Therefore it may contain both surfactants and builders such as the phosphates, metasilicates, and carbonates which can assist in emulsifying soils and suspending

dirt in aqueous solutions [24] and may be responsible for forming the opaque solution at higher concentrations.

### 3.5.2 Effect of Viscosity Modifiers on the Viscosity of the Formulations

Glycerol, PEG 200 and CMC were investigated as rheology modifiers for inkjet inks as they are water soluble, nontoxic, compatible with Synthappret BAP and are known to be able to modify the solution viscosity over a wide range at different concentrations [25-27]. The effect of the viscosity modifiers on the viscosity of the formulations containing a fixed amount of Synthappret BAP, surfactant, and NaHCO<sub>3</sub> is illustrated in Figure 3.18. It was observed from the viscosity dilution curves that there was a gradual increase of viscosity up to concentration of 45% glycerol, and after that level viscosity rose quickly with the increased concentration of glycerol. Similarly with PEG 200, the viscosity increased gradually up to a concentration of 25% PEG 200, and after that a steady increase of viscosity was observed with increasing concentration levels. Therefore it was apparent that a higher application level of glycerol and PEG was required to achieve the typical operating viscosity of the inkjet inks. However, for CMC, with a lower concentration (0.1-1%), higher viscosity was observed, due to CMC having a higher molecular weight than the other rheology modifiers. As the required viscosity of the inkjet inks was achieved at these lower concentrations, CMC was selected as the most effective viscosity modifier. Risio and Yan [22] demonstrated similar trend with the same types of viscosity modifiers in their bioink application.

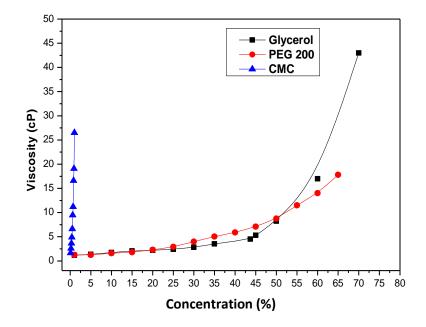


Figure 3.18 Viscosity Dilution Curves of Glycerol, PEG 200 and CMC

#### 3.5.3 Formulated Inks

Following the results obtained from the shrink resist finishing, surface tension optimisation and viscosity dilution curve studies, a range of inkjet inks were prepared to observe the operating jettability in the piezoelectric DMP. Moreover, all the formulations were prepared both with and without surfactants. In addition, one of the formulations was prepared in combination of CMC and glycerol, where glycerol functioned as a humectant as well as a viscosity modifier. Table 3.5 illustrates the formulated inks for the application in piezoelectric DMP application to observe the jettability performance.

Formulations	Viscosity Modifier	Range (wt %)	Synthappret BAP	Humectant (wt %)	Surfactant (wt %)	NaHCO <sub>3</sub> (wt %)
1	Glycerol	10-40			-	
	Glycerol	10-40			0.6	
2	PEG 200	15-35		_	-	
_	PEG 200	15-35	4		0.6	0.4
3	СМС	0.1-1			-	011
	СМС	0.1-1			0.6	
4	СМС	0.1-1		10	-	
	СМС	0.1-1		10	0.6	

Table 3.5 Range of Formulated Inks for the Application in DMP

### 3.5.4 Storage Stability of Formulated inks

The storage stability of the formulated inks is illustrated in Figure 3.19, and the stability observed by maintaining overnight at room temperature at approximately 20°C. The inks without any surfactants were observed to form an opaque solution, and the tendency to form a cloudy solution increased with increased concentration of viscosity modifiers. Moreover, the presence of higher amount of viscosity modifiers in the inks without surfactants altered the ink stability and blocked the cartridge channels and printhead after leaving for few days.

Chapter 3 Results and Discussion

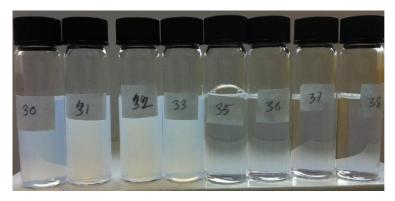


Figure 3.19 Storage Stability of Ink Formulation 2 in Table 3.14 (30-33: Without Surfactant, 35-38: With Triton X-100 as Surfactant)

In contrast the inks containing Triton X-100 as the surfactant formed homogenous and transparent solution, and the ink stability was not affected with increased concentration of the viscosity modifiers. The possible reason, of forming homogeneous solution by Triton X-100, could be its ability to solubilize higher concentrations of viscosity modifiers, and its HLB value (listed as 13.1) [21].

### 3.5.5 Jettability Performances of Formulated Inks

The formulated inks were tested in the DMP to establish their jettability under the "optimum" operation conditions: voltage: 25 -30 V, firing frequency: 5 KHz, meniscus vacuum: 5 inches  $H_2O$ . A 1.0 sec purge cleaning cycle was run before jetting of each ink to remove trapped air from the ink circuit and any dry ink deposits from the nozzle entrance. It was observed that the inks containing lower concentration of viscosity modifiers such as 15-35% glycerol, 15-20% PEG 200, and 0.1-0.2% CMC could not be jetted properly. In this case, the "chaotic" spraying of drops was observed initially and after running a cleaning cycle, inks came out from the cartridges and wetted the whole surface of the printhead facing the substrate. At lower concentrations, a long tail formed that was not absorbed by the printhead subsequently, and therefore it produced highly chaotic drops that were irreproducible in nature [28-30].

In contrast, it became more difficult to jet the inks at higher concentration, as the molecular weight increased [31]. With the increased concentration of viscosity modifier i.e. the inks containing viscosity modifiers at higher level such as 40-45% glycerol, 25-35% PEG 200 or 0.3-0.4% CMC with or without 10% glycerol (as humectant), the inks jetted well initially, but after few minutes of running became unstable and a few drops appeared at the tail similar to previously observed [28-30]. Moreover, wetting of the printhead surface was also observed with all the formulation combinations and the problem remained unsolved. Nevertheless out of all the inks tested, considering the drop size and velocity, the formulation containing 45% glycerol as the viscosity modifier performed best. However, it also became unstable after

printing for few minutes, and further research is necessary to overcome this technical difficulty.

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CHAPTER 4 CONCLUSIONS AND FUTURE WORK

### 4.1 Conclusions

After applying a range of shrink resist finishing formulations containing Synthappret BAP to cotton and wool fabrics, an initial formulation containing 40 g/L Synthappret BAP was successfully identified for inkjet ink development. In terms of dimensional stability control, Synthappret BAP was found to have significant effect on both wool and cotton, but a greater effect was observed on wool compared to the cotton fabrics due to the nature of felting shrinkage with wool. The SEM micrographs of the cotton and wool fabrics treated with Synthappret BAP indicated the presence of surface polymer and inter-fibre bonding. At an application level of 20-30 g/L, the Synthappret BAP imparted its best shrink resist effect on the wool fabric, whereas an application level of 40-50 g/L of Synthappret BAP was required to achieve the best effect on the cotton fabric. In contrast, Synthappret BAP does not have any beneficial effect on the dry crease recovery of both the unlaundered treated cotton and wool fabrics; however the dry CRA decreased for both the cotton and wool fabrics after the washing cycles. The Kawabata evaluation system for fabrics (KES-F) data indicated that the mechanical properties of the fabrics such as bending stiffness, shear stiffness, and shear hysteresis increased with higher polymer add on, but decreased after repeated washing cycles due to the breakage of inter-fibre bonding. While the selected mechanical parameters are regarded as sensitive indicators of softness, the overall primary and total hand values were also affected by the polymer additions and subsequent washing. The THV values of cotton fabrics decreased with higher polymer add-ons, however it increased for wool initially, and then decreased with higher polymer add-ons. The repeated washing cycles improved the THV of wool and cotton fabrics due to fabric softening.

The surface tension and viscosity of the initial formulation that was selected based on the results obtained in the traditional textile finishing, was optimised within the range of piezoelectric DMP application conditions. Of the two surfactants that were investigated, Kieralon Jet B Conc was found to be more efficient in term of reducing surface tension; however Triton X-100 was selected for ink formulation because of forming homogenous and transparent solution at higher dosing, whereas an opaque solution was formed with higher application levels for the Kieralon Jet B Conc. The effect of different viscosity modifiers such as glycerol, PEG 200, and CMC was investigated, and CMC was observed to be most effective in modifying the viscosity of the formulation. The desired viscosity was achieved at relatively lower concentration of CMC, whereas higher add-ons were required for glycerol and PEG 200.

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A range of inks, with or without surfactant, were prepared to test the jettability performances in piezoelectric DMP. However the inks without any surfactant were observed to form opaque solution after storing for few days, whereas the presence of surfactant in the inks offered stable, clear and homogenous solutions. However it was observed that the inks containing lower concentrations of viscosity modifiers could not be jetted properly. In this case, the "chaotic" spraying of drops was observed initially and after running a cleaning cycle, inks came out from the cartridges and wetted the whole surface of the printhead facing the substrate. In contrast, with increased concentrations of viscosity modifiers, there was acceptable jetting initially, but after few minutes of running the drop size and velocity, the formulation containing 45% glycerol as the viscosity modifier performed best and offered some potential for further development. However, in its current composition the jetting also became unstable after printing for few minutes.

### 4.2 Future Work

Digital finishing technology is rapidly developing and in the next twenty years will become one of the predominant commercial and chemical application technologies. Process automation in this new technology will lead to reduced labour cost, improved processing efficiency and lower environmental impact. Moreover, it will help to eliminate some of the processes from the textile value chain, thus helping to reduce heating, water and power consumption. This will lead to a reduction in carbon emissions produced by the textile industry.

This investigation on Digital finishing using Synthappret BAP in a piezoelectric DMP on textiles demonstrated that the polymer jetted well initially, however jet-stability needs to be improved. Therefore, further studies should be undertaken to investigate other parameters and compositional additives. As viscosity modifiers play a very important role in increasing the reliability and quality by controlling the drop formation and break-up process, other viscosity modifiers such as poly-propylene glycol, polyvinyl alcohol, ethylene glycol could be investigated as potential rheology modifiers for inkjet inks. Moreover, the improvement in jettability should be investigated by reducing the molecular weight of Synthappret BAP. In addition, other inkjet technologies such as thermal DOD or Continuous inkjet technologies could be investigated to identify the delivery technology associated with optimum jetting. The optimum application level of Synthappret BAP in inkjet ink formulations needs to be established to obtain comparable performance to conventional textile finishing.

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It would be of interest to extend the systematic approach followed in this thesis for ink formulation and jettability performance testing to other textile finishes. In addition, formulated inks can be deposited onto textile surfaces to deliver a range of novel effects such as textural, olfactory, liquid repellences, conductivity etc. However, in addition to the delivery of the effect chemical to the textile the actual effect of that finish on textile performance also needs to be established.