

Preparation and Characterisation of Inks for Jet Printing
onto Textile Materials

By

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The candidate confirms that the work submitted is his own and appropriate credit has been given where reference has been made to the work of others.

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Abstract

The feasibility of using thermal drop-on-demand ink jet printing to print pigmented ink systems onto textile materials was investigated.

Preliminary studies showed that a novel binder system, Synthappret BAP (traditionally used as a shrink resist treatment for wool), could be successfully incorporated within a screen ink formulation for printing onto cotton fabric. Such a printing ink produced a high quality print which offered the required fastness properties of a textile print whilst maintaining a soft fabric handle.

The cross-linking mechanism/properties of the Synthappret BAP were fully characterised. It was found that Synthappret BAP underwent rapid self cross-linking at elevated temperatures. There was no significant evidence of the cross-linking of the Synthappret BAP and the textile fibres. However, the Synthappret BAP was capable of (a) diffusing into the fibre matrix and (b) entrapping the pigment particles, thus, successfully fixing the pigment to the substrate. Such fixation resulted in a high degree of washfastness and rubfastness.

Following the initial success of applying Synthappret BAP as a binder for textile printing, various ink jet printing inks suitable for textile printing were developed. Such inks were tested for physical characteristics required of a typical ink jet printing ink and successfully printed using a desktop ink jet printer.

Successful printing of an array of textile materials was achieved.

Based on initial trials of such inks further investigation was carried out in order to improve/ensure the following criteria were met:

- Suitability for a one pack printing process.
- Excellent stability of inks including pH and freeze-thaw stability of pigmented inks thus giving indications on possible shelf life.
- Excellent printability on cotton and polyester.
- Excellent washfastness on cotton and polyester.
- Excellent fabric handle after printing.
- Acceptable rubfastness and lightfastness of printed cotton and polyester.

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List of Abbreviations

CAD	Computer Aided Design
CYMK	Cyan, Magenta, Yellow and Black
DEA	diethanolamine
DEG	Di(ethylene glycol)
DOD	Drop-on-Demand
dPa s	Deci Pascal seconds
dpi	Dots per inch
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-rays
EG	Ethylene glycol
FCS	Four Colour Set
FTIR	Fourier Transform infra red
HP	Hewlett Packard
IPA	Isopropyl alcohol (2-propanol)
mPa s	Milli Pascal seconds
NaOH	Sodium hydroxide
PEG 200	Poly(ethylene glycol) – molecular weight 200
Piezo	Piezoelectric
pL	Picolitres
SEM	Scanning Electron Microscopy
TEA	Triethanolamine
T _g	Transition glass temperature
TGA	Thermo-gravimetric analysis
TIJ	Thermal ink jet
µm	Micrometres

1 Introduction

The last 10 years have seen somewhat of a revolution within the textile printing industry. Whilst traditional printing methods still dominate, the advent of digital printing onto textiles has been seen especially in areas such as print proofing and bespoke designs. There is however, a need for the development of advanced ink formulations for the ink jet printing process which allow for excellent fastness properties whilst conferring an acceptable handle to the textile after printing. Recent years have seen the emergence of pigmented inks due to their durability and versatility in terms of their being non specific to any particular substrate. Current technology is however somewhat limited and commercial inks for ink jet printing onto textiles are in their infancy. Many problems are associated with such inks in terms of stability, ability to print, pre and post treatment of the fabric, resistance properties of printed substrates and handle of the printed fabric. As such a novel binder system was investigated for its possible use within an ink jet printing ink. Such a binder was unique in its application for such a use, as it had previously only been used as a shrink resist treatment for wool. The novelty of the binder lay in it being both self cross-linkable and water soluble. The advantages of such a binder are detailed below:

- Excellent stability (due to water solubility) compared with those used traditionally and within commercial ink jet inks.
- No requirement of a pre-treatment process.
- Minimal amount of post-treatment. Post-treatment consists of thermal curing at a relatively high temperature (120-200°C) for a short period of time (<3 minutes).
- Once cured the printed substrate offers excellent fastness properties.
- The printed and cured substrate has a soft handle, barely different from unprinted fabric.

As such a printing ink with the above attributes would rival any commercially available ink. A summary of inks currently available and their limitations for use in ink jet applications is given in Section 1.3.11.

This investigation is centred around the development of pigmented, water-based printing inks that give good printability and good colour strength after washfastness and rubfastness testing.

This chapter gives an introduction to a number of textile printing methods and relevant ink formulations and printing mechanisms.

1.1 Textile Printing

Textile printing is still very much dominated by traditional printing processes. The market is predominately taken up by screen printing. Recent years have however, seen a trend towards the use of ink jet printing for textiles, flags and banners and bespoke designs (Tanaka et al., 1999; Ross, 2001). An area in which ink jet printing is already established is in the field of print proofing. The process of print proofing is where a design is printed onto textile prior to the main production run using screen printing in order for the customer to see whether the design is acceptable. A flow diagram of the print proofing process can be seen in Figure 1.1.a and a comparison of the previously mentioned conventional method is seen in Figure 1.1.b.

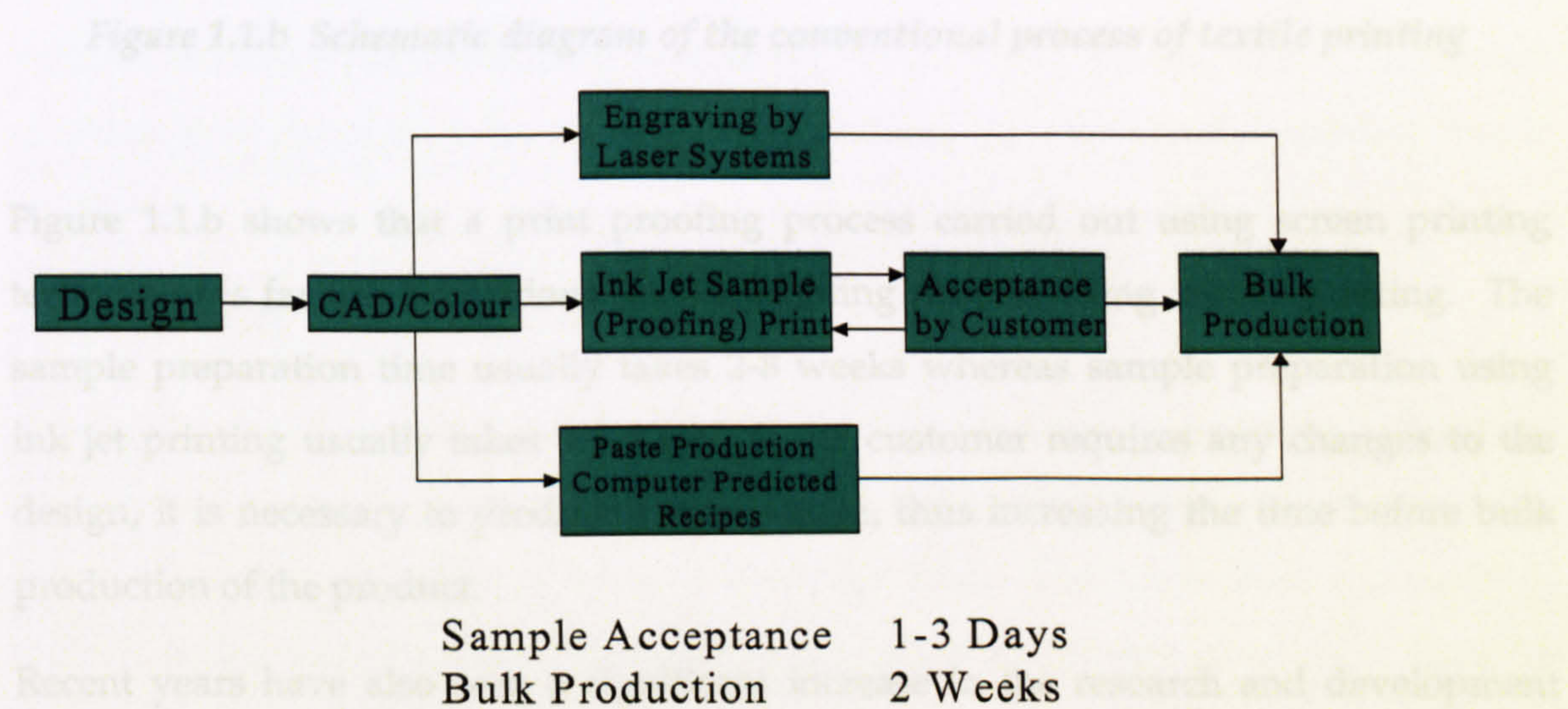


Figure 1.1.a Schematic diagram of a textile proofing process by ink jet

Figure 1.1.a shows that in a process where ink jet printing is used to produce a proof of the final print, the customer can accept or reject the design prior to the production of a screen. Such a print proofing process shortens the time between the submission of a design and a proof being created for the customer. The print proofing process using ink jet technology also does not require the slow and costly process of creating a screen for a sample design which may be rejected on viewing by the customer. Any changes

that are required by the customer can be made using computer based design software and a new proof produced in a short period of time.

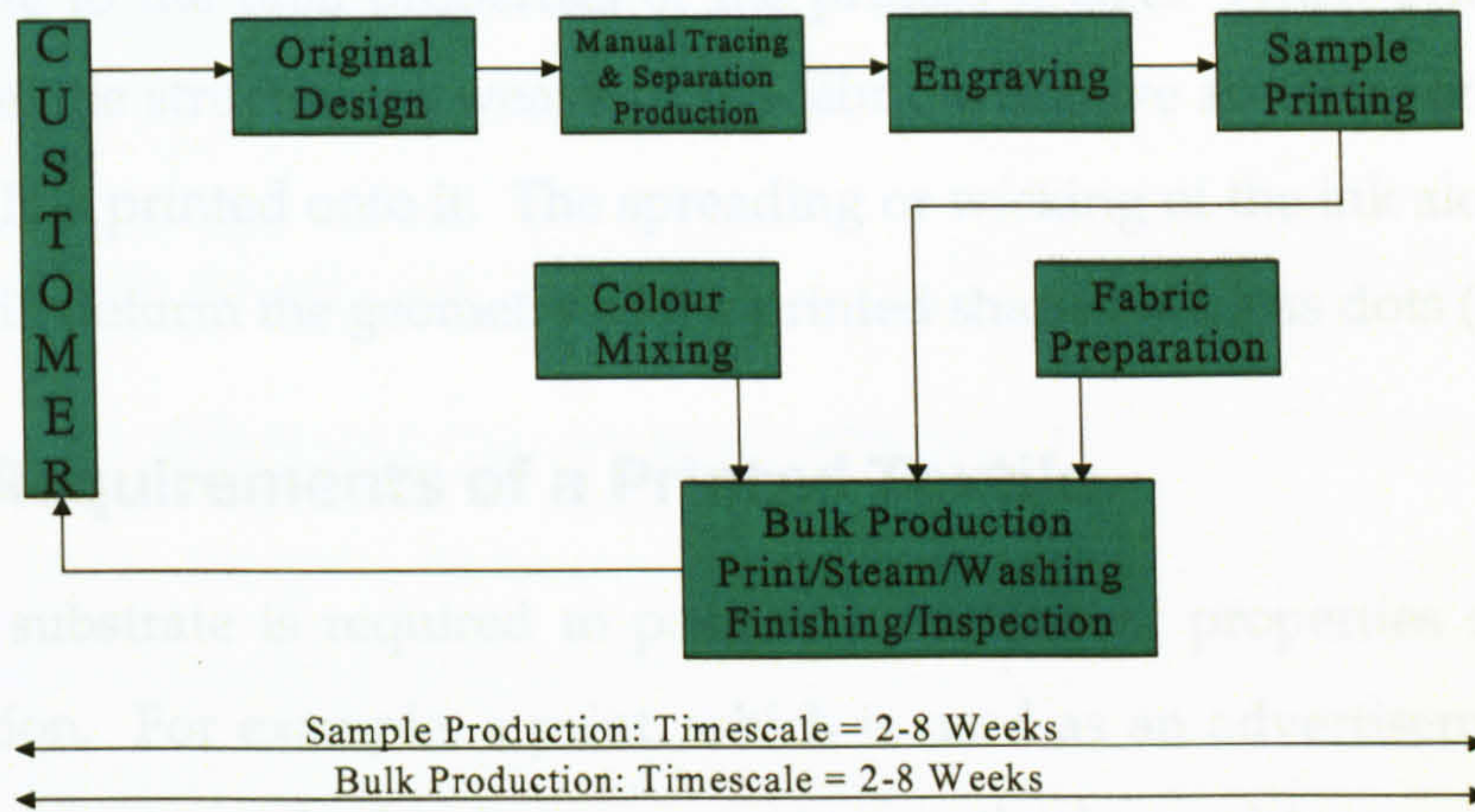


Figure 1.1.b Schematic diagram of the conventional process of textile printing

Figure 1.1.b shows that a print proofing process carried out using screen printing technology is far more laborious than a proofing process using ink jet printing. The sample preparation time usually takes 2-8 weeks whereas sample preparation using ink jet printing usually takes 1-3 days. If the customer requires any changes to the design, it is necessary to produce a new screen, thus increasing the time before bulk production of the product.

Recent years have also seen a significant increase in the research and development activities into ink jet printing on textiles. It is apparent to the author that large, industrial scale ink jet printing facilities will soon be available to textile printers. There are two ink types which can be chosen, depending on the application for which they will be used. Traditionally, dye based inks have been used due to their high image quality (Bugner and Bermel, 1997; Basak et al., 1999). However, most dye-based ink jet printing inks suffer from poor water-fastness when printed on common office printing paper. Thus, various attempts to develop colorants capable of improved water-fastness, when printed on various substrates, have been made; some of which have been successful (Lewis et al., 2001).

1.1.1 Effect of the Textile Substrate on the Printed Image

The type of substrate that is used has a significant effect on the quality and stability of the printed image. The penetration of the ink into the substrate, the structure of the substrate and the physical and chemical nature of the ink and the substrate will all contribute to the final properties of the printed image. When printing onto a textile substrate, the structure or weave of the fabric will have an effect on the quality of any straight line printed onto it. The spreading or wicking of the ink along the fibres of the fabric will deform the geometry of the printed shapes, such as dots (Dawson, 2003).

1.1.2 Requirements of a Printed Textile

Printed substrate is required to possess a number of properties relevant to its final application. For example, a print, which is used as an advertisement banner for two months, is not required to have as great a weathering resistance as a banner that may be used over a period of years. A printed textile that is used in a clothing application is required to have a good resistance to washing. In each case, the end use of the printed substrate is of paramount importance in determining the relative print stability that is required.

1.2 Screen Printing Technology

Essentially, screen printing may be described as an extension of stenciling. That is to say, a screen contains a pattern of image and non image areas where ink can only come into contact with the substrate through the image areas. The screen itself comprises of a mesh, which is traditionally composed of silk, but often consists of synthetic fibres or metal threads, tightly stretched over a frame. The pores of the mesh are 'blocked' in the non-image areas and left open in the image area. A schematic representation of a typical screen can be seen in Figure 1.2.a.

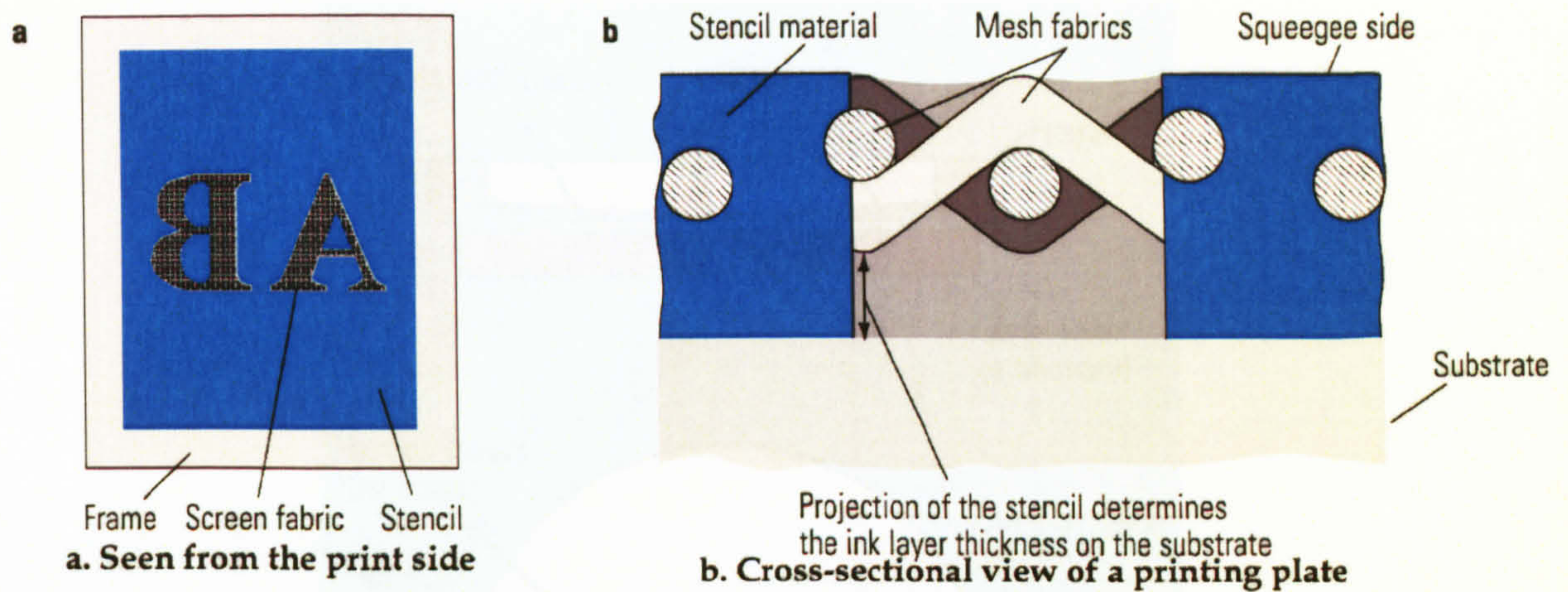


Figure 1.2.a Schematic diagram of a screen used for screen printing (Kipphan, 2001)

In order for an image to be created on a substrate the screen must be flooded with ink and have a squeegee drawn across it thus forcing the ink through the image areas and onto the substrate (Birkenshaw, 1993; Walenski and Kipphan, 2001).

There are two major types of screen printing, namely flatbed and rotary screen printing, which are commercially employed.

1.2.1 Flatbed Screen Printing

Flatbed screen printing consists of a screen pulled tightly across a frame which is held parallel to the substrate. The substrate is held onto a printing table so that it is taut and the screen placed on top of it. The screen and substrate are held firmly in place, either by clamps or by vacuum. Once the screen is in place, the ink is applied and forced through onto the substrate by a squeegee (Hawkyard, 1994; Kipphan, 2001; Tippet, 2001). A schematic representation of this process is given in Figure 1.2.b.

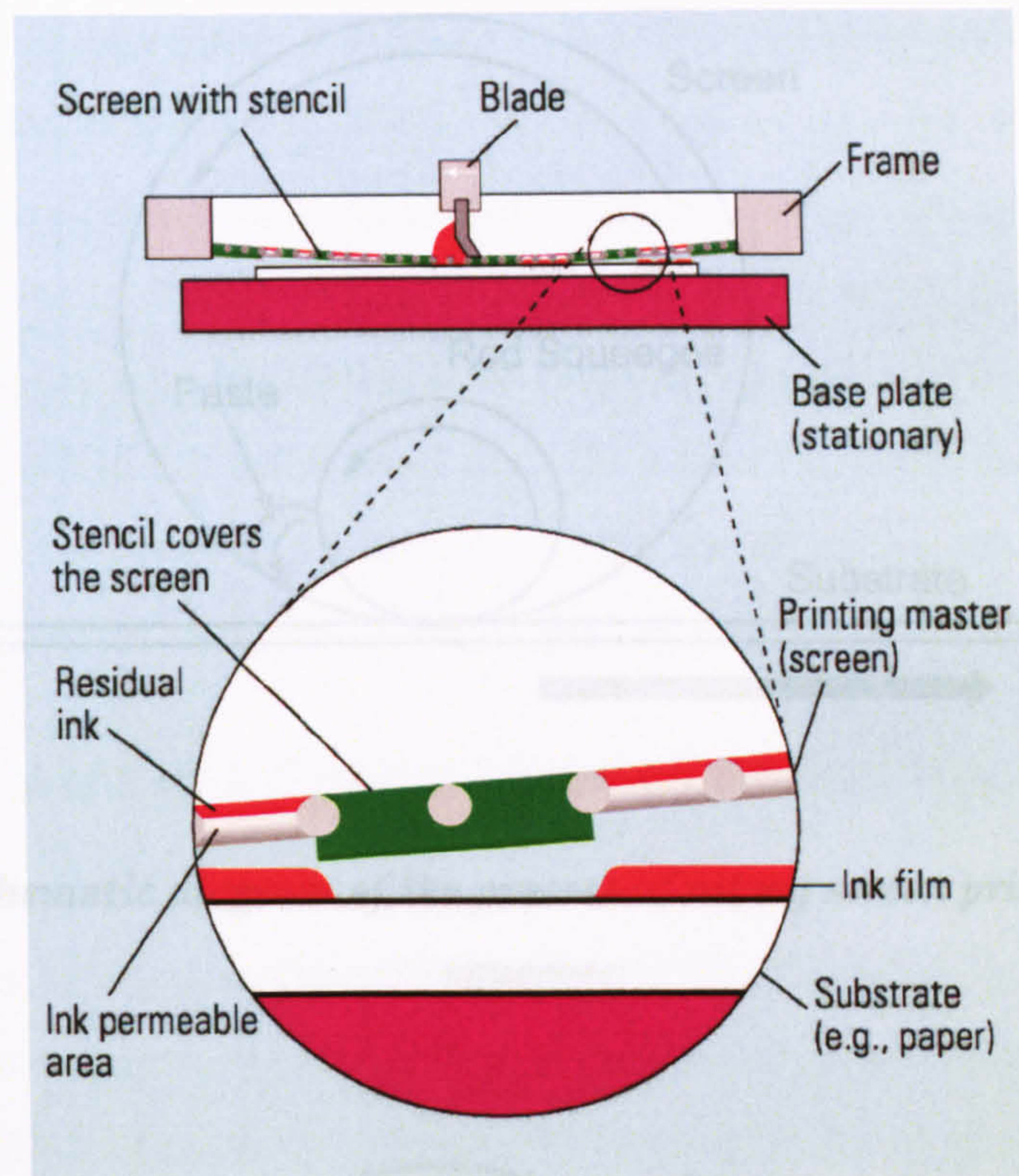


Figure 1.2.b Schematic diagram of the mechanism of flatbed screen printing (Kipphan, 2001)

1.2.2 Rotary Screen Printing

In rotary screen printing, the screen itself the form of a cylinder. Rotary screen printing can be described as a continuous printing process as it involves the continuous rotation of the cylindrical screen which is always in contact with the substrate (Hawkyard, 1994; Tippet, 2001). The print paste is fed into the cylinder and as with flatbed screen printing, is forced through the image areas of the screen by application of a squeegee. An outline of the rotary screen printing process is given in Figures 1.2.c and 1.2.d.

A rotary screen allows for closer contact of the screen with the substrate although it does require larger driers in order for complete drying to be achieved at high speeds of 30-70 m/min. Faster speeds are possible, however this is limited by substrate type and length. The rotary screen process is often used where a repeat pattern is required, such as in the printing of curtains (Hawkyard, 1994; Kipphan, 2001).

1.2.3 Mechanism of Screen Printing

In screen printing processes, when the print paste is pushed between the squeegee

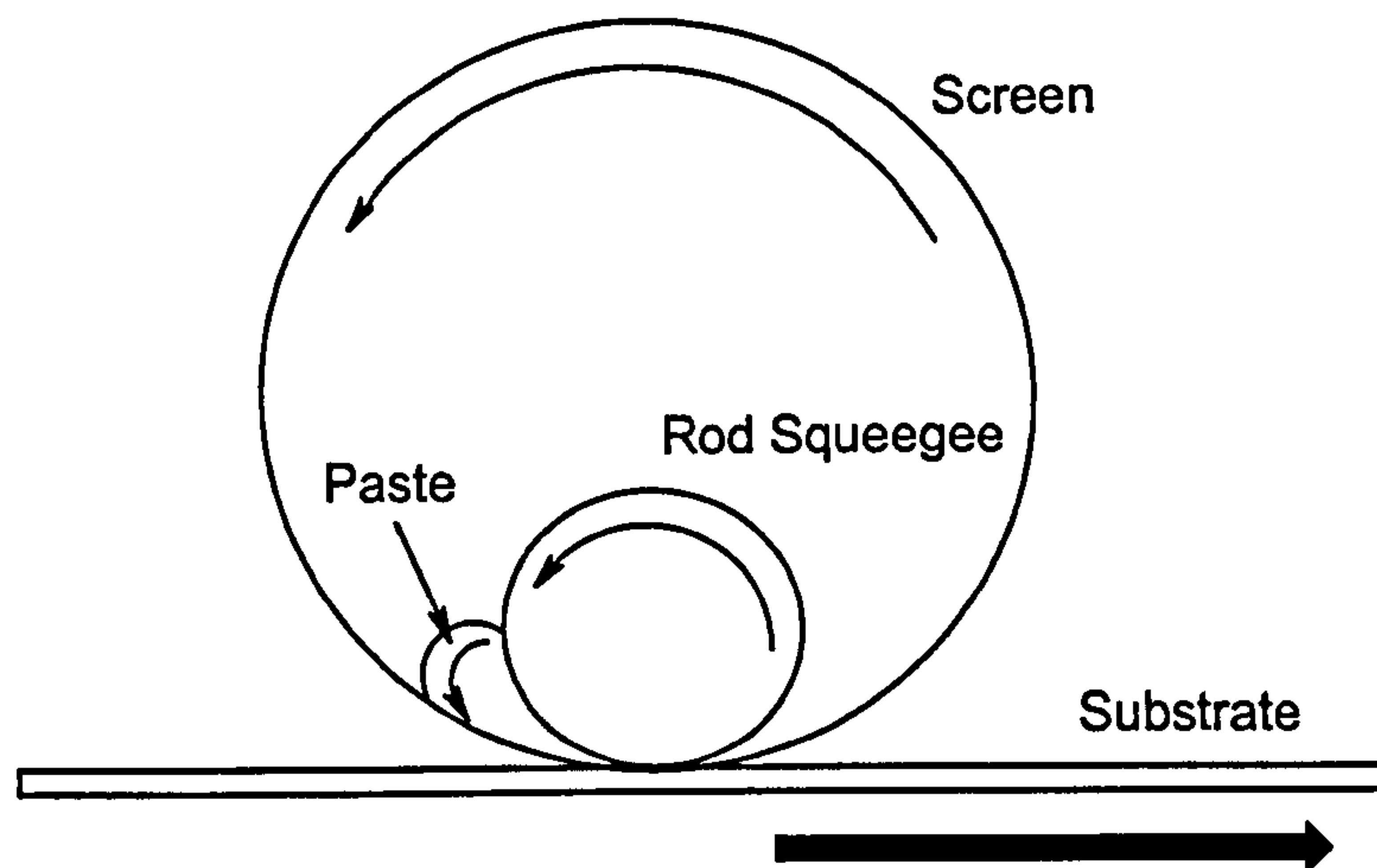


Figure 1.2.c Schematic diagram of the process of rotary screen printing using a rod squeegee

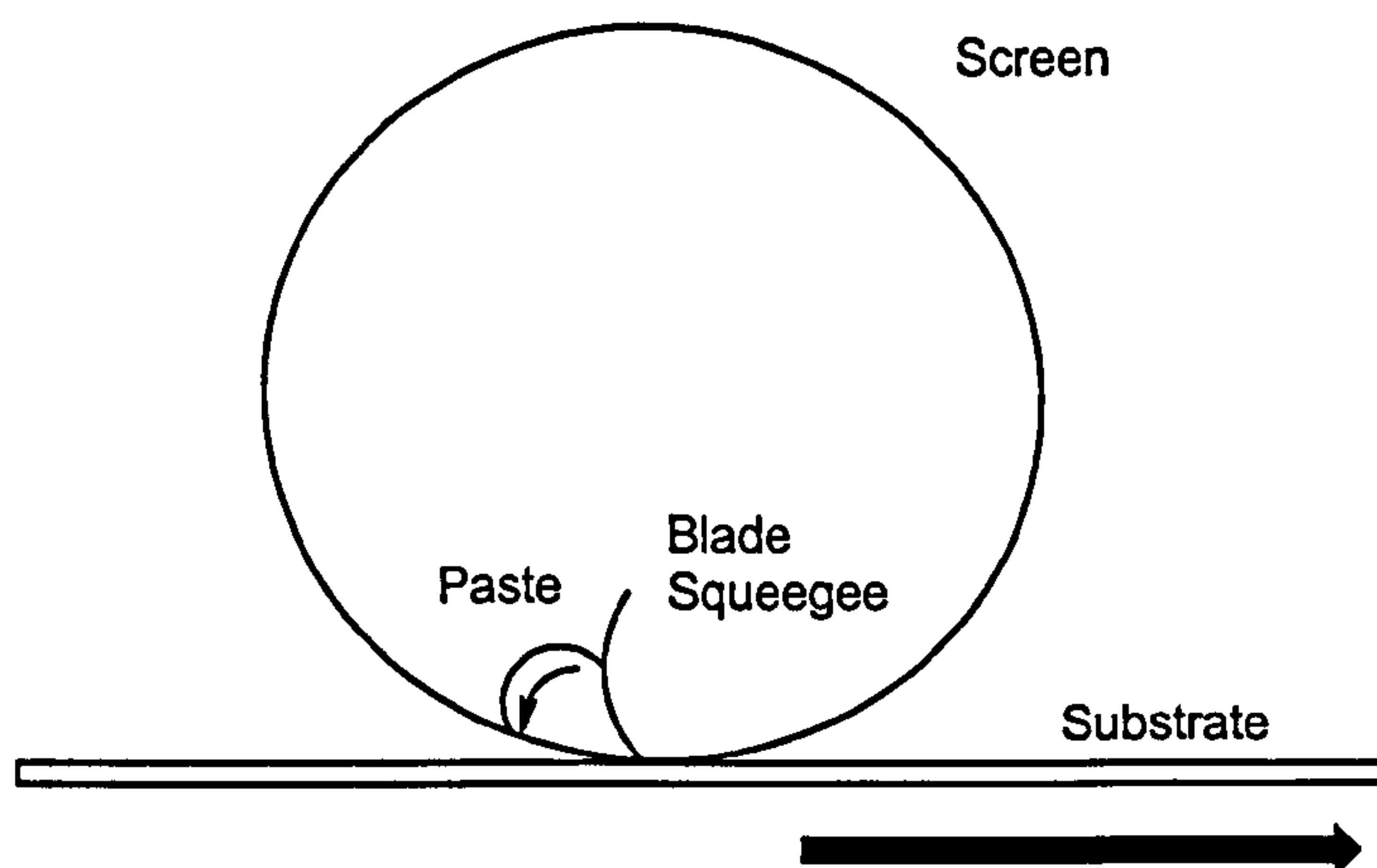


Figure 1.2.d Schematic diagram of the process of rotary screen printing using a blade squeegee

A rotary screen allows for closer contact of the screen with the substrate although it does require larger driers in order for complete drying to be achieved at high speeds of $30\text{--}70\text{ m min}^{-1}$. Faster speeds are possible, however this is limited by substrate type and length. The rotary screen process is often used where a repeat pattern is required, such as in the printing of curtains (Hawkyard, 1994; Kipphan, 2001).

1.2.3 Mechanism of Screen Printing

In screen printing processes, when the print paste is positioned between the squeegee

and the screen, a hydrodynamic pressure results. This pressure depends on the type of squeegee being used (Hawkyard, 1994). When a rod or roller squeegee is used there are two moving surfaces which bring their boundary layers of print paste into a wedge (seen in Figure 1.2.d). The pressure induced, in this case, is greater than that on application of a blade type squeegee, if all other factors remain constant. Ultimately however, the amount of ink transferred onto the substrate, is dependent on the size of the holes in the image areas of the screen and the ability of the substrate to accept the print paste, as well as the magnitude of the applied pressure.

1.2.4 Components of a Typical Screen Printing Ink

The requirements pertaining to the components of a screen printing are unrestricted to a great extent due to the dexterity of the process. That is to say that the viscosity and surface tension of a screen ink are of minor importance when compared to a process like ink jet printing, although, the physical properties that are required of the ink are dependent on the substrate and its application. Traditional screen printing is seen to deposit an ink layer of about 12 μm , gravure printing gives a layer of 7 μm and offset lithograph a thickness of 2 μm (Leach et al., 1955; Walenski and Kipphan 2001). In terms of screen printing onto textiles, a typical formulation is given in Table 1.2.a (Barker, 1993; Hees et al., 2002).

Table 1.2.a Components of a typical screen printing ink and their relative concentrations

Ink component	Concentration within the ink formulation in terms of mass (%)
Water	10%
Emulsifier	%
Thickener	4%
White Spirit	62%
Catalyst solution	3%
Binder	15%
Pigment dispersion	5%

It should be noted that for a water based formulation the white spirit would be replaced by water. The advantage of completely water based formulations is in the handle imparted to the textile. The role of the components within a screen ink formulation, listed in Table 1.2.a, will now be discussed further.

Water/White Spirit

Essentially the water or white spirit within a screen ink formulation acts as the bulk solvent and the carrier for the other constituents of the ink. As this investigation is concerned with aqueous ink formulations, water would be the only solvent used. The choice of solvent also acts to determine the drying rate of the printed substrate. As such, it is sometimes preferable to include volatile solvents which evaporate at a faster rate (Barker, 1993).

Emulsifier

Emulsifier is an important ingredient if white spirit is included within the ink formulation. The emulsifier acts to stabilise the oil-in-water emulsion where the oil is the white spirit (Barker, 1993).

Thickener

The role of the thickener within a screen printing ink is to control the viscosity of the formulation. Typically, a screen ink has a viscosity of 1.5 – 2 Pa s although inks with much greater viscosities can be printed. Practically, a screen ink is supplied with a greater viscosity than is required and solvent is added to produce an ink of the required final viscosity.

Catalyst

The incorporation of a catalyst within a screen ink formulation is to aid the cross-linking of the binder onto the textile substrate. The aim of the inclusion of the catalyst is therefore to reduce the time required to cure the ink.

Pigment

It is commonplace for a filler or extender such as china clay to be included into a screen ink in order to lower the cost of production and increase the opacity of the print. Such fillers also aid in controlling the consistency of the ink. The actual pigment provides the colour of the ink and in order to obtain the required hue, 5% or less pigment may be needed. The final application of the printed textile usually determines the pigment choice in terms of the required properties of the printed fabric.

Binder

The role of the binder within a screen ink formulation is to provide fixation of the ink to the textile. Often the binder may be an acrylate co-polymer which cross-links in the presence of a catalyst when heated. Other binders used include resins and plastisols. Further discussion of binders which are commercially used within the screen printing industry follows in a later section. It should be noted that, typically, a screen ink for printing onto textiles requires curing at 160°C for 2 – 3 minutes in order to achieve the desired fastness properties.

The investigation reported here focuses on the role of the binder within a water-based printing ink in terms of its application and fastness properties conferred to the printed substrate. As such, some details on the various types of binders used in screen printing inks for textiles are given in the following section.

1.2.5 Commercially Available Binders for Textile Printing

It was suggested that when considering fixing a pigment to a textile substrate, a binder already used in a textile printing ink such as a screen ink would provide the starting point for an ink jet formulation (Hees et al., 2002). Several textile binders are available which, when applied as part of a screen printing ink give the required fastness characteristics along with an acceptable handle.

1.2.5.1 Helizarin Binder TW

BASF supplies a number of textile binders in the Helizarin range. Helizarin Binder TW is a self cross-linking polyacrylate which is supplied as a dispersion in water and is miscible with water at all proportions. Helizarin Binder TW can be applied within a pigmented ink at levels of up to 10% by weight of formulation. Helizarin Binder TW is designed to give very good general fastness properties whilst conferring excellent handle to the fabric. A drawback of this particular binder is its poor resistance to dry rubbing and as such, the addition of a silicone based auxiliary within an ink formulation is recommended. Once printed onto the required substrate as part of an ink formulation, Helizarin Binder TW is fixed by the application of hot air. The recommended cure conditions for this system are 150°C for 4-5 minutes. This puts a time constraint on how quickly the print can be processed. The recommended viscosity range of application of this binder is 40-70 dPa s which is more than 100 times greater than that required for ink jet. However, the Helizarin Binder TW itself has a

viscosity below 30 mPa s so could be used in an ink jet formulation at low levels. The problem with the inclusion of such a binder within an ink jet system would lie in the stability of the dispersion and its compatibility with other constituents of the ink. The white cloudy nature of the dispersion may also cause problems with colour characteristics when pigment levels are low and the amount of ink applied to the substrate is limited (BASF, 2001).

1.2.5.2 Synthomer 5130

Synthomer produces a wide range of print paste binders, for example Synthomer 5130, for use in the printing of textiles. Synthomer 5130 is a latex which is suitable for pigmented water-based systems. It is compatible with and often used alongside cross-linking agents such as melamine resins or acrylic binders with pH adjustment. Once applied to the substrate, a thermal drying process equivalent to 150°C for 5 minutes is required to fix the print. Synthomer 5130 is known to give soft hand characteristics whilst providing the print with excellent wet and dry rub resistance. That is to say that the printed fabric feels very similar to unprinted fabric whilst conferring the appropriate fastness properties required from a textile print. The viscosity of Synthomer 5130 is 25-300 mPa s. This high viscosity suggests that for incorporation within an ink jet ink, the amount used would be limited in order to meet the strict requirements of physical parameters of the ink jet process. Whether a small amount would provide the required fastness properties is unknown. The reliance on additives to aid the cross-linking of the product may also cause problems in terms of viscosity and in adding an extra complication to an ink jet system which must be finely balanced. A further problem with the inclusion of a melamine resin as a cross-linking aid lies in the fact that tends to produce a yellowing of the fabric upon curing (Synthomer, 2001).

1.2.5.3 Impranil DLN

Bayer manufactures binders for use within inks for the printing of textiles. Impranil DLN is an anionic aliphatic polyester polyurethane dispersion with a solids content of approximately 40%. Impranil DLN is a low viscosity dispersion with a flow time of below 70s when measured using a 4 mm flow cup at 23°C. Impranil DLN can be used within an ink formulation alongside cross-linking agents such as melamine resins. Once printed, the substrate is dried at temperatures between 80°C and 150°C. If a cross-linking additive is present, on evaporation of the water, the substrate is heated

for up to 2 minutes at 150-160°C. In terms of its possible use within an ink jet printing ink, the dispersion stability is important. That is to say that once part of an ink formulation, it is important that the Impranil DLN remains well dispersed. There are also concerns over the inclusion of cross-linking additives which may act to disturb other components of the formulation and produce a yellowing of the substrate on curing (Bayer, 2001).

1.2.5.4 Other Possible Binders for Textile Printing

Other types of binder that may be used within an ink for the printing of textiles include resins, polyvinyl propylene and carboxy functional polyvinyl alcohol. However, use of each of these binders within an ink jet printing ink would cause problems in terms of their viscosity and dispersion stability within such formulations (Barker, 1993).

1.3 Ink Jet Printing Technology

Ink jet printing is essentially a non-impact technology in which droplets of ink are ejected from a small orifice and directed onto a specific area on a substrate in order to form an image.

1.3.1 History of Ink Jet Printing

In 1951, Elmqvist patented the first ink jet device based on the theories of Rayleigh (Rayleigh, 1878; Elmqvist, 1951). During the 1950's and early 1960's, computer systems were becoming more advanced and as a result the need for a high speed electronic method of printing grew. Sweet established that it was possible to break up a stream of ink into droplets of uniform size and spacing by applying a pressure wave pattern to an orifice (Sweet, 1965).

In 1976, IBM introduced the first printer based on a continuous ink jet system whereby electrically charged ink droplets were deflected into a gutter for recirculation on passing an applied electric field while uncharged droplets were seen to remain travelling straight until hitting the substrate and forming an image. In tandem with this project, a method of drop on demand (DOD) printing was developed. By 1977, the first continuous ink jet colour image printer pioneered by Applicon of Burlington, Massachusetts became commercially available. The first DOD ink jet printer PT-80 using piezoelectric technology, pioneered by Zoltan, Kyser and Sears was launched by Siemens also in 1977 (Zoltan, 1974; Kyser and Sears, 1976).

In 1979 a second drop on demand ink jet system known as “bubble-jet” was developed by Canon in which the piezoelectric transducer was replaced by smaller thermal alternatives (Endo et al., 1979). This technology was also adapted by Hewlett-Packard around the same time which they named “thermal” ink jet. This led to a more widespread production of desktop DOD printers and subsequently the first disposable ink cartridge was created (Vaught et al., 1984). Current technology allows for resolutions improving from 300 dpi to 600 or 720 dpi and even in some cases as high as 2880 dpi. In 1999, Epson introduced a printer (Stylus 900) which offered 1440 × 660 dpi by ejecting ink droplets as small as 3pL. With this capability, it equals the world’s best lithographic printing (Pond, 2000).

1.3.2 Introduction to Ink Jet Printing

Ink jet printing is an ever evolving technology with a rapidly increasing number of patent applications. The increased number of patent applications in the field of ink jet printing is mainly due to the significant, worldwide research and development interest since the first commercialisation of the ink jet printing technology by Hewlett Packard and Cannon in 1984. Today, ink jet printing is a fairly mature technology. This is true particularly in the areas of ink jet printing on paper, desktop ink jet printing, wide format (poster size) ink jet printing and industrial scale, high-speed (usually continuous stream) but relatively low-resolution ink jet printing.

However, ink jet printing still attracts an increasing amount of research and development interests. In fact, such interest has grown steadily throughout the last decade. Figure 1.3.a shows the number of patents granted each year from 1990 to 2002 (Lin, 2003).

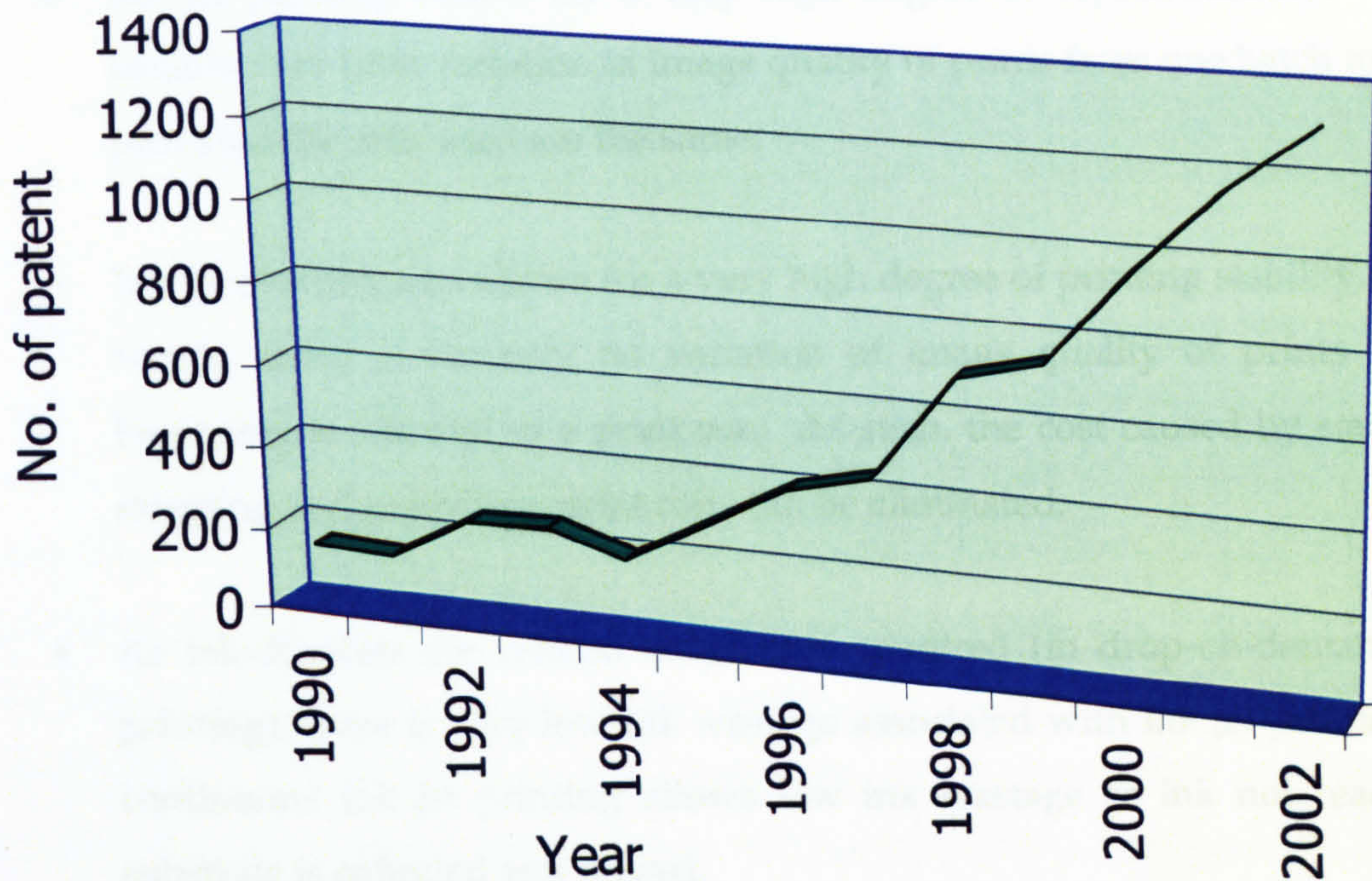


Figure 1.3.a Number of patent applications relevant to ink jet printing

Compared to conventional printing processes, ink jet printing has significant advantages. Such advantages include the following: (Lin and Guthrie, 2001).

- Ink jet printing process does not require the use of printing plates and therefore, time-consuming plate making/plate mounting operation.
- As no printing plate making is required, there is no need for usually time-consuming colour separation process.
- As ink jet printing technology allows direct printing from graphic design software (via microcomputer) to printer, there is no need for the "traditional proofing". Moreover, any modification made to the image can be incorporated into the final print conveniently.
- Ink jet printers are usually much less expensive than the conventional printing presses.

Following are several advantages of ink jet printing that are less well-known: (Lin and Guthrie, 2001).

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

Ink jet printing technology is particularly suitable for printing of inks that contain expensive ingredients. Typical examples of expensive ingredients include photochromic colorants, thermochromic colorants for anti-counterfeit applications (Lin, 2003) and biochemicals.

Due to it being a non-impact process, ink jet printing offers great versatility in terms of the varied substrates that can be printed. Emerging markets include plastics, printing of circuit boards and of electronic displays. For industrial applications ink jet printing is currently used for graphics, signs, labels, textiles and flags and banners (Tanaka et al., 1999). While continuous ink jet is used for fast, quick change processes such as printing use by dates on produce, it is generally accepted that for the most part drop-on-demand ink jet printing is preferred. There are two major types of drop-on-demand print-heads namely thermal and piezo jet. Piezo ink jet print-heads are more widely used in wide format industrial applications (Dante et al., 1999).

1.3.3 Types of Ink Jet Technology

As mentioned previously, ink jet printing does not require the presence of an image carrier or plate in order to transfer ink to the required substrate. In ink jet printing a digital image can be converted directly into a printed image without the need for an image carrier. Although there are different types of ink jet printing, each has similar characteristics. All ink jet techniques are non-impact processes which form an image on the substrate via the ejection of ink droplets from a series of small orifices. The simplicity of the process allows for a range of applications within the printing industry. Essentially, there are two types of ink jet printing which are extensively used in industrial applications, these being continuous and drop-on-demand ink jet technologies. A breakdown of these processes and their different types is given in Figure 1.3.b. In terms of market share, drop-on-demand is predominant as it offers higher quality prints whereas continuous ink jet printing tends to be used for simple designs printed at a high speed, such as sell by dates on cans.

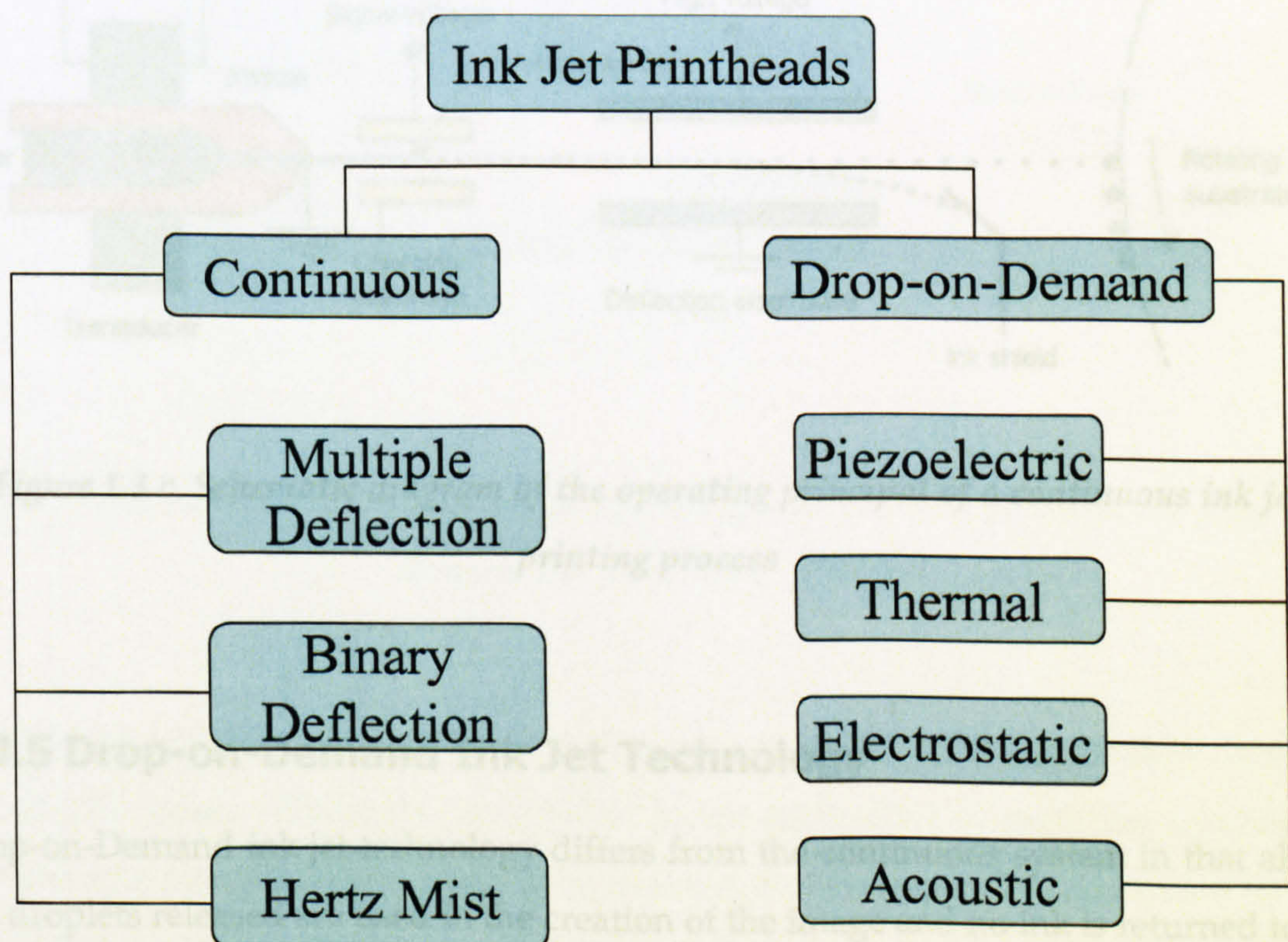


Figure 1.3.b Types of ink jet printing technology

The main ink jet technologies will now be discussed in greater detail.

1.3.4 Continuous Ink Jet Printing Technology

In a continuous ink jet system, ink droplets are released in a continuous stream. Inks used in continuous ink jet inks contain electrolytes. Therefore, on passing a charging electrode some of these droplets become charged. The ink droplets which have become charged are then deviated from their original direction on passing a high voltage deflection plate (Davison, 1995). In general, the charged droplets are deflected onto the substrate thus forming the required image and the uncharged droplets are collected in a gutter and pumped back to the body of ink in the cartridge (Kipphan, 2001; Davison, 1995). In some cases the reverse method is used, i.e. the uncharged droplets form the image and the charged droplets are returned to the reservoir. These methods are known as the "raster scan method" and the "binary continuous ink jet system" respectively (Le, 1998). A diagram outlining the principle of continuous ink jet printing is shown in Figure 1.3.c.

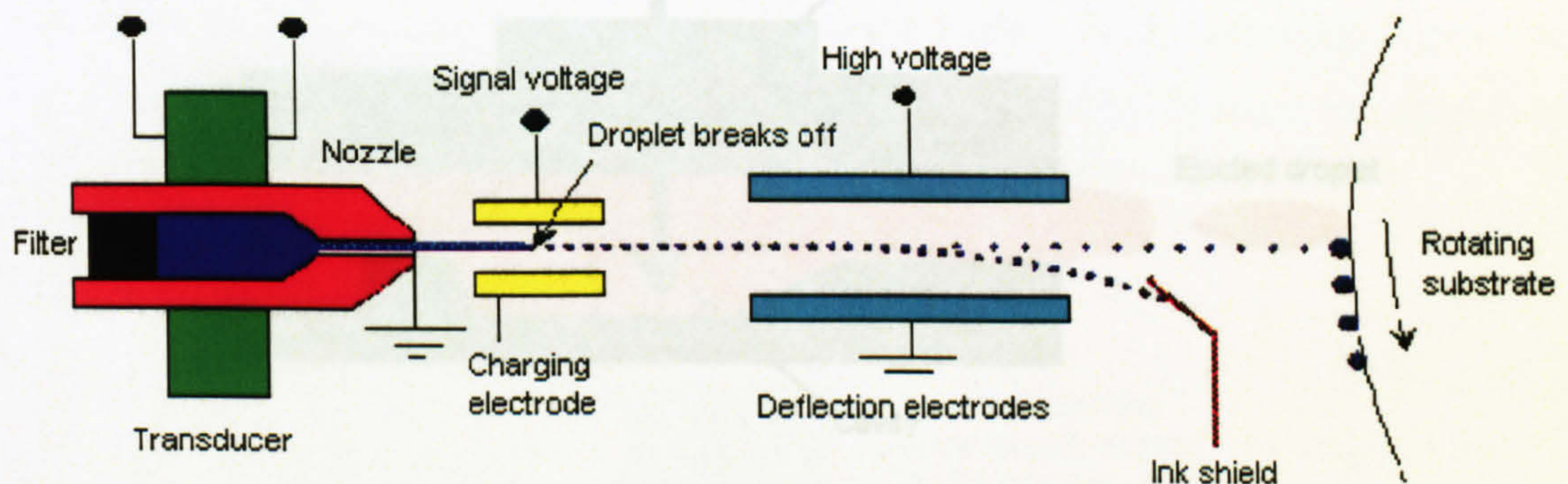


Figure 1.3.c Schematic diagram of the operating principal of a continuous ink jet printing process

1.3.5 Drop-on-Demand Ink Jet Technology

Drop-on-Demand ink jet technology differs from the continuous system in that all the ink droplets released are used in the creation of the image and no ink is returned to the reservoir. The droplets of ink are not charged and thus there is no deflection involved. The print-head is located as close as possible to the substrate in order to reduce the distance travelled by the ink droplet. As a result these types of system are more popular for office use. There are two major types of drop-on-demand print-heads, namely thermal and piezoelectric (Piezo) jet. Piezo ink jet print-heads are more widely

used in wide format industrial applications (Dante et al., 1999), whilst both have a share of the more traditional desktop market.

1.3.5.1 Piezoelectric (Piezo) Ink Jet Printing Technology

Piezo ink jet is one of the simplest forms of drop on demand printing where ink droplets are ejected by the action of an oscillating piezo crystal. This technology involves the application of an electric charge to the cartridge nozzles. The applied electric charge acts to excite small piezo crystals contained within the print-head. Once stimulated, these piezo crystals change shape and as a result squeeze the ink inside the chamber resulting in the release of an ink droplet from the nozzle. In real time, this process occurs many times per second to produce a “vibration” of the piezo crystal and a stream of ink droplets is expelled from the cartridge. A diagram of a piezo ink jet system is given in Figure 1.3.d.

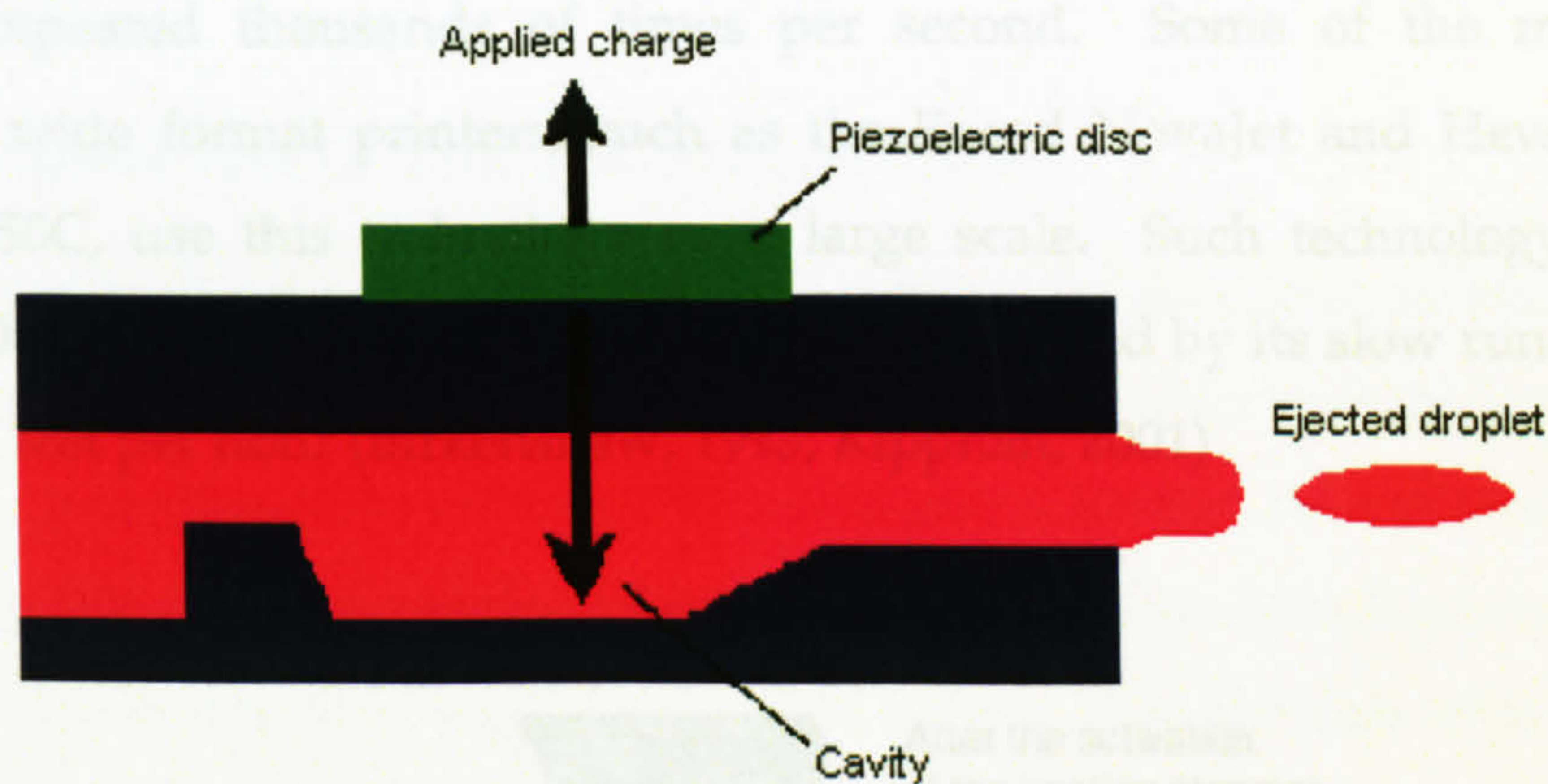


Figure 1.3.d Schematic diagram of the operating principle of a piezoelectric drop-on-demand ink jet printing process

In piezoelectric based ink jet printers, the ink supply is located separately from the actual print-head. Whilst this may be an inconvenience when replacing print-heads, piezoelectric print-heads are seen to have a greater life span when compared to their bubble-jet counterparts (Dawson, 2003).

1.3.5.2 Thermal Ink Jet Printing Technology

Thermal or bubble-jet ink jet printing involves a process of superheating where a heating element flashes to temperatures of up to 350°C within a tube filled with ink. As the ink is heated, vapour bubbles are formed almost instantaneously. Once

nucleated, the bubble formed thermally isolates itself from the heating element and as such, no further heat can be conducted by the ink (Henseleit et al., 1992; Rembe et al., 2000). The phase transition of liquid to vapour gives rise to a volume expansion of around 50 times. This volume expansion acts to force a droplet from the print-head onto the surface of the receiving media. The operating principle of a bubble-jet ink jet printer is given in Figure 1.3.e. The ink leaves the print-head after $10\mu\text{s}$ due to a pressure of about 100 atmospheres being created. The heating element then cools and the initial steam created condenses back to a liquid creating a vacuum which acts to pull ink from the reservoir to replace that which has been ejected. Due to the speed at which this process occurs, it is only the ink in the immediate surroundings of the heater which is heated and the remaining ink is left cool. To help ensure that the ink remains below 65°C , a heat sink is included within the print-head which acts to dissipate the heat energy away from the heater and avoid over heating of the ink. This process is repeated thousands of times per second. Some of the most popular commercial wide format printers, such as the Encad NovaJet and Hewlett Packard 650C and 750C, use this technology on a large scale. Such technology gives print quality of 300 to 600 dpi, although the process is hindered by its slow run speeds of 10 to 20 square feet per hour (Birkenshaw, 1993; Kipphan, 2001).

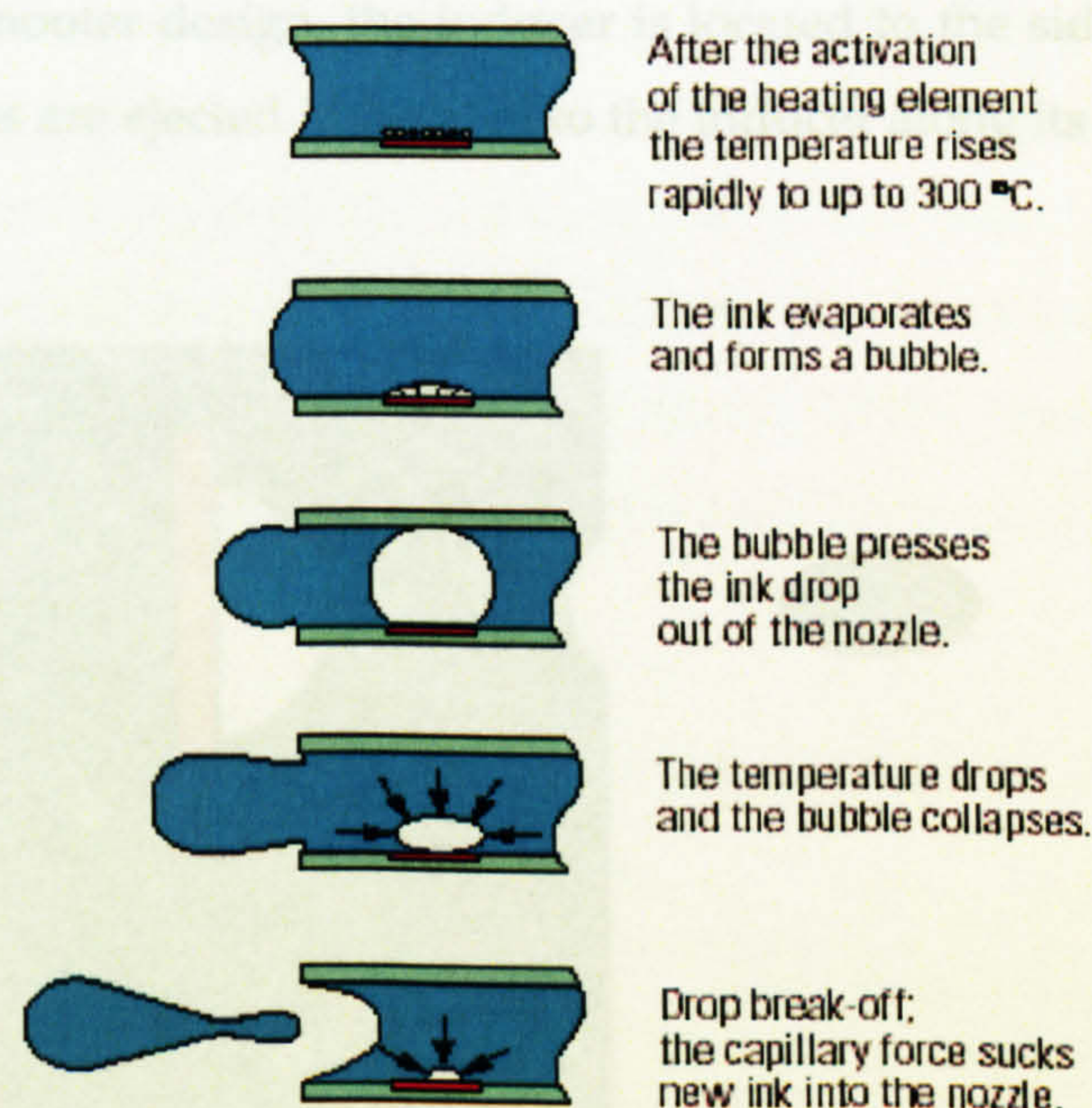


Figure 1.3.e Schematic diagram of the operating principle of a thermal ink jet printing process (Kipphan, 2001)

In a bubble-jet printing system it is common for the print-head and the ink supply to be contained within the same unit. This allows for easy replacement of the ink and of the print-head should any nozzle blocking or other defects occur (Dawson, 2003).

In this technology and in its piezoelectric counterpart, the concentration of any dissolved or suspended solids near to the nozzles may exceed the solubility of any remaining liquid components of the ink. The reduced amount of solvent within this proximity may result in deposition of solid aggregates around the nozzles. If this build up of aggregates becomes excessive, the release of ink droplets from the print-head will be affected and the subsequent printed image will lose quality.

When discussing ink droplet release, it should be noted that each ejected droplet is seen to have a volume of $100\text{-}200 \times 10^{-12}$ litres. Each droplet also has a diameter of about $40 \mu\text{m}$ which will correspond to a printed image which has a resolution of 600 dpi (Dawson, 2003).

1.3.6 Composition of Ink Jet Print-Heads

Two types of print-head design dominate the market: the roof-shooter shown in Figure 1.3.f and the side shooter shown in Figure 1.3.g. In a roof-shooter design, the droplet inducer, be it a heating plate or piezoelectric crystal, is located behind and in line to the nozzles. The ink droplets are ejected in a plane which is perpendicular to that of the inducer. In a side-shooter design, the inducer is located to the side of the nozzles. In this case, the droplets are ejected in parallel to the inducer along its plane (Le, 1998).

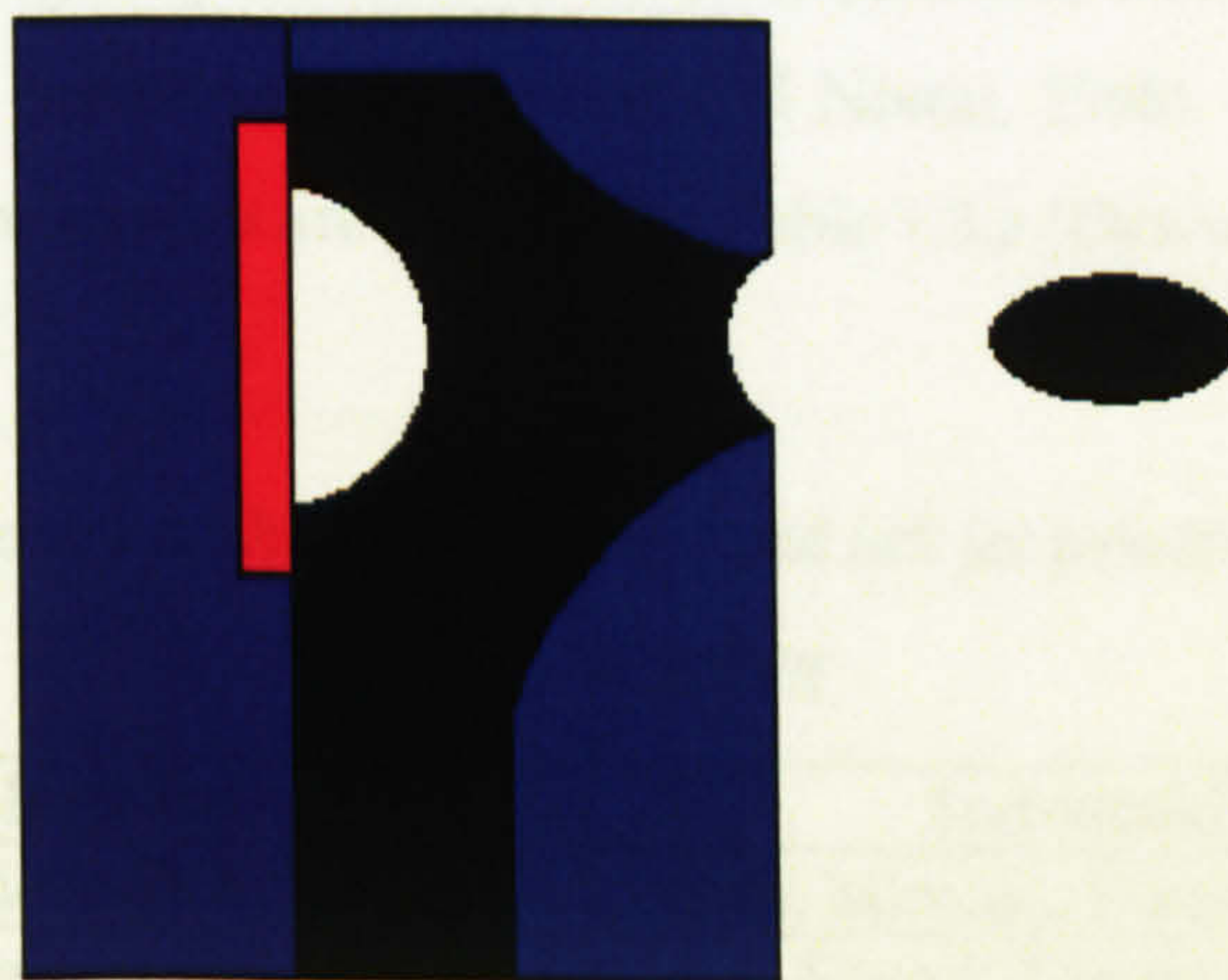


Figure 1.3.f Schematic diagram of a roof-shooter design ink jet print-head

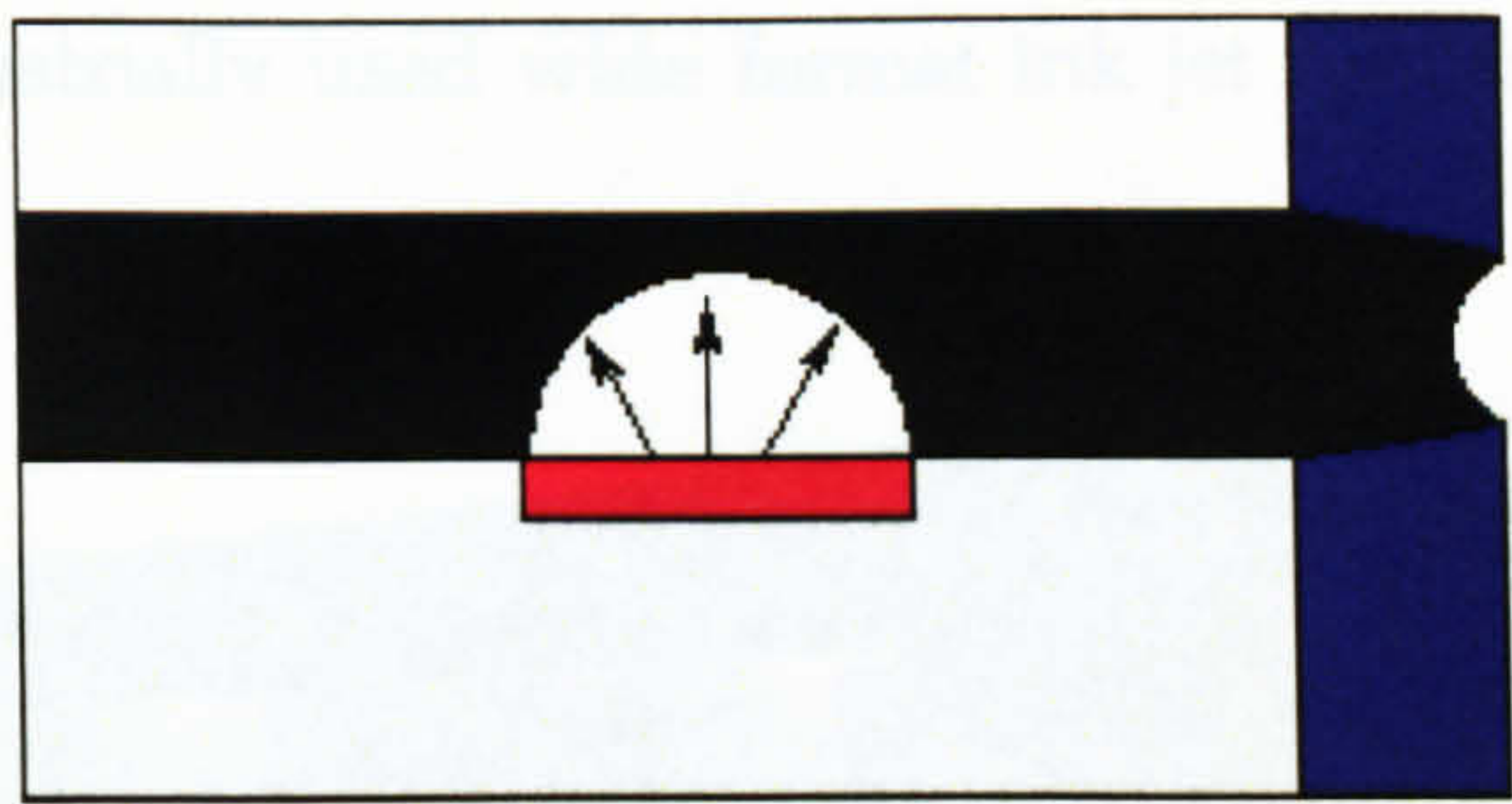


Figure 1.3.g Schematic diagram of a side-shooter design ink jet print-head

Ideally, in order to reduce any evaporation of solvent from the print-head, which may increase the likelihood of aggregation, the nozzle would be capped between firings. In practice, this would compromise the print speeds attainable. The time spent by an ink jet nozzle without firing a droplet is known as its latency. Geometric considerations mean that for the same ink formulation, the latency time of a roof-shooter design is greater than that of a side-shooter (Kipphan, 2001).

1.3.7 Wide Format Ink Jet Printers for Textile Printing

It is now becoming commonplace in industry to find large format ink jet printers ranging from 1 to 5 metres wide. Such printers are used for a variety of applications and substrates e.g. billboard advertisements, large hangings from buildings and logos for aircraft tail fins (Kipphan, 2001; Frost and Lahut, 2003). These large scale printers are now used in the printing of textiles. Essentially, wide format printers use the same technology employed by desktop ink jet printers, only on a larger scale. Therefore, the three major technologies (piezoelectric drop on demand, thermal drop on demand and continuous ink jet) predominate (Yandell and Nixon, 1998). Some of the companies which use such technologies are outlined in Table 1.3.a (Dawson, 2000).

Table 1.3.a Overview of the industrially used ink jet printing techniques for textile printing

Technology Employed	Industrial Users
Piezo DOD	Vutek, Mimaki, Epson, Stork Sapphire
Thermal DOD	Encad, Canon, ColorSpan
Continuous (binary charge)	Stork Truprint
Continuous (multiple charge)	Stork Amathyst, Zimmer Chromatex

Examples of two industrially used wide format ink jet printers are shown in Figure 1.3.h and Figure 1.3.i.



Figure 1.3.h Stork Sapphire wide format ink jet printer

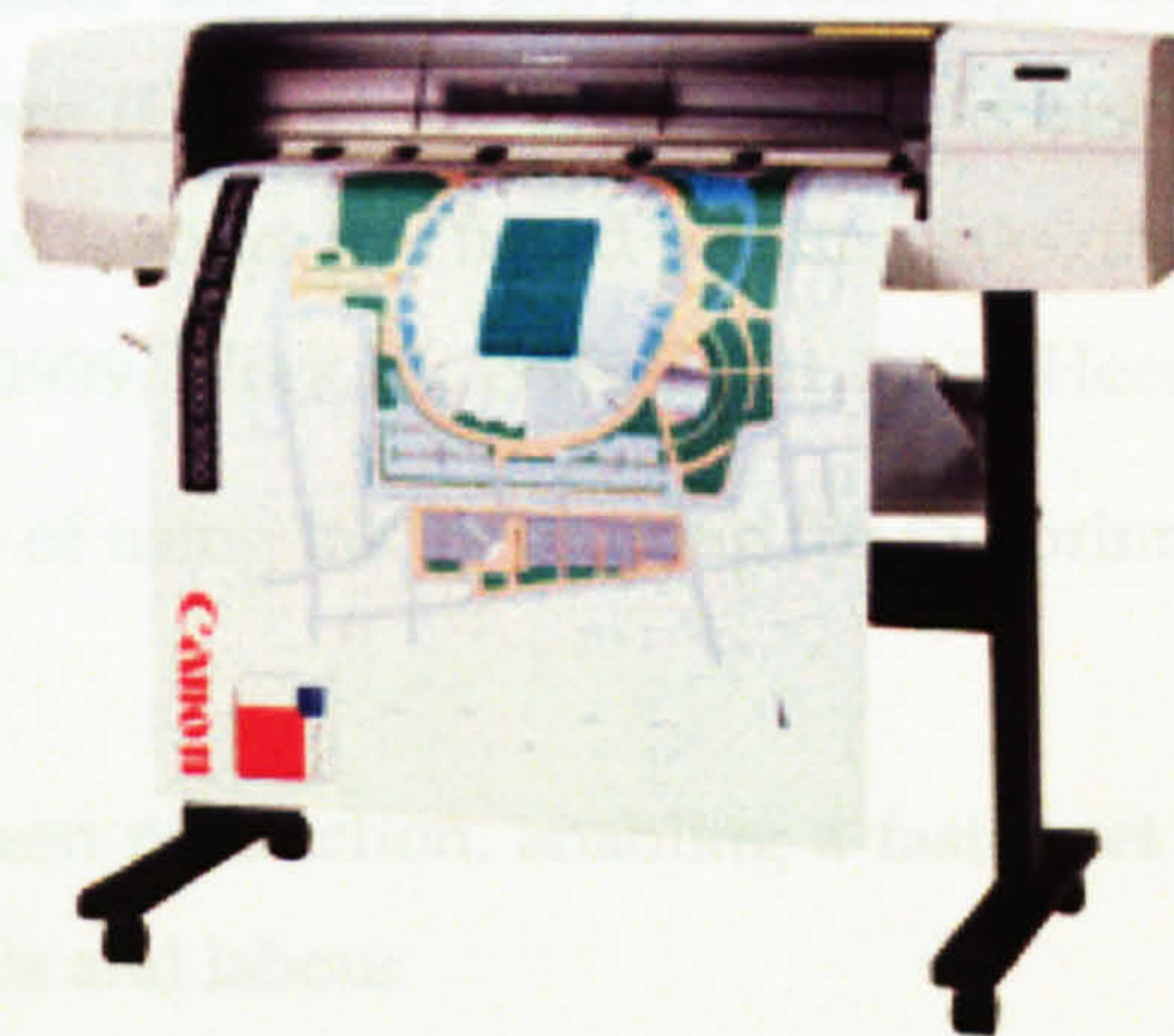


Figure 1.3.i Canon BJ-W3000 wide format ink jet printer

There are four major aspects of performance of wide format ink jet printers which industry is concerned with: (Frost and Lahut, 2003).

- Printing should be sustainable at high frequencies
- Nozzles should direct the ink jets accurately
- There should be uniformity between channels
- There should be wide operating latitudes

In terms of industrial applications print-heads which use piezoelectric technology are favoured due to their versatility. Inks of higher viscosities (20 mPa s and over) jet far

better using this technology which also allows for use of oil based, solvent based and UV curable ink formulations (Frost and Lahut, 2003; Russel, 2003).

Printed images, depending on the printer used and the final application of the substrate, usually have a resolution of 20-600 dpi. Wide format printers have variable print speeds. The speed of printing is determined by the resolution of the print and the width of the substrate. Whilst the speed of printing is continually increasing as the industry evolves, typically, print speeds of 1-3 m²/h are observed (Kipphan, 2001; Frost and Lahut, 2003).

1.3.8 Advantages and Disadvantages of Ink Jet Printing onto Textiles

In terms of textile printing, ink jet printing is still in its infancy. Traditional techniques dominate the industry, however, there are forecasts which suggest that with the development of print-heads and inks, ink jet technology may enter the market to a larger extent in the future (Hees et al., 2002). There is also a suggestion that whilst current ink jet technology favours dye based printing inks, the future lies in pigmented systems (Deverakonda, 1999; Work III, 1999; Grant, 2001; Hees et al., 2002).

Some of the advantages of using ink jet printing for the printing of textiles include the following:

- No need for screen production, enabling a faster set up and cost reduction in terms of materials and labour
- Any design may be printed. Due to the fact that all designs come from computer based software, the design can be printed directly onto the substrate
- Reduced cost of set up. Once the initial printer and computer software has been bought, the only further costs incurred are in replacement of ink and maintenance of equipment. The need for production workers is also reduced, thus reducing costs further
- There is no need for colour separation. Screen printing requires a different screen to be used for each colour applied to the substrate. Ink jet printing uses a colour mixing process which allows for virtually all colours to be produced
- An ink jet printer requires far less factory space than a conventional screen printer

- The ink jet printing process allows for short runs and bespoke designs with quick change over between prints
- The size of a design repeat is unlimited. The size of a screen will control the size of the pattern which can be used in a repeat

As with any technology, there are some drawbacks in the use of ink jet for textile printing on a large scale. Some of the disadvantages of ink jet printing of textiles include the following:

- The speed of print production. Ink jet printing currently allows for up to 200 m/h whereas screen printing is able to print up to 5000 impressions per hour.
- Restrictions of ink formulations. Ink jet printing has parameters in terms of viscosity, surface tension and particle size, which must be strictly adhered to. Screen printing is more versatile and these physical properties are less important.
- Problems may occur in terms of blocking of the print-head. Due to the restrictions of an ink jet ink, when considering the size of the nozzles and possible aggregation of the colorant, clogging can be a problem. Screen printing can be a more reliable print method.
- Not only are there problems in terms of the physical parameters when considering the amount of colorant and binder to use within a system, the amount of ink which is actually deposited onto the substrate via the medium of ink jet is far less than is the case with more traditional printing methods.
- Some colours are difficult to print using the colour mixing process associated with ink jet technology. Often such problems are associated with the depth of shade achievable using only four colours, namely, cyan, yellow, magenta and black. However, this problem is reduced by the addition of "spot" colours such as green and navy blue. Screen printing allows for any colour to be created and printed.
- Ink jet inks are required to have a longer shelf life than screen printing inks, typically up to 2 years due to the fact that they may rest within a print cartridge over a large period of time. Screen inks may be made up on the day of printing and generally have shelf lives of up to three months. It is possible for a screen printing ink to be formulated on the day of printing.

Whilst it is clear that there are several advantages in the use of ink jet as a technology to print textiles, especially in terms of short runs and bespoke designs, limiting factors appear to be the speed of printing, stability of the inks and the number of possible different substrates.

1.3.9 Influence of Textile Substrates on the Quality of Ink Jet Printed Images

A major problem associated with the printing of textiles lies in the vast array of textile substrates available and in creating an ink with suitable resistance properties for such an application. Due to the vastly different properties required for textile application as opposed to paper substrates, new ink formulations specific to textiles will have to be developed.

Tincher et al. suggested the following criteria as a guide to the type of formulation for use on textiles (Tincher et al., 1998):

- Viscosity < 10cps
- Surface tension > 40mN/m
- Post processing - thermal or UV only
- Colorants - both dyes and pigments
- Dry crockfastness > 4 (AATCC Test outlined in Section 2.3.11)
- Wet crockfastness > 3.5 (AATCC Test outlined in Section 2.3.11)
- Minimum change in fabric hand
- Applicable to a wide range of fibre types
- Water based or 100% curable
- High colorant loading
- Low cost.

These specifications were set out purely as a basis to start from as there is no one specific formulation set out and accepted as being the best possible for use on a textile substrate. However, it was recognised that ink droplets needed to be of consistent and uniform size. As a result, the viscosity and surface tension of the formulation must be controlled very strictly. It was also stated that the ink formulation required to colour a textile material is likely to contain both dye and pigment (Tincher et al., 1998).

1.3.10 Status Quo of Ink Jet Printing onto Textiles

As discussed previously, there is currently a large amount of research carried out in the field of digital printing onto textiles. Some of this research concerns the use of dyes as the colorant in the ink formulation. However, there has been a trend towards the development of pigmented ink systems.

1.3.10.1 Dye-Based Ink Jet Printing Systems

Dye-based inks are very effective in terms of the printing process, the stability of the formulation and the colour gamut available. Reactive dyes are favoured by ink makers due to their solubility in water (Work III, 2000). However, a problem associated with the use of dyes arises in their being substrate specific. For example, reactive dyes are used to dye cellulosics whereas polyester requires the use of disperse dyes and silks and wool needs the use of acid dyes (Galea, 1993; Gutjar and Koch, 1994; Gutjar and Koch, 1994; Ross, 2001). Further problems are encountered in the fixation of any prints. When considering an ink that uses a reactive dye as the colorant, it is necessary to pre-treat the substrate with the chemicals which are required to fix the dye to the fabric (Gutjar and Koch, 1994; Provost, 1995; Ross, 2001). Inks containing disperse dyes as the colorant encounter problems in terms of stabilising the particles within the ink formulation. Fixation of the prints is achieved by stentering of the fabric at elevated temperatures ($>160^{\circ}\text{C}$) (Gutjar and Koch, 1994). Due to the need for ink formulations that are capable of printing a range of textiles, the use of dyes is limited and pigmented systems would appear to be the preferred option.

1.3.10.2 Pigmented Ink Jet Printing Systems

Typically, pigmented inks are produced via a step of formulation of a pigment concentrate. Preparation of a pigment concentrate usually involves a process of mechanical shearing of the pigment within a liquid medium containing a dispersing agent. The aim of this step is to produce a pigment paste in which most of the agglomerates and aggregates are broken up into smaller particle units. Such smaller particles are kept apart in a suspension due to the effect of the dispersing agent providing stability usually sterically or electrostatically (Lin, 2003; Belmont, 2001; Hatada and Tanaguchi, 2001). The pigment concentrate can then be blended with other necessary components such as humectants, binder(s) and surfactants to form an ink formulation.

In general, where good durability and light fastness are required, pigmented systems are preferred (Gregory, 1993). This is borne out by the fact that 48% of the textile printing sector is concerned with pigment printing (Hees et al., 2002). Recently, there has been significant progress in the development of pigmented inks for ink jet applications (Dante et al., 1999).

However, there are several drawbacks in the use of pigments for ink jet applications due to the relatively low dispersion stability of the pigments within the generally low viscosity ink jet ink formulations. Such low dispersion stability is mainly due to the lack of polymeric binder at an adequate concentration. (Lin, 2003) Thus, the pigment particles may flocculate or agglomerate leading to the blocking of the jet nozzles within the print-head (Work III, 1999). A significant factor that has been widely used for the assessment of the status of pigment dispersion is the particle size within the ink formulation. Ideally, for ink jet applications, a particle size of 0.5 μm or under is required. Smaller particles allows for improved stability, optical density, colour gamut, gloss and light fastness (Bugner and Bermel., 1997), this is discussed further in Section 1.4.3.3. To be suitable for ink jet printing, an ink must also have the required viscosity profile for a specific print-head (Hees et al., 2002). Although pigment loading has an effect on it, the viscosity profile of an ink is largely governed by polymeric components of the ink such as binders and humectants.

Once all the problems associated with stability have been overcome, the major problem lies in how to bond the pigment to the fabric to give the durability required (Work III, 1999). Ideally, to achieve the best fixation of pigment to the fibre, similar binder systems as those used in the screen printing process would be used. However, incorporating such ingredients at the required concentrations may raise the viscosity of the ink formulation to levels higher than is acceptable for the ink jet printing process as detailed above (Work III, 1999). Other binders which can be used include resins. Binders based on resins also encounter problems when printing textiles as they can confer an unacceptable stiffness to the fabric (Tincher and Yang, 1999).

1.3.11 Status Quo on the Research into Pigmented Ink Jet Inks for Printing Textile Substrates

A number of companies have been developing ink jet inks specifically for the printing of textiles over recent years. Such inks are required to have the required fastness properties for their particular application whilst conferring an acceptable handle to the

printed fabric.

1.3.11.1 Irgaphor Pigmented Ink Jet Inks

Ciba has introduced a set of pigmented inks known as the Irgaphor range. Such inks appear offer excellent fastness properties after a curing process involving heating to 200°C for 2 minutes. However, Irgaphor inks can, in some cases, confer a stiffer hand to the fabric than is preferred (Ciba peciality Chemicals, 2002).

1.3.11.2 Helizarin Pigmented Ink Jet Inks

It has been reported that BASF have developed two pigmented inks for ink jet printing of textiles. These are Helizarin P inks that are used in piezo ink jet printers and Helizarin H inks, which have been developed for thermal systems (Hees et al., 2002). The application of these inks to textile involves a possible five step process which is detailed as follows (Hees et al., 2002).

1. Application of a pre-treatment to the fabric – (optional). Such a pre-treatment is usually for specific recipies.
2. An image is ink jet printed onto the fabric.
3. The printed fabric is dried.
4. Application of a post treatment. The post treatment is again concerned with specific recipes of binders developed for specific fabrics.
5. The ink is fixed to the textile by application of temperatures of 150°C for 5 minutes.

The approach used by BASF is therefore at minimum a “two pack” process where the pigment and textile binder are applied separately to the substrate. The idea behind this is to increase the reliability of the ink within the print-head whilst achieving the required handle and fastness properties of the fabric. The problem with such a system lies in the amount of time and energy that is used in comparison to a “one pack” process where the pigment and binder are combined within an ink formulation. The need to incorporate the binder and pigment within the ink in the future was also detailed within the paper (Hees et al., 2002). However, it is noted that incorporating the binder within the pigmented ink formulation may require the development of the polymer systems used.

1.3.11.3 Artistri Pigmented Ink Jet Printing Inks

Another company that developed ink jet inks for textile printing is DuPont who introduced their Artistri range of inks to the market. These inks provide advanced colour choices and DuPont offers a colour control management system to enhance the colour attributes of the prints (DuPont, 2002).

1.3.11.4 Research into Pigmented Ink Jet Inks Containing Emulsion Polymers

Grant reported the development of pigmented ink jet inks incorporating water-based emulsion polymers (Grant, 2001). The suitability of such polymers was tested alongside acrylic and styrene-acrylic emulsions. The ink formulations prepared by Grant were printed and thermally cured at 150°C for 3-4 minutes. Once cured, the prints were assessed for their fastness properties and graded using grey scales. The rubfastness and washfastness of each of the prints using acrylic or styrene-acrylic as the binder were seen to be poor having a grey scale value of 1 in each case. The acrylic copolymer when combined with a cross-linker provided greater stability of the print although the wet crockfastness was still below 3. Addition of thickening agents such as propylene glycol and polyethylene glycol to the acrylic copolymer/cross-linker blend gave some improvements to the fastness properties although the viscosity was increased. Whilst these are encouraging results, the fastness properties are lower than would normally be preferred (Grant, 2002).

1.3.11.5 Research into Pigmented Ink Jet Inks Containing Resins

Tincher and Yang also reported the process of ink jet printing of pigmented inks onto textiles (Tincher and Yang, 1999). The use of resins as a binder within the ink formulation was discussed. The problems encountered when using resins lie in the handle conferred to the fabric and the viscosity of the formulation. Tincher and Yang have overcome these problems by the formation of lattices of suspended polymer molecules which have low viscosities even with high pigment loadings. In order to deposit the required amount of ink to the substrate, 4 print passes were required (Tincher and Yang, 1999).

1.3.11.6 Other Research into Pigmented Ink Jet Printing Inks

Other research on the ink jet printing of textile substrates using pigmented inks has been reported (Tincher et al., 1998). These pigmented inks are however, concerned with UV technology and have problems with viscosity as a result of the monomers and

oligomers required within the ink. The presence of acrylates within UV curable systems may also cause irritation to the skin.

When considering the research outlined in this section, there appears to be a need for a pigmented ink which could be jetted onto a range of textiles via a “one pack” process. The ink had to comply with the physical properties required for ink jet printing whilst producing prints which had appropriate handle as well as the required fastness properties. Ideally, the ink should also have an acceptable cure rate in order to reduce the time and costs of the operation.

1.4 Design and Manufacture of Inks for Ink Jet Printing

When formulating an ink jet ink, there are several components which can be incorporated depending on the end application of the ink. Some of the typical constituents of an ink jet ink, along with their functions, are shown in Table 1.4.a.

Table 1.4.a Components of a typical ink jet ink for printing onto textiles and their relative concentrations

Ink Component	Function	Concentration (%)
Water/Alcohols	Solvent	35-80%
Other solvents	Humectant (e.g. glycols)	5-30%
Dye/Pigment	Colorant	1-10%
Buffer	pH control	0.1-1%
Latex/Polymer	Binder, promotes fixation	1-3%
Surfactant	Wetting agent	0.2-2%
Ink Component	Function	Concentration (%)
Anti oxidant	Prevents oxidation	>1%
Conductive salt	Charging element in continuous systems	>1%
Additives	Defoamer, dispersants etc	>1%

Each of the ink components shown in Table 1.4.a is briefly described as follows.

Solvent

Solvent acts as the primary vehicle to carry the colorant and other ingredients. Typically in ink jet systems, water, methyl ethyl ketone or alcohols, such as isopropanol are common solvents. In thermal ink jet applications, the solvent is required to be the vapourisable component of the ink (Hauser and Reiniger, 1992).

Humectant

Humectants are typically liquids of low volatility which are incorporated into an ink formulation to alleviate any unnecessary evaporation of the ink and to give a smoother print. Most common examples of humectants in ink jet inks are glycols such as ethylene glycol and diethylene glycol. Where viscosity is less of an issue, polyethylene glycols or glycerol may be used although usually in combination with other glycols to provide a required viscosity and good latency (Fuji et al., 1985; Katsen et al., 1996).

Colorant

Colorants used within an ink jet formulation are either dyes or pigments depending on the application. Typically, dyes are used due to their high solubility, colour strength and gamut although there are arguments that pigmented inks offer superior print quality (Cheng et al., 2002). Recently, there has been a trend to move away from dyes in favour of using pigments. Such a move increases the versatility of the inks especially within the area of textile printing due to pigments being non substrate specific. (Work III, 1998).

Buffer

The presence of a buffer within an ink formulation is usually for pH adjustment in order to stabilise a particular component contained within the ink. Typically, inks are required to have a pH of 7-9 which also will prevent any unnecessary corrosion of the print-head.

Binder

The primary role of the binder is to achieve image permanence. That is to say it is required to prevent smudging of the printed image and in the case of textile printing to impart wash fastness properties. Common binders within aqueous systems include latexes, polyvinyl alcohols and polyvinylpyrrolidone. Binders must be used according to viscosity parameters. Other examples of binders used are hydroxypropyl cellulose and hydroxyethyl cellulose (Henseleit et al., 1992).

Surfactants

There is a wide range of surfactants available which vary in their use for a particular application. Most commonly used surfactants are wetting agents which act to reduce the surface tension of an ink formulation to enhance its wetting characteristics on the substrate. If a rapid drying after printing is required, the addition of a drying agent may be considered. Drying agents do however carry the risk of nozzle clogging and therefore more practical methods such as the inclusion in the system of wetting agents are usually employed. Other surfactants can be used in ink jet systems to enhance fastness properties such as light fastness agents and mar and abrasion resistors.

Anti Oxidants

Anti oxidising agents are used to reduce any oxidation which may take place within the ink cartridge.

Conductive Salts

Conductive salts are present only in inks used in continuous ink jet systems. Conductive salts become charged on application of an electric field and deflect either onto the substrate or into the gutter for recycling depending on the continuous process being used.

Other Additives

There is an array of additives which may be included to give certain properties to an ink. These may be defoamers to negate any foaming within the print-head; dispersants to stabilise a pigment suspension or chelating agents which complex metal ions and thus prevent clogging around the nozzle orifice. Ideally these additives should be kept to a minimum.

It should be noted that it is not necessary for an ink to contain all the components described above and in most cases the ink will be tailored for its particular application.

1.4.1 Choice of Colorant for Ink Jet Printing onto Textiles

The colorant and its relative concentration within an ink system determines the colour of the substrate in terms of its chroma and hue. In general, when formulating an ink the two colorants of choice are dyes and pigments. There are two ink types which can be chosen depending on the application. Traditionally, dye based inks have been used due to their capability of producing high image quality (Bugner et al., 1997; Dante et al., 1999). However, where good durability and light fastness is required, pigmented

systems are preferred. This is born out by the fact that 48% of the textile printing sector is concerned with pigment printing (Hees et al., 2002). A representation of current and future colorants for used in ink jet printing of textiles can be seen in Figure 1.4.a and Figure 1.4.b.

The pie charts show an increase in the use of direct to textile colorants i.e. pigments and disperse direct dyes which take the form of particulates within an ink formulation.

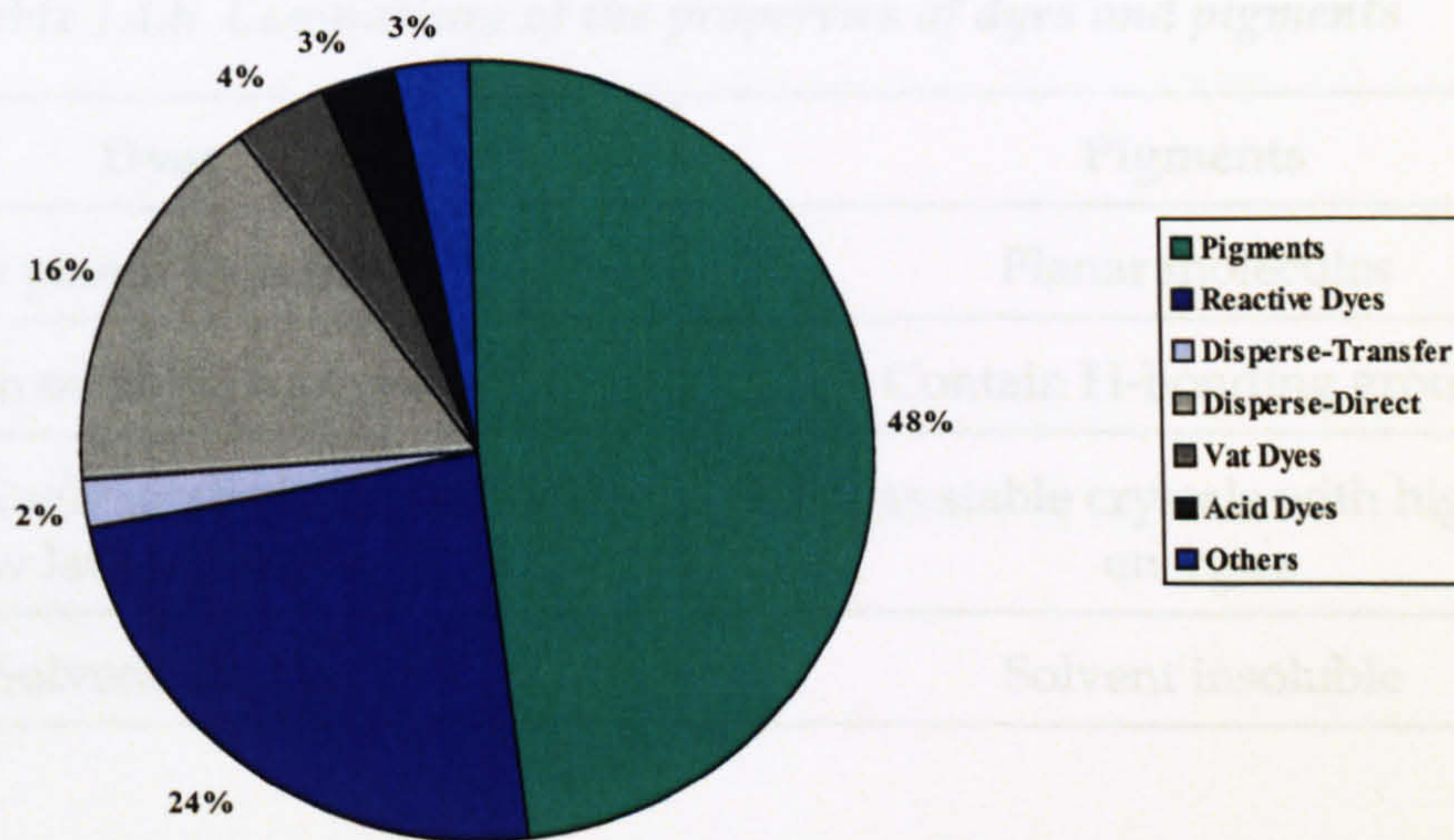


Figure 1.4.a Textile printing in 2001 by colorant class

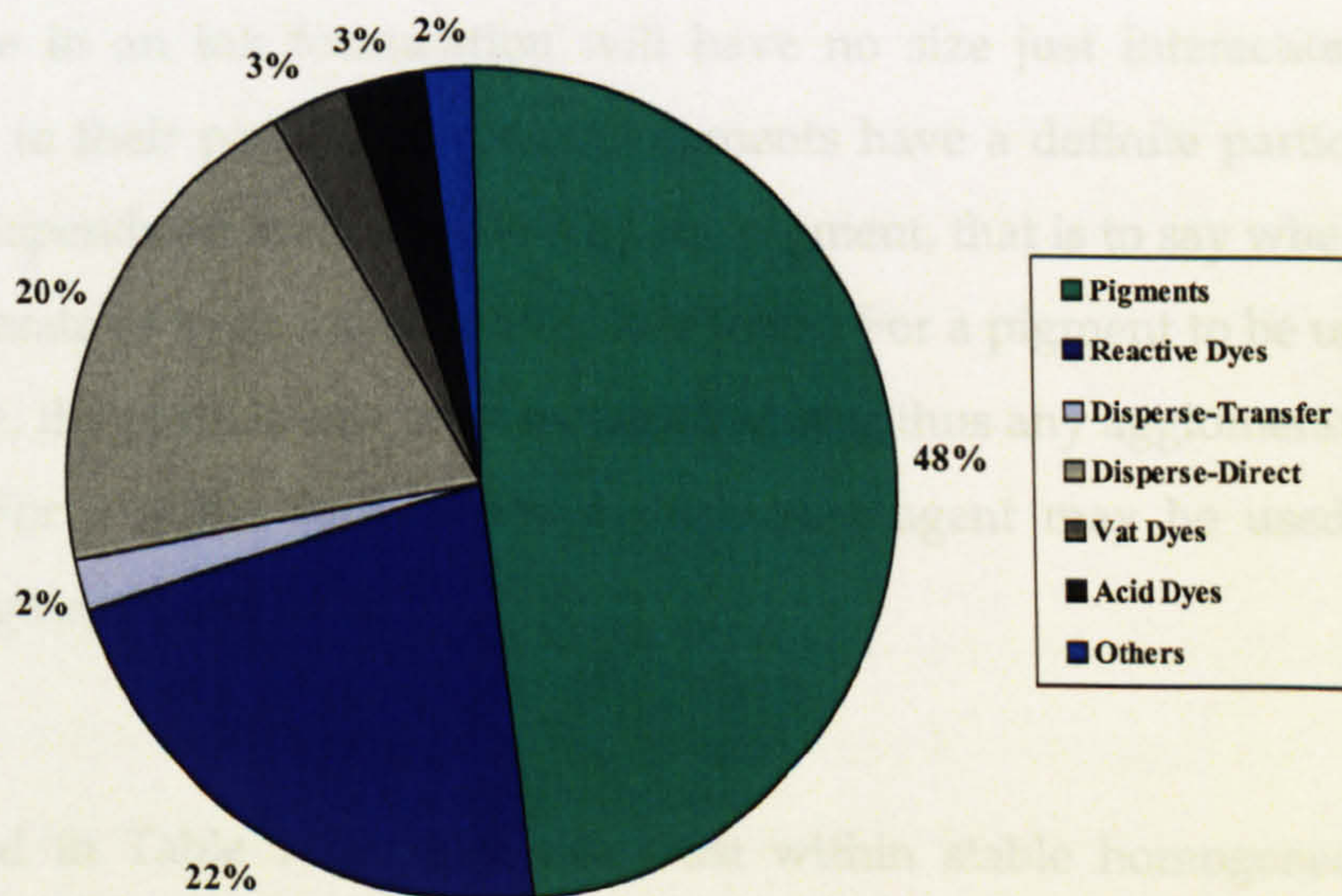


Figure 1.4.b Projected textile printing in 2011 by colorant class

As mentioned previously, there has been significant progress in the development of pigmented inks for ink jet applications in recent years (Dante et al., 1999). The characteristics of dyes and pigments are summarised and compared in Table 1.4.b. It should be noted that a dye exists in a monomolecular state whereas pigments are found in particulate form. As a result, dyes possess a greater surface area than pigments.

Table 1.4.b Comparison of the properties of dyes and pigments

Dyes	Pigments
Non planar molecules	Planar molecules
Contain solubilising groups	Contain H-bonding groups
Exist as relatively unstable crystals with low lattice energies	Exist as stable crystals with high lattice energies
Solvent soluble	Solvent insoluble

Dyes and pigments can be compared in a number of areas in order to determine their suitability for a particular application (Gregory, 1993; Hauser and Buhler, 1998).

Particulate/Molecule Size

As mentioned above, dyes exist in a monomolecular state and are solvent soluble therefore once in an ink formulation will have no size just interaction within the system. Due to their particulate nature, pigments have a definite particle size. The particle size depends on the form taken by the pigment, that is to say whether it is part of an agglomerate or in its lowest particulate form. For a pigment to be used in an ink jet application, the particle size must be kept low and thus any agglomeration kept to a minimum. For a stable formulation a dispersing agent may be used to separate individual pigment particles.

Ease of Use

As mentioned in Table 1.8.a, dyes can exist within stable homogeneous solutions whereas pigments can only be used as meta-stable heterogeneous dispersions. Therefore, in terms of application and stability, dyes would be considered easier to use than pigments.

Availability

Over 5000 dyes are commercially available in comparison to less than 400 pigments. It should also be noted that dyes are considered to be more synthetically flexible.

Cost

In general, pigments are considered to be cheaper than dyes although in some cases dyes may be a more cost effective option. For example, it is possible for a 1% solution of dye to give the equivalent optical density of an 8% pigment dispersion.

Colour Gamut

It is a general opinion that dyes are able to give a better range of colours than pigments.

Transparency

Dye based colorants are noted to have a superior transparency than pigments. As a result, dyes are used in applications where transparency is required and pigments in cases where a degree of opacity is needed.

Light Fastness

Light fastness is variable in both dyes and pigments. The light fastness required by the printed substrate is dependent on the desired application. Pigments generally have a superior light fastness compared to dyes and as such are preferred for use in applications such as car paints and outdoor use where a high light fastness is required. Other applications may not call for such fastness properties and therefore colorants of a moderate light fastness may be used (Tanaka et al., 1999). The reason for the superior light fastness properties of pigments is due to their larger surface area. This means that if attacked by photofading agents, for instance ultraviolet radiation, the crystalline particulate structure of the pigment dissipates the energy and thus slows the rate of the photofading.

Water Fastness

Dyes have variable water fastness whereas pigments are generally accepted to exhibit excellent properties in this area. Therefore, where application involves exposure of the substrate to outdoor elements, pigmented systems are preferred.

For the purposes of this investigation, due to the nature of the substrate and its possible end use, pigments were chosen as the colorant of choice.

1.4.2 Choice of Binder for Ink Jet Printing onto Textiles

Binders used in conventional screen printing have previously been detailed and their limitations outlined. The purpose of this investigation is to identify a possible binder for use within an ink suitable for ink jet printing onto textile substrates. Ideally, a polymer capable of self cross-linking should be used to limit the inclusion of any cross-linking additives. The binder should be stable within an aqueous medium, ideally being soluble in water to avoid any potential problems with emulsion or dispersion stabilities. Once included within an ink jet ink, the binder should be of an acceptable viscosity at a high enough quantity in order to confer the required fastness properties to the printed substrate.

1.4.3 Requirements of the Properties of an Ink for Ink Jet Printing onto Textiles

In order for it to be viable for ink jet printing, an ink must have certain physical properties due to the physical limitations of jetting. These properties include viscosity, surface tension and particle size as well as ink/substrate interactions such as waterfastness (Kang, 1991). Ideally, for ink jet applications, a particle size of 0.5 μm and under is required. Small particle size allows for improved stability, optical density, colour gamut, gloss and light fastness (Bugner et al., 1997). For it to be suitable for ink jet printing an ink must also have the required viscosity profile for a specific print-head (Hees et al., 2002). The requirements of an ink jet ink are summarised in Table 1.4.c.

Table 1.4.c Physical properties required by an ink jet ink

Physical Property	Requirement
Particle size	<1 μm
Viscosity	2-30mPa s
Surface tension	35-60mNm ⁻¹
pH	7-9

In terms of ink jet printing, the three physical properties of a pigmented ink which are of paramount importance are viscosity, surface tension and particle size. These three

properties are now discussed further.

1.4.3.1 Viscosity Requirements of an Ink Jet Ink

Viscosity is a measure of the thickness of a liquid in terms of its internal resistance to flow (Hawaii Space Grant College, 1996; Nevins, 2000).

In terms of ink jet printing the viscosity is a very important parameter. For it to be a viable option for ink jet printing an ink is required to have a viscosity of 2-20 mPa s (Hudd, 1992; Macfaul 2003; Davison, 1995). However, this is not always the case as inks with a viscosity of up to 45 mPa s have been printed and wax based inks start as solids.

1.4.3.2 Surface Tension Requirements of an Ink Jet Ink

The surface tension of a liquid is defined as the attraction of that liquid to any surface with which it may make contact. If the surface tension is high, then the attraction between the liquid and contact material is low and conversely if the surface tension is low, the attraction between the liquid and the contact material will be high (Nevins, 2000).

In terms of ink jet printing aqueous ink jet inks are required to have a surface tension of 25-60 mNm⁻¹ (Hudd, 1992; Macfaul, 2003; Early, 2001). Surface tension, in conjunction with other physical parameters, such as viscosity, is important to ink jet printing as it aids to control the following: (Macfaul, 2003)

- Droplet formation,
- Wetting of the required substrate,
- Transition of ink through the chamber and nozzles and
- Position of the meniscus within the print-head

1.4.3.3 Particle Size Requirements of a Pigmented Ink Jet Ink

As mentioned in Section 1.4.1 pigments, when contained within an ink formulation exist as heterogeneous dispersions. The degree of dispersion of a pigment is the extent to which the pigment in question has been broken down into its primary particles. The more aggregates that are broken down, the lower the average particle size becomes.

In terms of measurements of particle size, what is often obtained is a particle size distribution. A particle size distribution can be described as the relative amount of

material measured as a function of its size. A number of properties of the measured sample may be used in the calculation of such a distribution according to relative amounts. These properties include:

- The number of particles measured,
- The total particulate area measured and
- The mass or volume of particles

As the particle size of a pigment decreases, so its surface area increases. It is suggested by SpecialChem that the larger the surface area of the pigment particles within an ink formulation the greater its colour strength. This concept is represented in Figure 1.4.c.

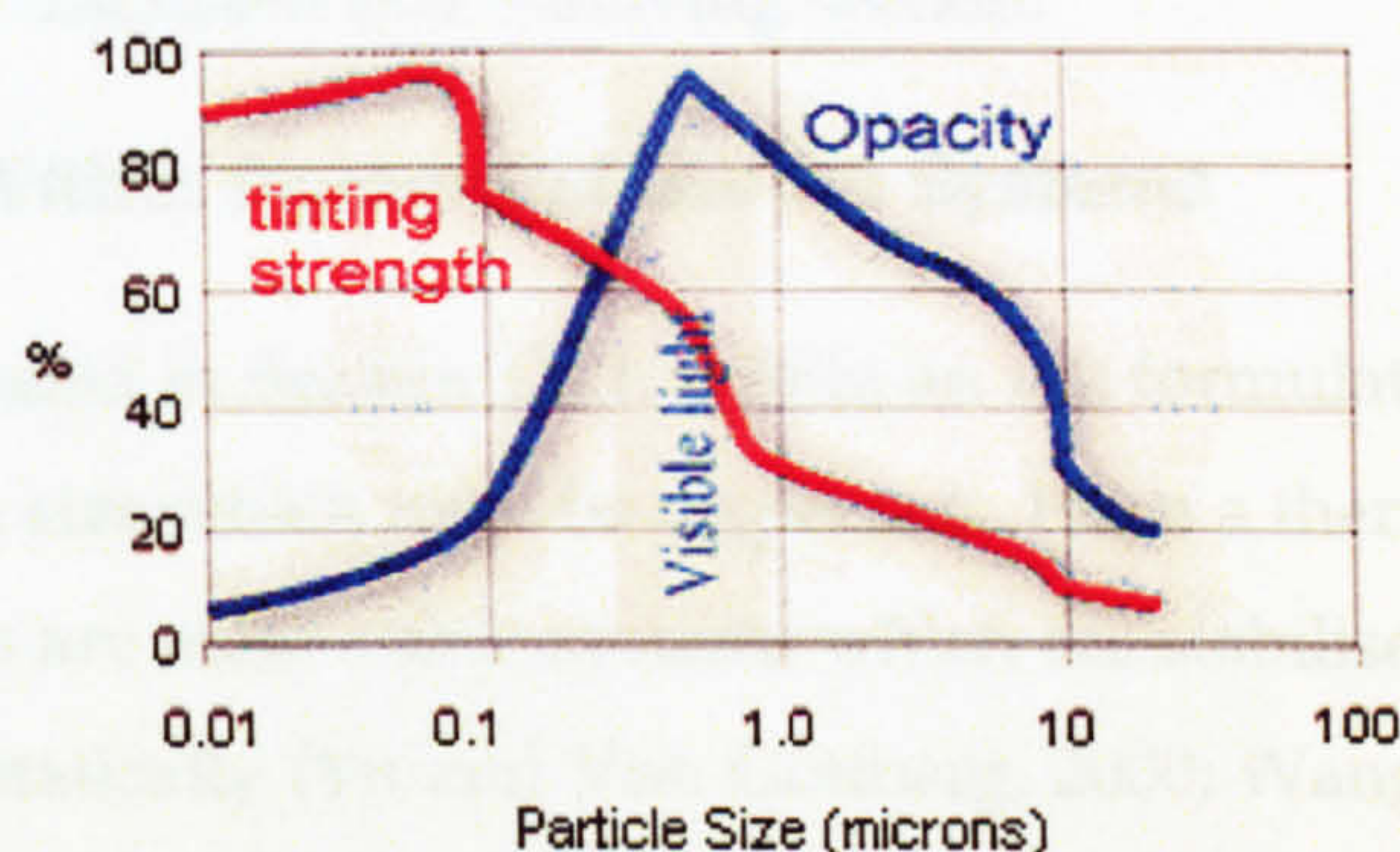


Figure 1.4.c Representation of the effect of particle size on tinting strength and opacity (SpecialChem, 2003)

Figure 1.4.c shows that as the particle size of a pigment increases (up to ~ 0.8 nm) the tinting strength of that pigment increases. Most pigments have an optimum particle size at which the opacity is at its greatest. However, as the particle size is increased further (> 0.8 nm), the opacity obtained decreases markedly. The colour strength of the pigment is also increased as the particle size is decreased (SpecialChem, 2003).

The dispersibility of a pigment is dependent on the size distribution and the amount of agglomeration. The reduction in size of any agglomerates and larger pigment particles allows for easier dispersion and subsequently better stability once dispersed.

If any agglomeration or oversized particles are present within an ink formulation, the following problems may arise while ink jet printing:

- Flocculation can cause irregularities in the colour strength,

- Printed images may be scratchy due to incomplete coverage of the substrate and
- Print-head nozzles may become blocked due to aggregation of larger particles

As previously mentioned, it is generally accepted that in order for a pigmented ink to be a viable option for ink jet printing, a particle size of below $1\mu\text{m}$ is required, although, a particle size of below $0.5\mu\text{m}$ is preferred (Kang, 1991; Macfual, 2003).

1.4.4 Issues Affecting Stability Within an Ink Jet Printing Ink

When considering an ink for application via ink jet printing, the inks stability is of great importance in terms of the jetting operation and the image printed onto the substrate. Considerations of the stability of the ink after printing i.e. its lightfastness, washfastness etc are discussed in a following section.

1.4.4.1 Stability Within Pigmented Ink Jet Systems

As previously discussed in Section 1.4.1, within an ink formulation a pigment exists as particles of a certain size which must be dispersed. From a thermodynamic standpoint pigment dispersions are meta-stable systems which are stabilised in some way usually sterically or electrostatically (Yu and Von Gottberg, 2000; Wang, 2002; Belmont, 2002). In order to be effective, a pigment dispersion must be stabilized within the ink formulation. Such stabilisation is usually carried out in one of two ways which are described in the following sections (Galloway et al., 2001; Belmont, 2002).

1.4.4.2 Electro-Static Stabilisation

Electro-static stabilisation is based on the process of forces of repulsion either anionic or cationic. The pigment particles are given either a positive or a negative charge and once in dispersion these charges repel each other. This electro-static repulsion prevents any joining of pigment particles to form aggregates (Yu et al., 2001). The process of electro-static stabilisation is shown in Figure 1.4.d.

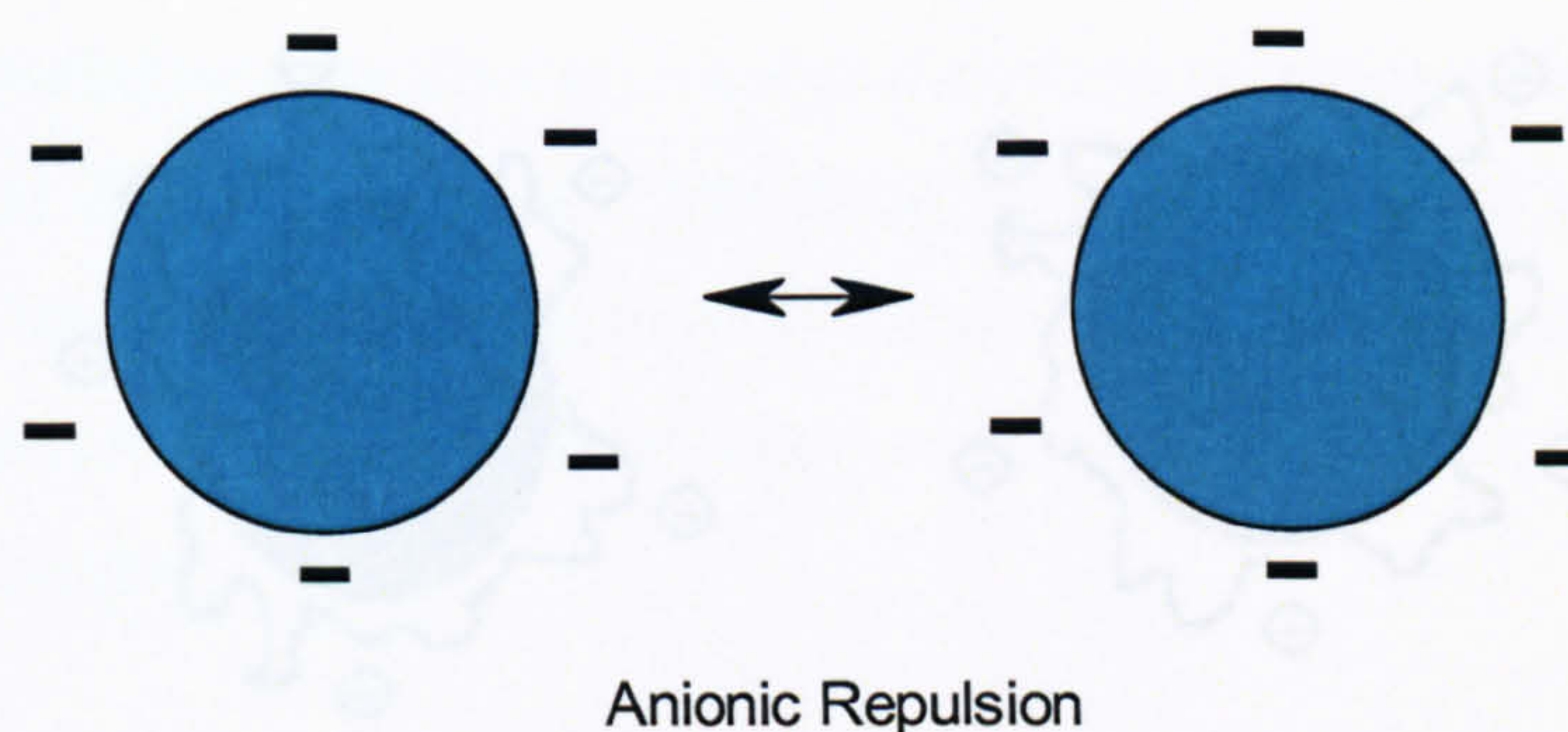


Figure 1.4.d Schematic diagram of the process of electro-static stabilisation

1.4.4.3 Steric Stabilisation

In steric stabilisation, polymeric molecules are either attached or adsorbed onto the surface of the pigment. Such polymeric molecules prevent the pigment particles from getting close enough to each other to form aggregates (Yu et al., 2001; Yu and Von Gottberg, 2000). An example of steric stabilisation is shown in Figure 1.4.e.

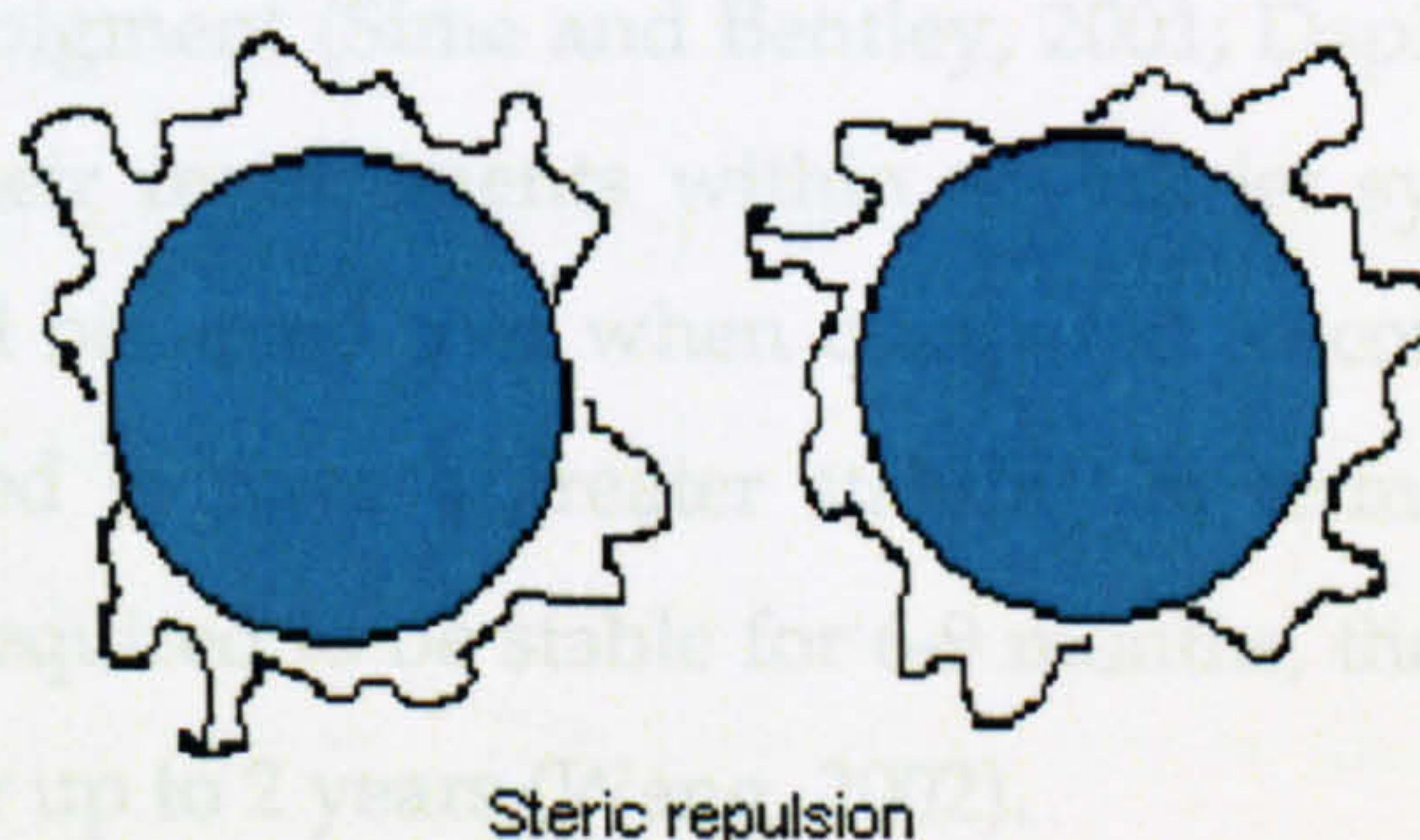


Figure 1.4.e Schematic diagram of the process of steric stabilisation

1.4.4.4 Hybrid Stabilisation – Electro Steric Stabilisation

A further form of stabilisation exists where the two types discussed combine to increase the stabilising effect. This is known as electro steric stabilisation. In this case the groups attached or adsorbed onto the surface of the pigment also possess a charge (Yu et al., 2001; Yu and Von Gottberg, 2000). An example of electro steric stabilisation is shown in Figure 1.4.f.

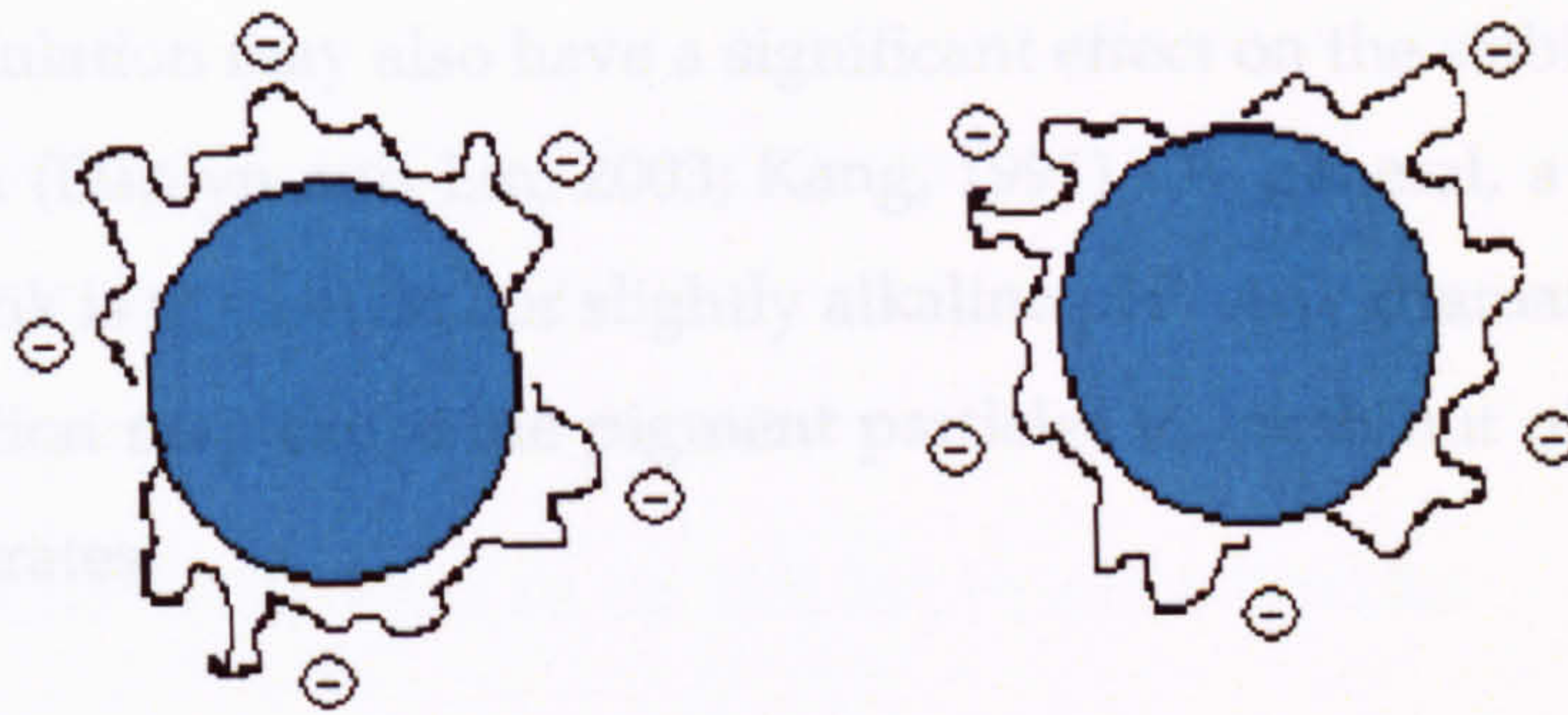


Figure 1.4.f Schematic diagram of the process of electro steric stabilisation

1.4.5.3 Viscosity of a Pigmented Ink Formulation

1.4.5 The Use of Pigments within an Ink Jet Ink Formulation

Pigment particles may flocculate or agglomerate leading to the blocking of the jet nozzles within the print-head. A number of factors may affect the stability of pigments within an ink jet ink, these being viscosity, surface tension and pH. However, it is acknowledged that the limiting factor in terms of the stability of an ink jet ink lies in the particle size of the pigment (Sime and Bentley, 2001; Daplyn and Lin, 2003). Each of these factors and their requirements within an ink jet system were discussed in Section 1.4.3. It should be noted that when compared to conventional printing inks, ink jet inks are required to have a greater stability in terms of shelf life. Whereas conventional inks are required to be stable for 6-9 months, their ink jet equivalents are required to be stable for up to 2 years (Wang, 2002).

A number of authors have reported tests that may be carried out in order to assess the relative stability of an ink jet ink formulation. The major factor that is discussed is the effect of certain conditions on particle size. Some of the conditions which affect stability and particle size are now discussed.

1.4.5.1 Thermal Stability of a Pigmented Ink Formulation

In order for an ink to have a certain shelf life, it is required to be stable in varying extremes of temperature. This is often simulated by the application of a freeze thaw test in which the inks are frozen for 24 hours before being heated at temperatures up to 60°C for 24 hours. This cycle is repeated a number of times for as long as six weeks (Bugner and Bermel, 1997; Sime and Bentley, 2001). It should be noted that this will not only test for the stability of the pigment, but also of other components of the ink such as binder.

1.4.5.2 pH Stability of a Pigmented Ink Formulation

The pH of a formulation may also have a significant effect on the stability of a pigment contained therein (Daplyn and Lin, 2003; Kang, 1991). In general, a pigment is most stable when the ink is at a neutral or slightly alkaline pH. Any dramatic changes in the pH of a formulation may cause the pigment particles to crash out of their dispersion forming agglomerates.

1.4.5.3 Viscosity of a Pigmented Ink Formulation

The viscosity of a formulation may also be an important factor in determining the stability of a pigmented ink. Given that an ink jet ink is required to have a much lower viscosity than a conventional printing ink, the use of polymers to provide dispersion stability is limited. It is therefore necessary to reduce the pigment particle size to as low as is possible, thus providing a greater chance of stability over a period of time (Wang, 2002).

1.4.6 Performance Requirements for Printed Textile

Once printed, a piece of textile is required to possess certain parameters in terms of its relative durability. The required fastness properties will vary according to the application of the printed textile. The printed textile is also required to exhibit the required colour characteristics for its end application. In order to assess the relative stability of a print, a number of tests may be carried out. The major tests used will now be discussed further.

1.4.6.1 Washfastness Testing of a Printed Textile

Once it has been printed a textile substrate is required to be tested for its washfastness. Washfastness tests demonstrate how the process of washing affects the colour strength of a fabric. Any fading is compared to that of a known standard i.e. greyscales in order for any change in the observed colour of the sample to be assessed.

1.4.6.2 Rubfastness Testing of a Printed Textile

Also known as crockfastness, rubfastness is a measure of the stability of a coloured print in terms of its resistance to surface abrasion.

1.4.6.3 Lightfastness Testing of a Printed Textile

Lightfastness is a measure of the degree of fading of a printed substrate when exposed to light. Depending on the colorant used the lightfastness of the substrate will vary. As discussed in Section 1.4.1, it is generally accepted that pigmented systems have a better lightfastness than their dye based equivalents.

1.4.6.4 Colour Characteristics of an Ink Jet Printed Textile

Ink jet printing uses a process of subtractive colour mixing to produce the required design. Thus, the primary colours used are cyan, magenta and yellow, which absorb red, green and blue light respectively. When these colours are mixed together in varying amounts, it is possible to create a range of colours encompassing the primary and secondary colours. A representation of such colour mixing can be seen in Figure 1.4.g (Lucas et al., 1996).

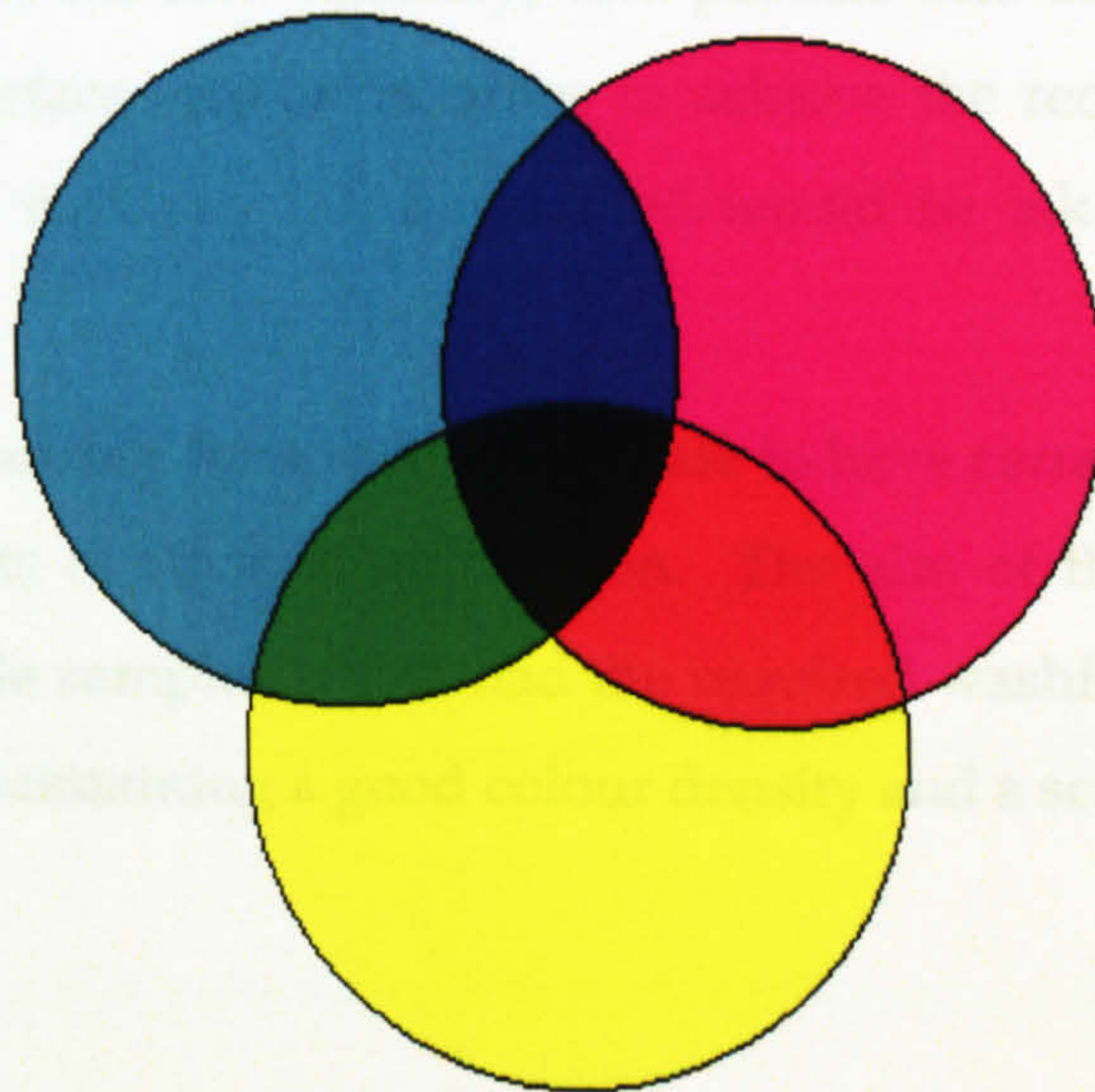


Figure 1.4.g Schematic diagram showing the principle of subtractive colour mixing with CMYK

It should be noted that in the ink jet printing process a separate black is used as the black created by the mixing of cyan, magenta and yellow is often not sufficiently dark. It is also becoming common within the textile printing industry for ink jet printers to provide spot colours such as navy blue and green to compliment the standard colours and provide a greater colour gamut with a better depth of shade (Gordon, 2001).

1.5 Aims and Objectives

The aim of this investigation was to identify a possible binder for use within an ink suitable for ink jet printing textile substrates. Ideally, a polymer capable of self cross-linking would be used to limit the inclusion of any cross-linking additives. The binder should be stable within an aqueous medium, ideally being soluble in water to avoid any potential problems with emulsion or dispersion stabilities. The binder, once included within an ink jet ink, should be of acceptable viscosity whilst being a high enough quantity in order to confer the required fastness properties to the printed substrate.

Once a possible binder had been identified, investigation into colorants was required. The aim of this investigation was to incorporate a pigment alongside a self cross-linkable binder within an ink formulation in order to print a wide range of textile materials. Such an ink formulation was required to adhere to the parameters required for ink jet technology, i.e. low viscosity, low particle size and high stability whilst having the correct surface tension in order to achieve the required jetting. Once all parameters had been met, any ink formulated would be ink jet printed onto textile materials.

Once printed, it is necessary for a textile substrate to have certain properties in order to meet the requirements of its final application. The aim of this investigation was to produce printed textile samples which had the required washfastness, rubfastness and lightfastness whilst maintaining a good colour density and a soft fabric handle.

2 Experimental

During this investigation, a number of materials, methods and characterisation techniques were used in the formulation and testing of inks for jet printing onto textile materials. These are detailed in the following sections.

2.1 Materials

During the course of this investigation, several materials were used in the formulation of inks for screen and ink jet printing. These materials are detailed in the following sub-sections.

2.1.1 Pigments

During the investigation, three different types of pigment were used in the formulation of inks for jet printing onto textile materials. In order for it to be suitable for use in an ink jet printing ink, the pigment must adhere to the following requirements once in dispersion:

- the pigment must have colloidal stability;
- the pigment should not increase in particle size;
- the pigment should be compatible with the solvent and other constituents of an ink;
- the pigment should have a small particle size, preferably below 0.5 μm .

Once printed the pigment needs to impart an acceptable optical density and chroma whilst achieving the required fastness properties (Yu and Von Gottberg, 2000).

The following pigments were used during the course of this investigation.

2.1.1.1 Pigment Choice 1 – Toner Pigments

Toner pigments are specially produced tonergrade pigments which are usually used within resin based systems. Toner pigments were chosen for this investigation due to their low particle size prior to any dispersion. Typically, Toner pigments have a particle size below 1 μm , which can be reduced further with the aid of a dispersant and milling. The lightfastness of such pigments is also excellent with values of 7-8 depending on the colour (Clariant, 2000). The Hostaperm pigments used for the

formulation of screen printing inks are detailed in Table 2.1.a and the Toner pigments used for ink jet inks are detailed in Table 2.1.b.

Table 2.1.a Hostaperm Pigments

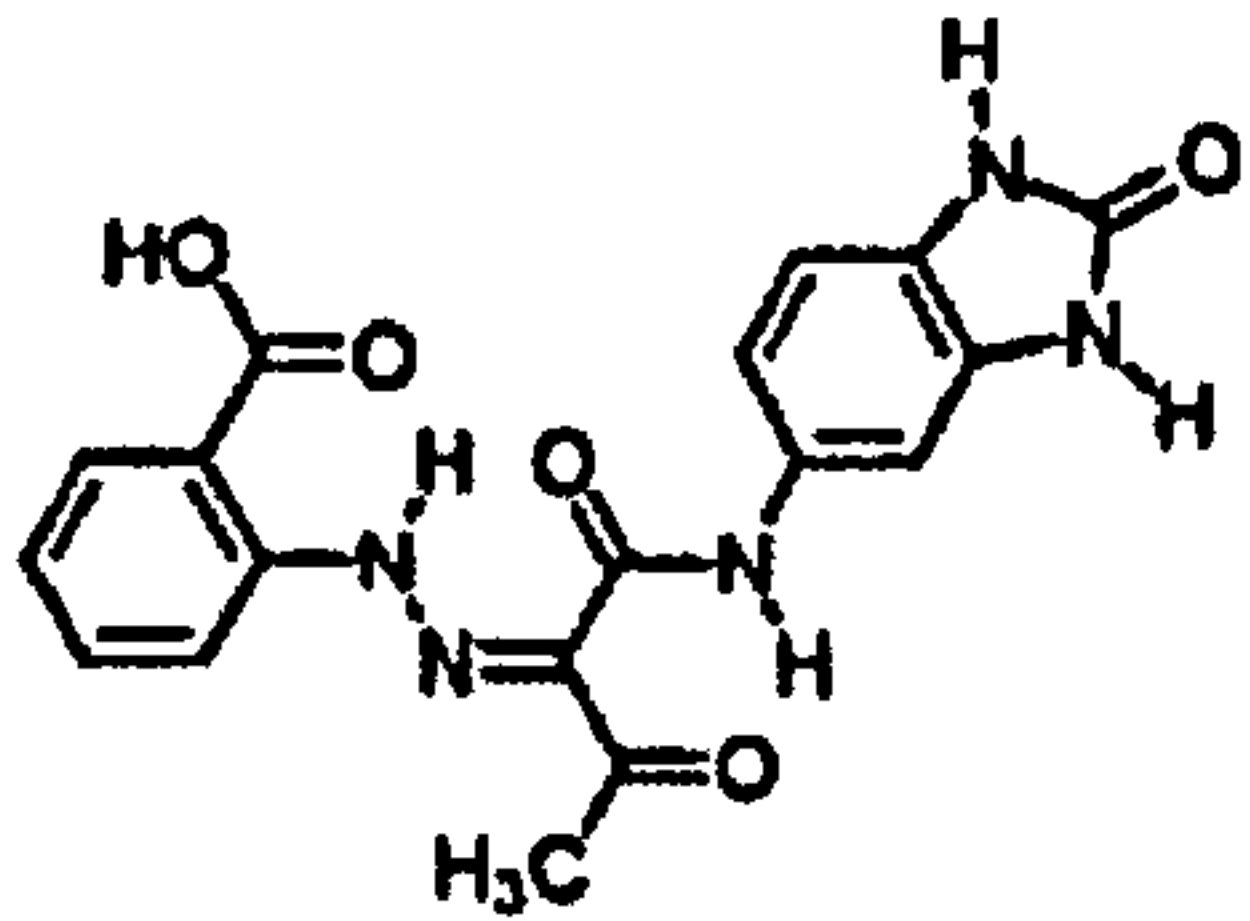
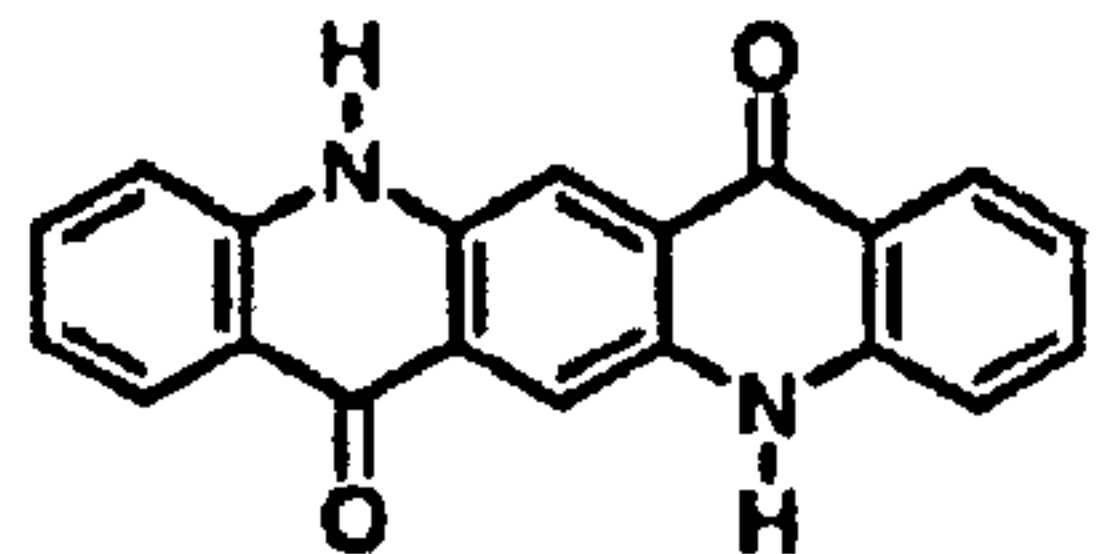
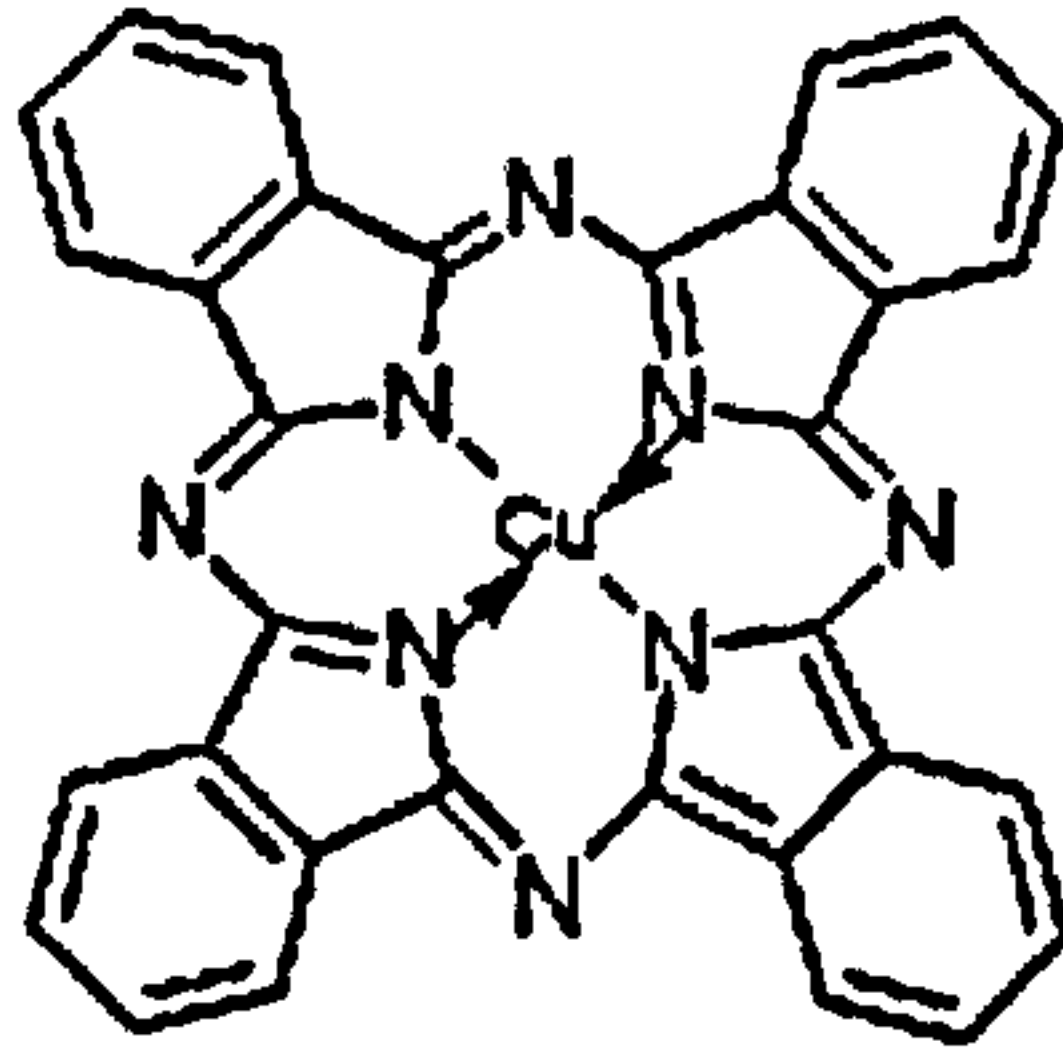
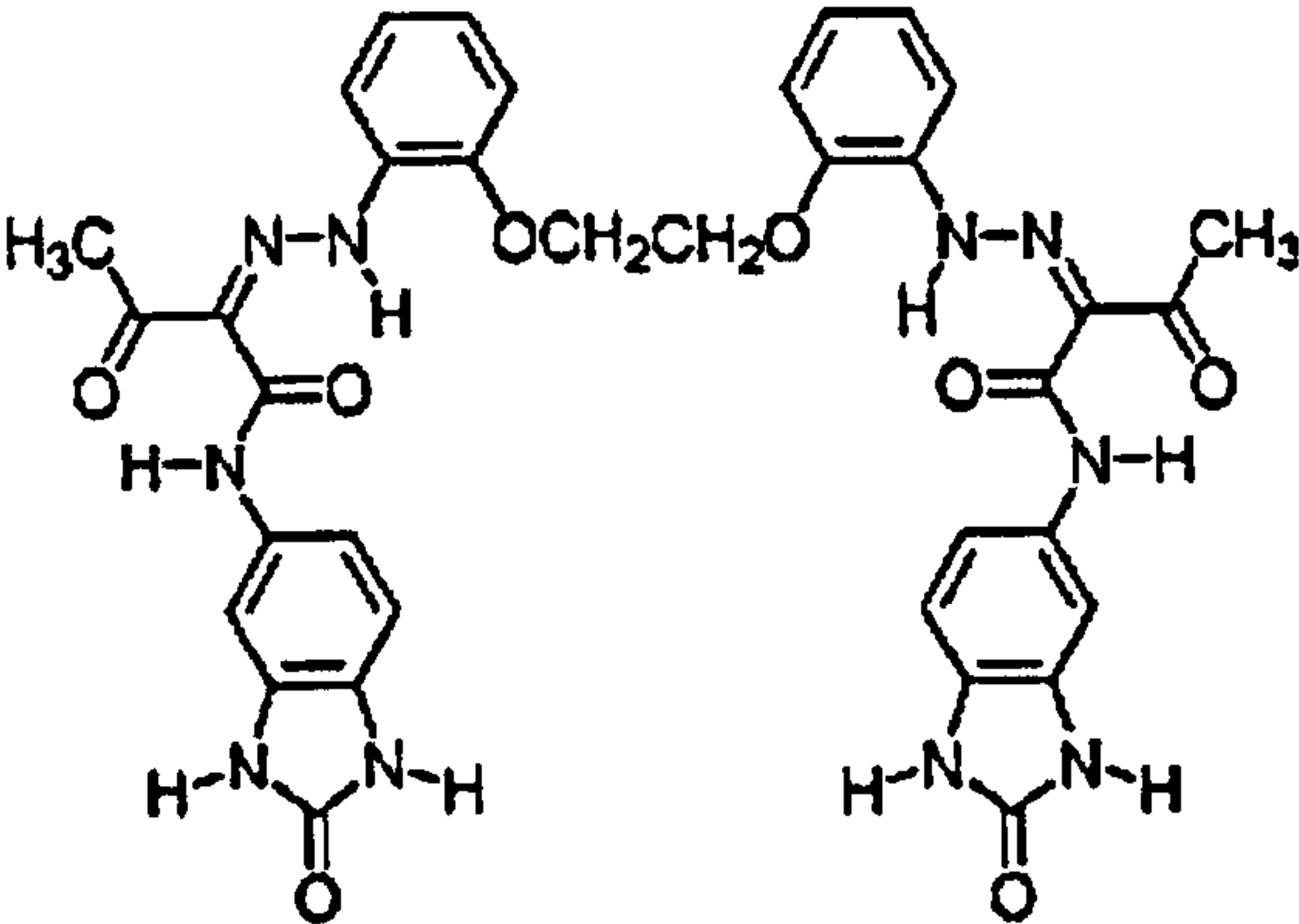
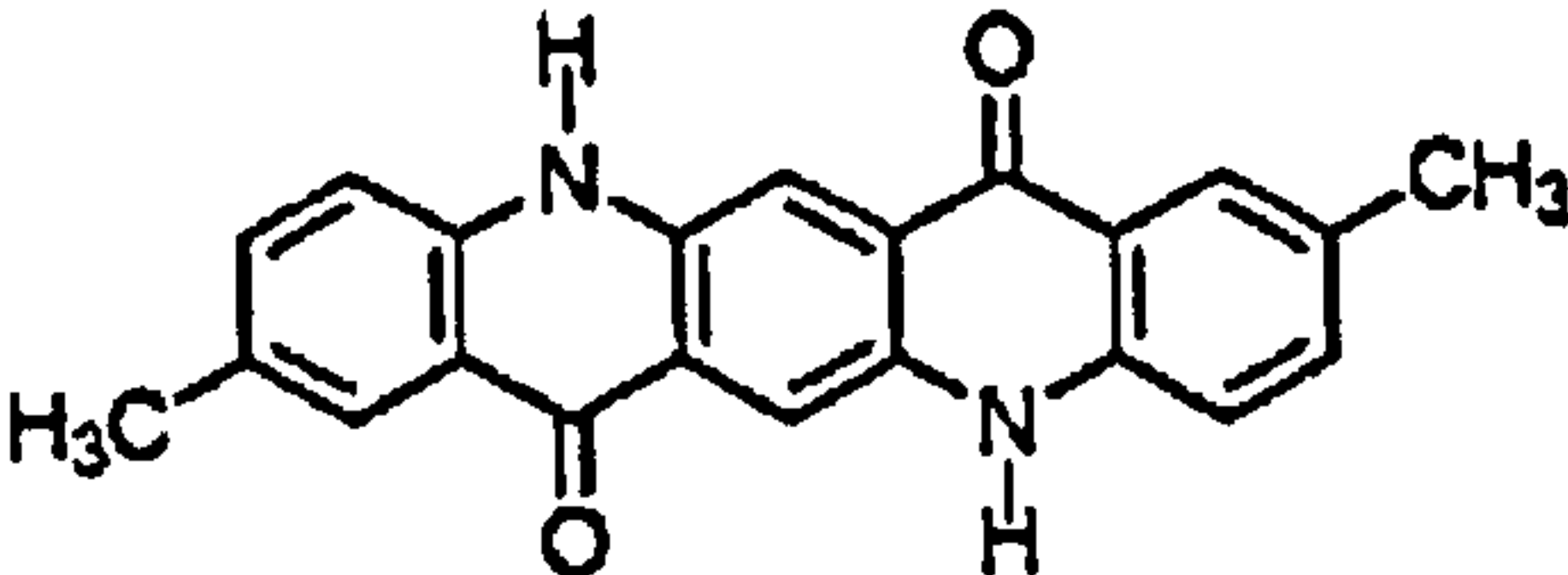
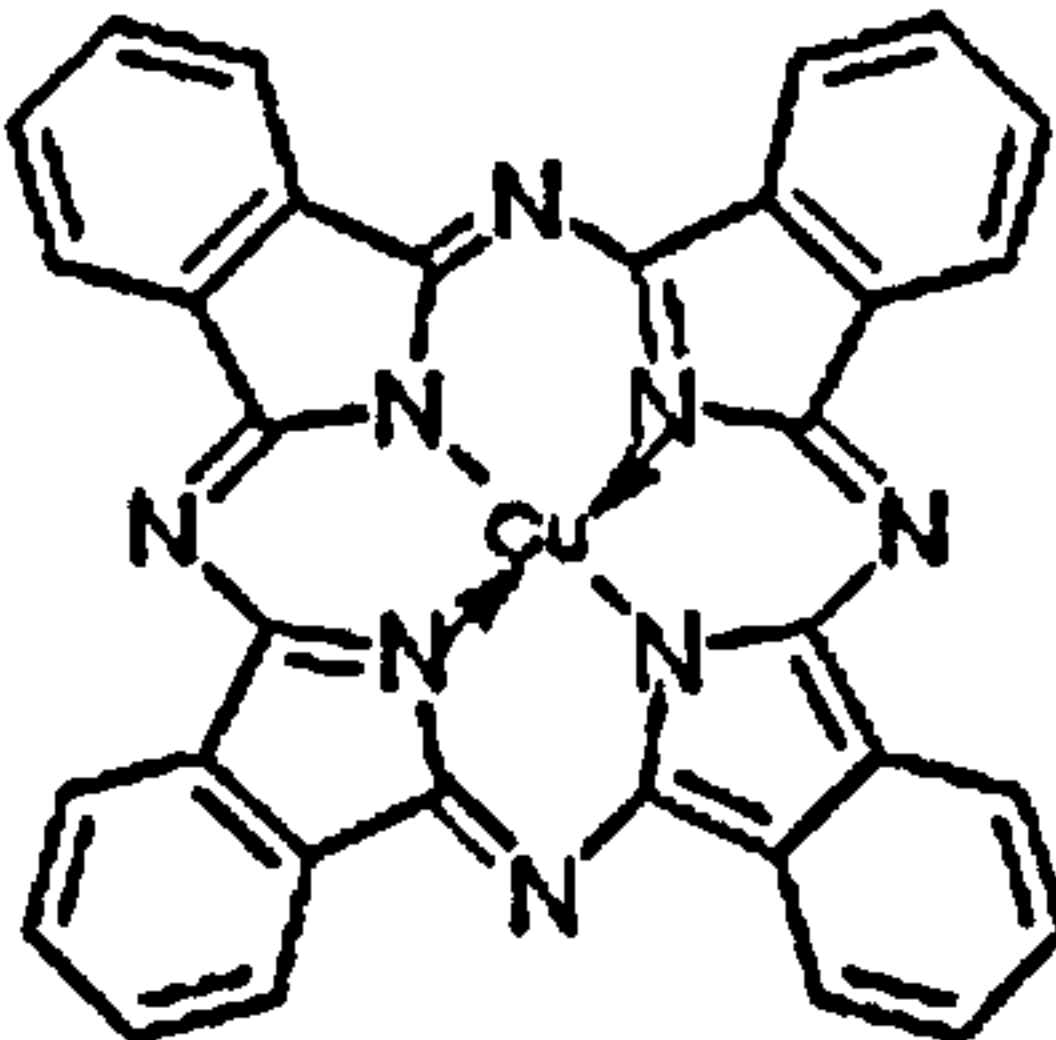
Commercial Name	Pigment C.I. Number and Structure	Supplier
Hostaperm Yellow	<div>Pigment Yellow 151</div> <div></div>	Clariant, Calverley Lane Horsforth, Leeds, West Yorkshire, UK
Hostaperm Red E5B 02	<div>Pigment Violet 19</div> <div></div>	
Hostaperm Blue	<div>Pigment Blue 15:3</div> <div></div>	
Hostaperm Black	Almost pure carbon	

Table 2.1.b Toner Pigments

Commercial Name	Pigment C.I. Number and Structure	Supplier
Toner Yellow HG	<div>Pigment Yellow 180</div> 	Clariant, Calverley Lane Horsforth, Leeds, West Yorkshire, UK
Toner Magenta E02	<div>Pigment Red 122</div> 	
Toner Cyan BG	<div>Pigment Blue 15:3</div> 	
Toner Black	Almost pure carbon	

2.1.1.2 Pigment Choice 2 – Microlith™ Pigments

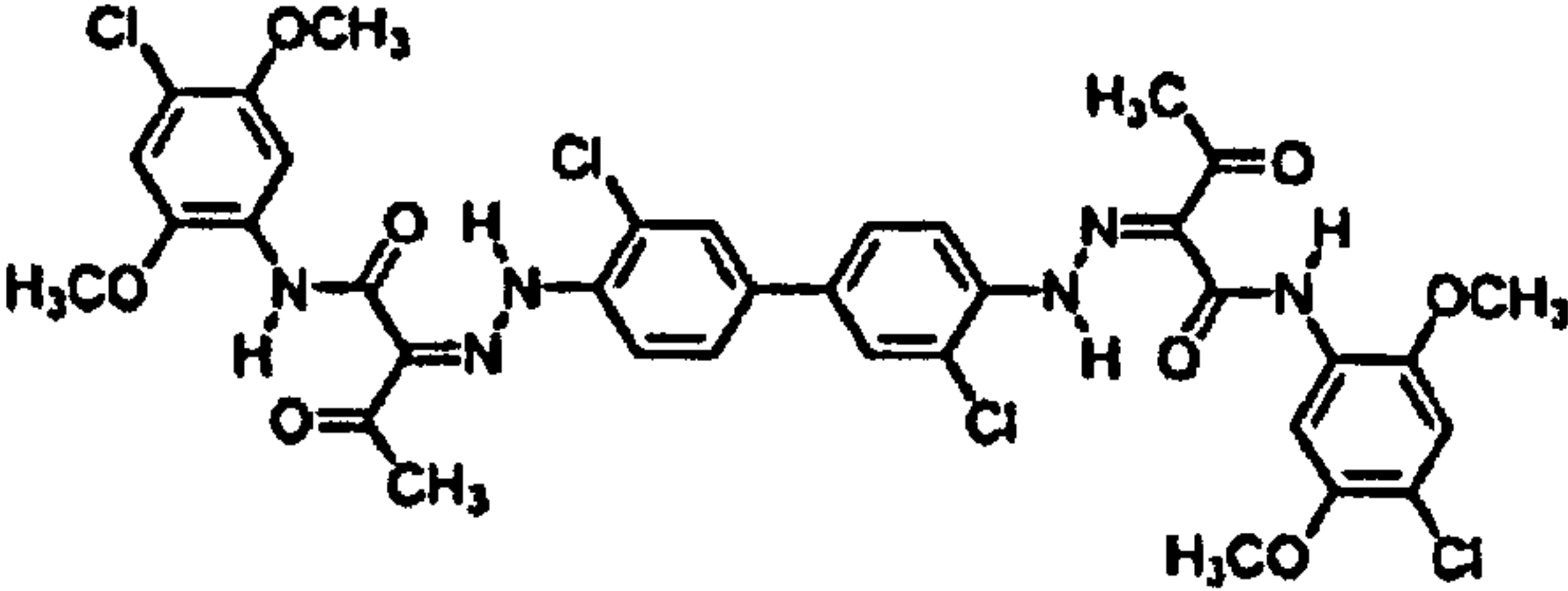
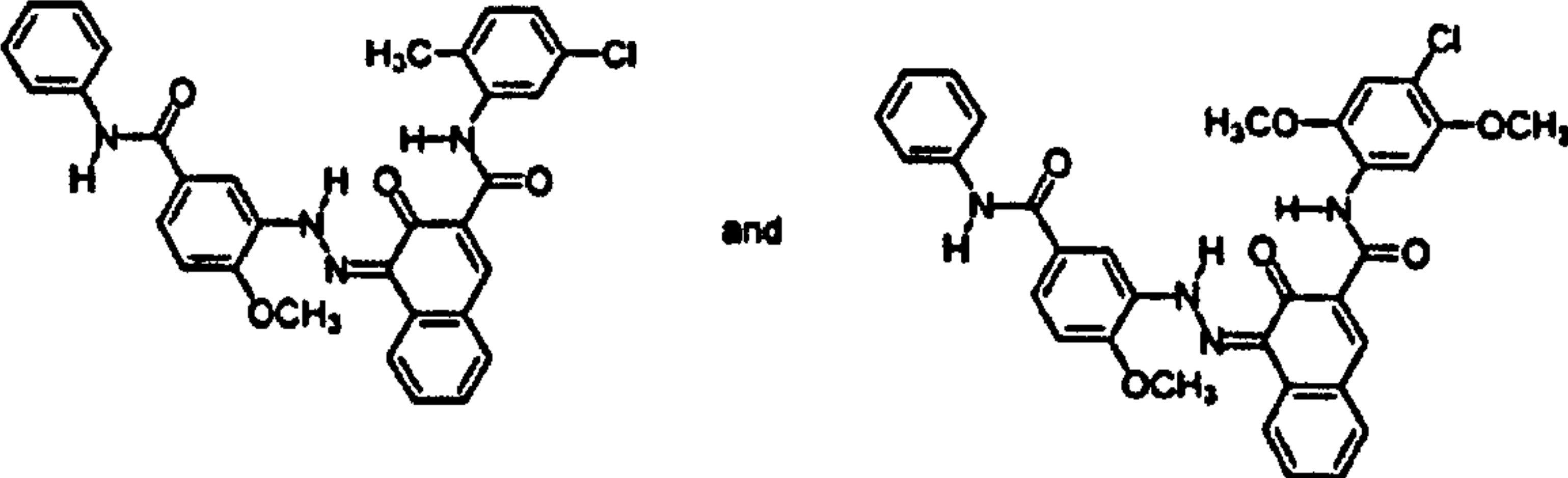
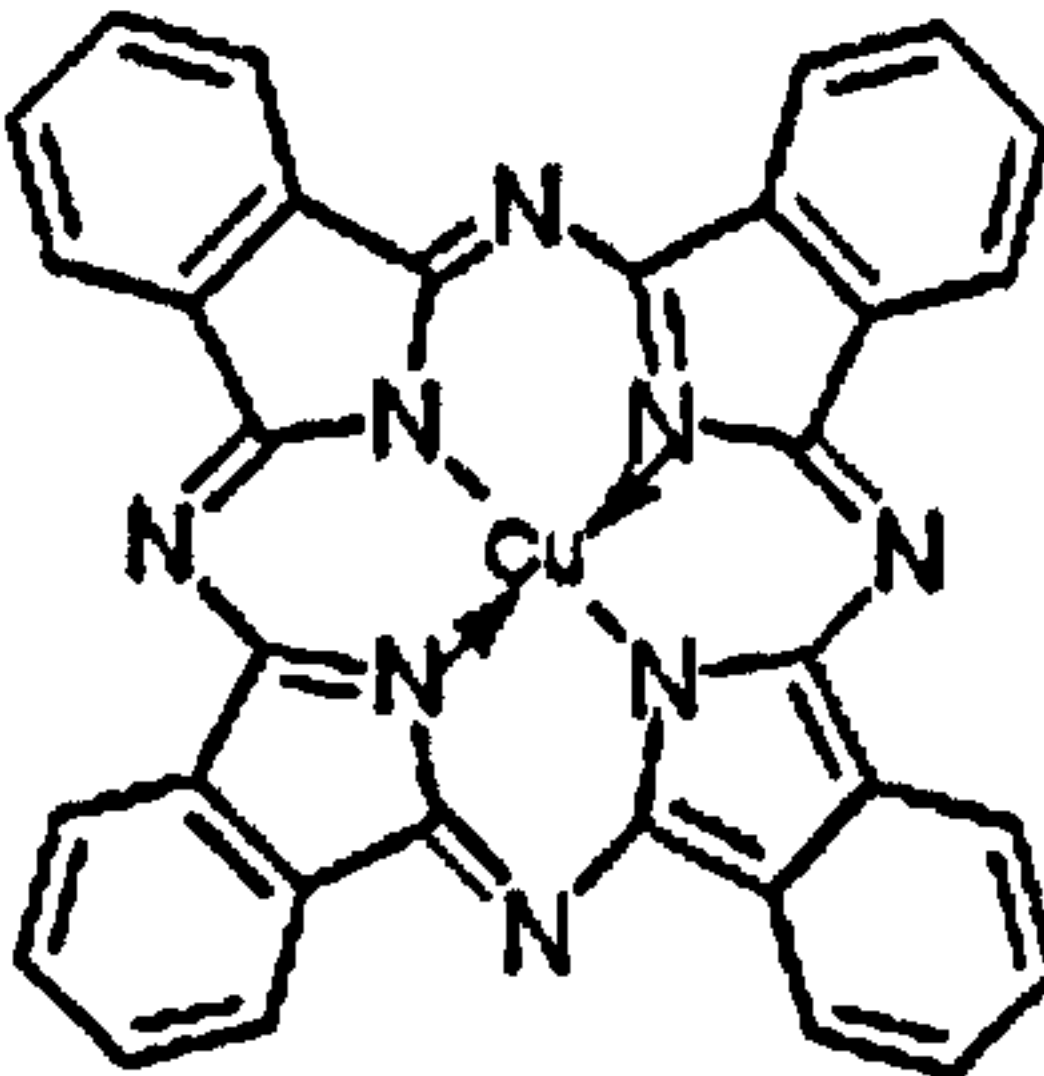
Microlith pigments are supplied in crystalline form and require the formulation of a pigment paste concentrate prior to their subsequent inclusion within an ink formulation. The details of such a pigment paste are as follows:

- Pigment 25%
- Water 54%

- IPA 20%
- Ammonia 1%

Microlith pigments carry a surface modification of an acrylic resin. The acrylic resin is well soluble in alkaline water and will produce solutions of low viscosity (Ciba Speciality Chemicals, 2001). This allows for extremely stable formulations to be produced. Details of Microlith pigments can be seen in Table 2.1.c.

Table 2.1.c Microlith Pigments

Commercial Name	Pigment C.I. Number and Structure	Supplier
Microlith Yellow 2R-WA	<p>Pigment Yellow 83</p> 	Ciba Specialty Chemicals PLC, Charter Way, Macclesfield, Cheshire, UK
Microlith Magenta B-WA	<p>Pigment Red 184</p> 	
Microlith Blue 4G-WA	<p>Pigment Blue 15:3</p> 	
Microlith Black	Almost pure carbon	

2.1.1.3 Pigment Choice 3 – Cab-O-Jet Pigment Dispersions

In the technology employed by Cabot Corp., stabilising groups are attached to the pigment surface. The stabilisation groups are introduced by a surface modification reaction of the pigment with diazonium salts. Figure 2.1.a shows the reaction carried out in order to obtain a diazonium ion (Yu and Von Gottberg, 2000). The diazonium ion thus obtained is coupled to the required pigment thus giving the pigment a soluble group, represented by R in Figure 2.1.a and Figure 2.1.b. Such soluble groups are either COOH⁻ or SO₃⁻. During this investigation only pigments containing SO₃⁻ were used as the presence of hydrogen ions in the COOH⁻ group may act to prematurely cross-link the binder used.

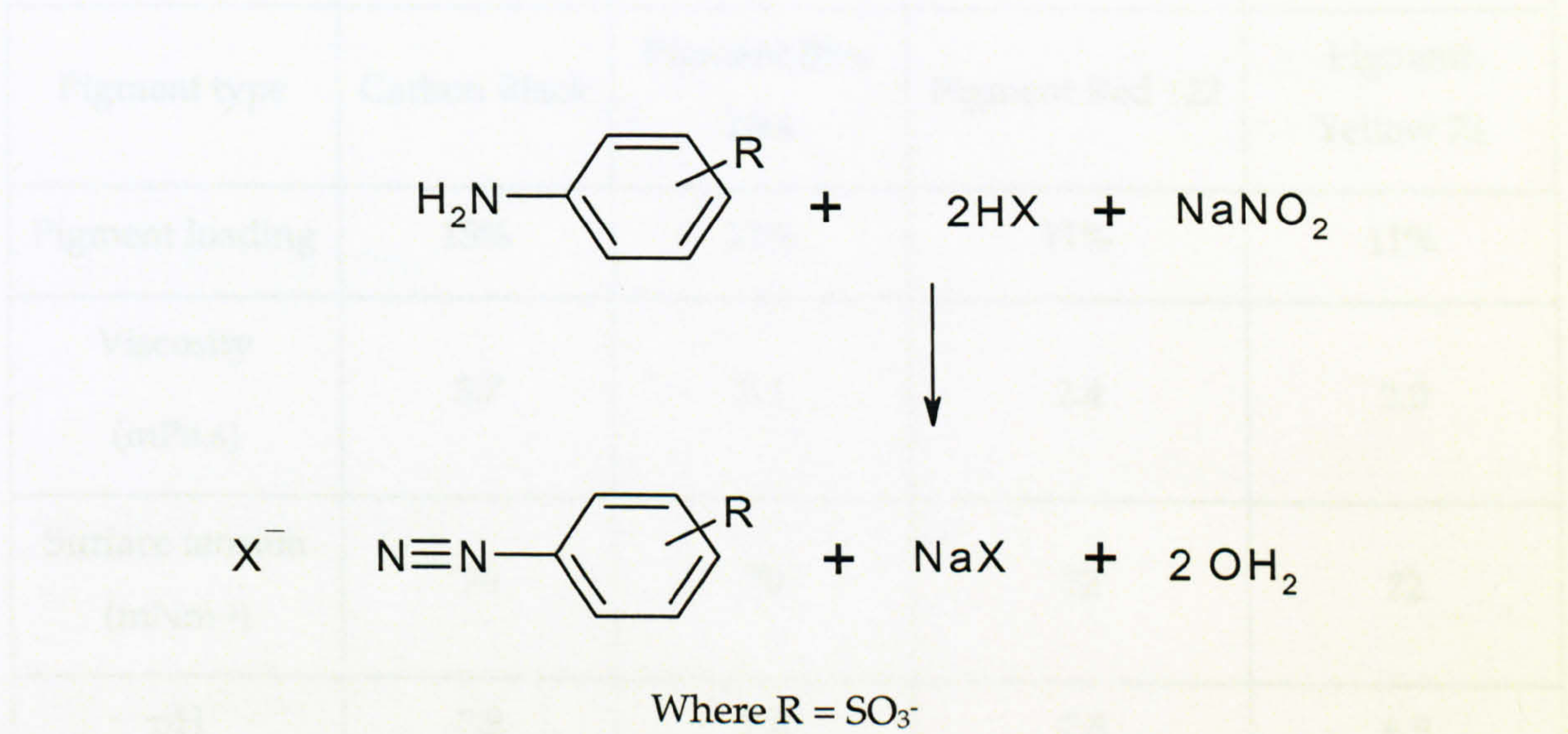


Figure 2.1.a Diazotisation reaction

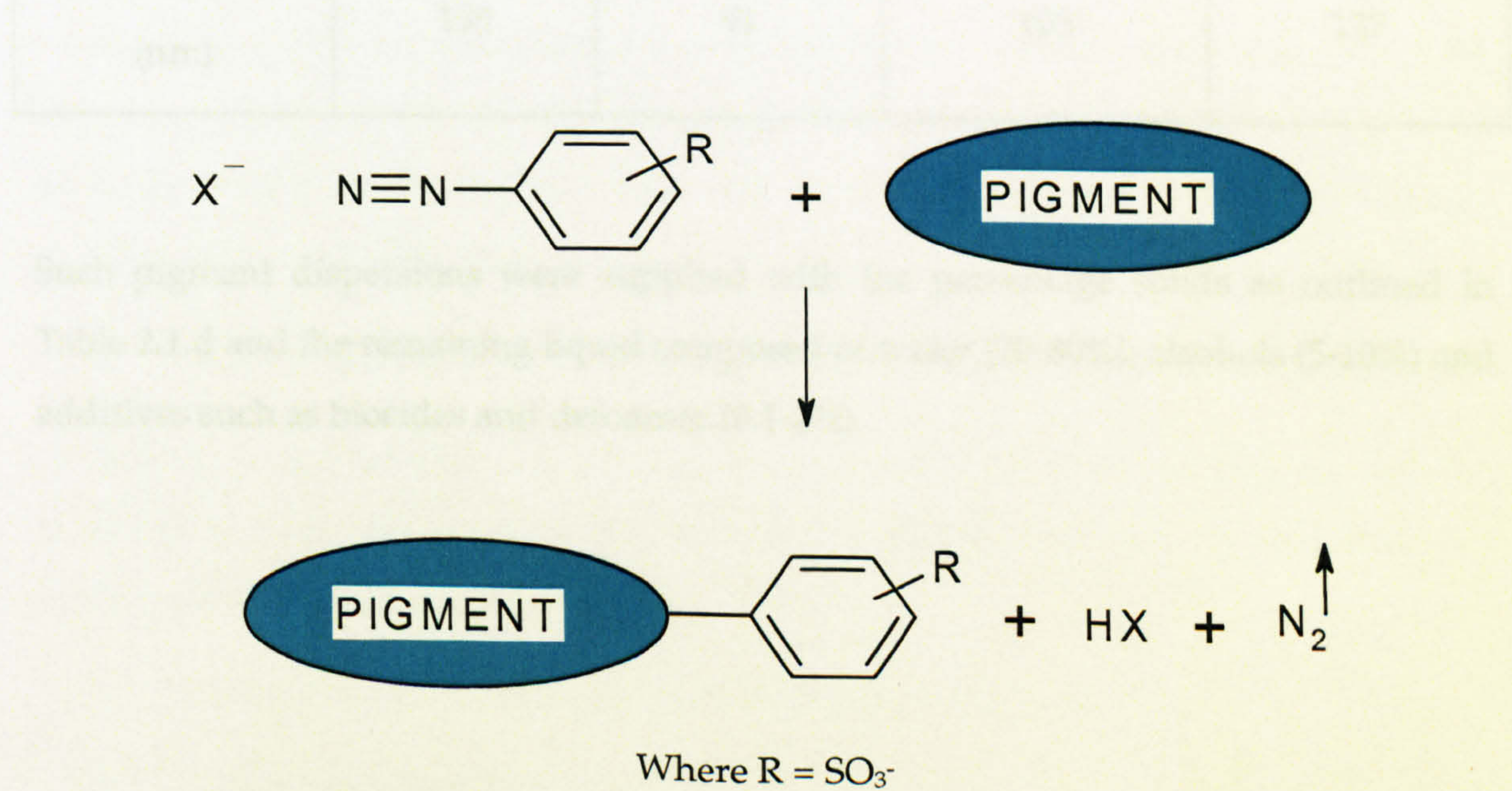


Figure 2.1.b Coupling reaction of the diazonium ion to the pigment

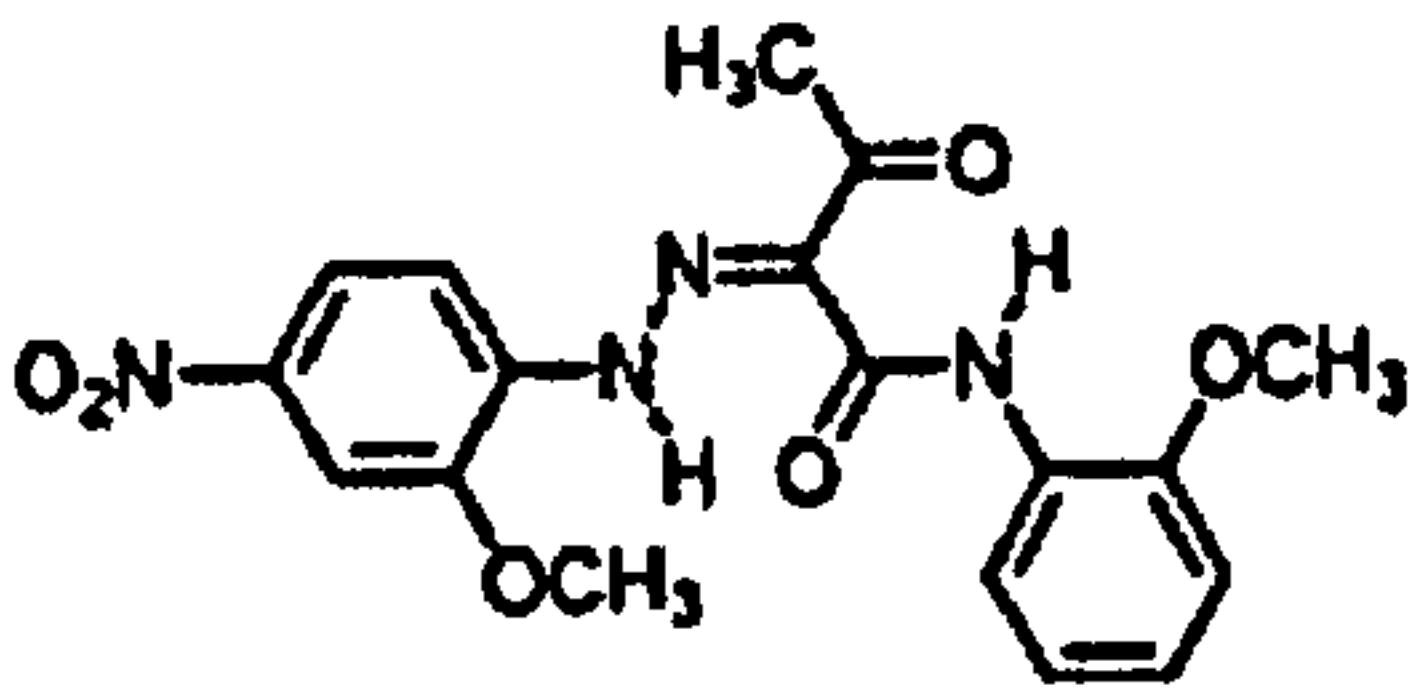
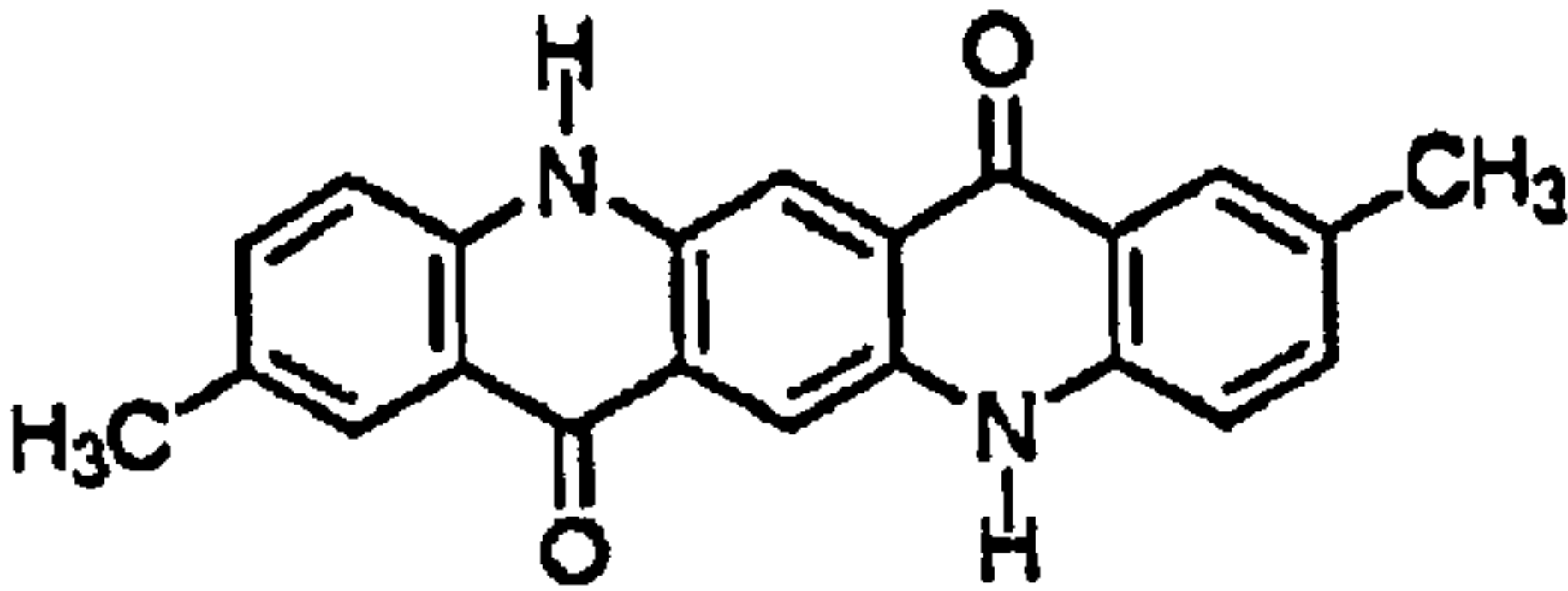
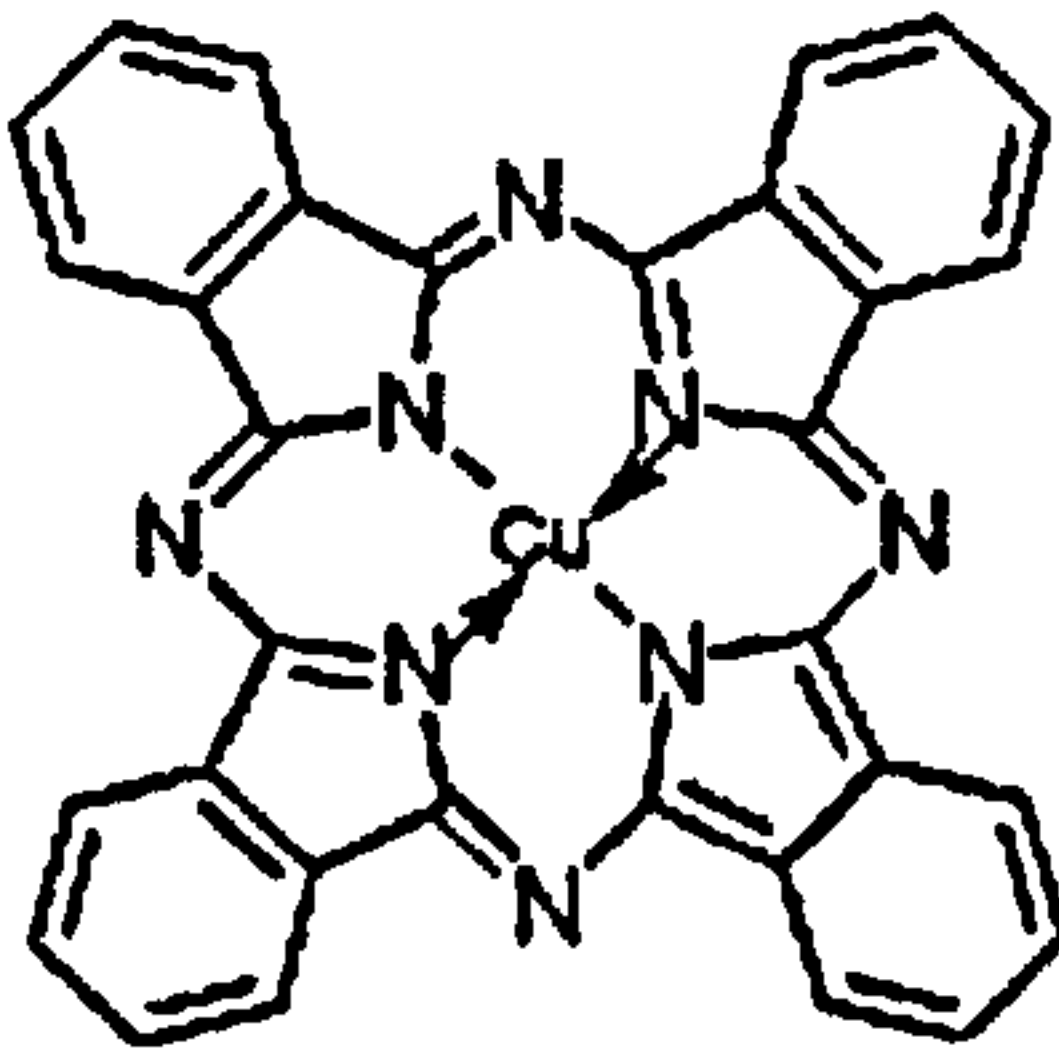
A four colour set of Cab-O-Jet pigments was chosen. The details of the physical properties of Cab-O-Jet pigment dispersions, as supplied by Cabot Corp., can be seen in Table 2.1.d. Further information on these pigment dispersions can be seen in Table 2.1.e.

Table 2.1.d Properties of the Cab-O-Jet pigment dispersions

Physical properties	Cab-O-Jet Black 300	Cab-O-Jet Cyan 250 C	Cab-O-Jet Magenta 260 M	Cab-O-Jet Yellow 270 Y
Pigment type	Carbon Black	Pigment Blue 15:4	Pigment Red 122	Pigment Yellow 74
Pigment loading	15%	11%	11%	11%
Viscosity (mPa.s)	3.7	2.1	2.4	2.0
Surface tension (mNm ⁻¹)	70	70	72	72
pH	7.8	7.0	7.5	6.5
Particle size (nm)	130	91	105	137

Such pigment dispersions were supplied with the percentage solids as outlined in Table 2.1.d and the remaining liquid composed of water (70-80%), alcohols (5-10%) and additives such as biocides and defoamer (0.1-2%).

Table 2.1.e Cab-O-Jet pigment dispersions

Commercial Name	Pigment C.I. Number and Structure	Supplier
Cab-O-Jet Yellow 270Y	<div>Pigment Yellow 74</div> <div></div>	Cabot Corporation Lees Lane, Stanlow, Ellesmere Port South Wirral, UK
Cab-O-Jet Magenta 260 M	<div></div>	
Cab-O-Jet Cyan 250 C	<div></div> <div>Pigment Blue 15:3</div>	
Cab-O-Jet Black 200/300	Almost pure carbon	

2.1.2 Binder

In this investigation, Synthappret BAP was employed as a binder system within an ink for jet printing of textile materials, although this was not its intended primary use. The following sections detail the intended primary use of Synthappret BAP along with an explanation of why Synthappret BAP was chosen as a binder for use in an ink jet printing ink for printing onto textiles.

2.1.2.1 Application of Synthappret BAP as a Shrink Resist Treatment

According to the product information, Synthappret BAP is a “product for anti-felt finishing of wool and wool blends without pre-chlorination” and its properties and applications are listed as: (Bayer, 2000)

- Improved dimensional stability and abrasion resistance
- Reduced pilling and snagging
- Finish is resistant to washing and dry cleaning

- No reduction in colour fastness

Traditionally, Synthappret BAP is used in shrink resist treatments of wool (Fleischfresser, 1982; Guise and Freeland, 1984). Synthappret BAP is the water soluble bisulphate adduct of a polyisocyanate polyurethane (Bayer, 2000; Cook and Fleischfresser, 1985), but is also described as a (poly)carbamoyl sulphonate (Guise and Freeland, 1984; Rippon, 1985). Synthappret BAP is known to self cross-link, a reaction that is enhanced in the presence of a sodium bicarbonate due to a slight increase in pH (~ pH 8) (Bell et al., 1985; Cook and Fleischfresser, 1985) as shown in Figure 2.1.c.

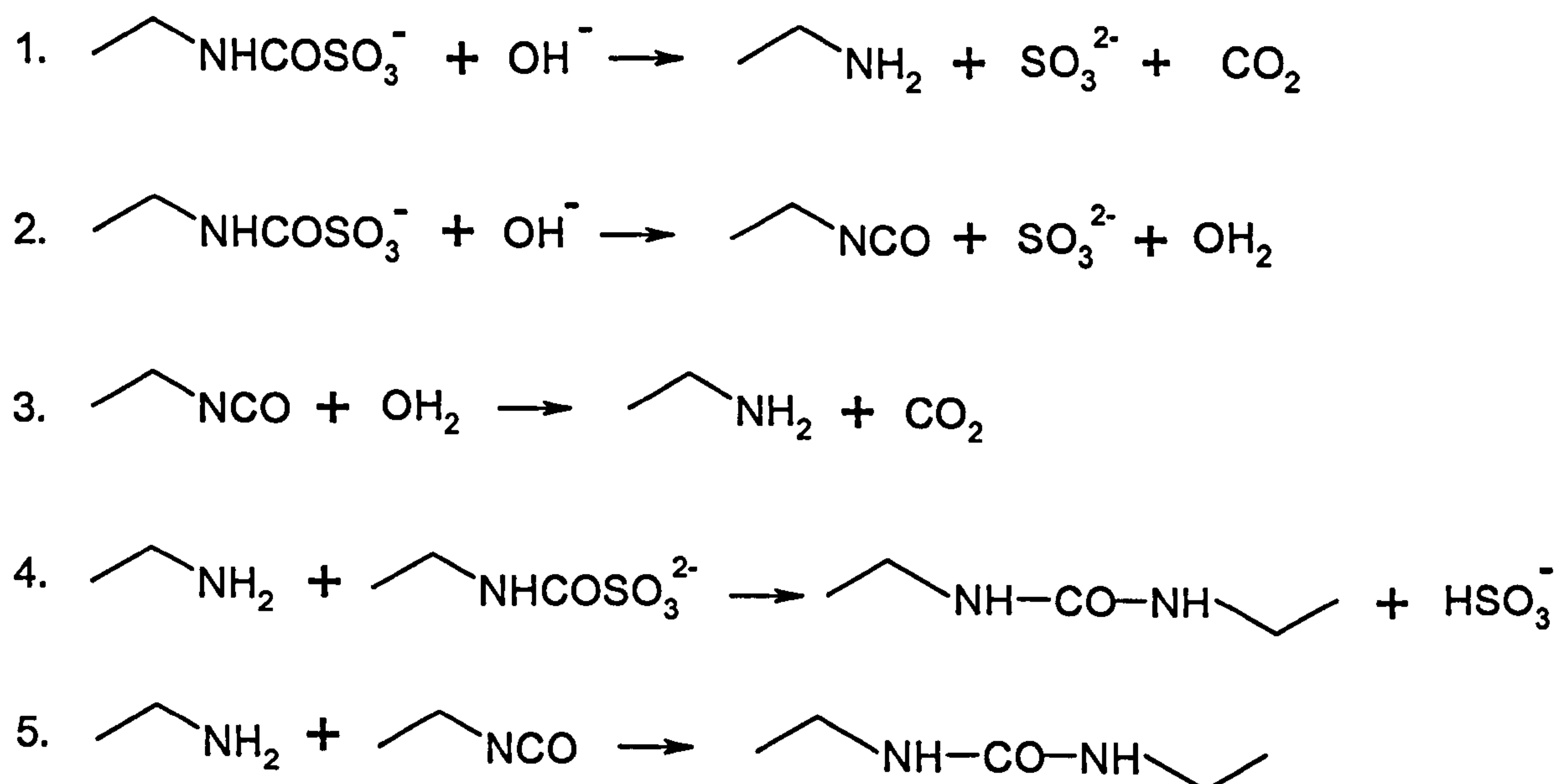


Figure 2.1.c Mechanism of cross-linking of Synthappret BAP

The idea behind the concept of shrink resist treatments of textiles (predominantly wool and wool blends) is to coat the fibres of the textile with a polymer which acts to prevent any felting of the fabric when subjected to washing (Lewis, 1992). Often Synthappret BAP is applied to the fabric being treated in a pad batch method in a mixture with a polyurethane dispersion and this is referred to as the Sirolan BAP process (Lewis, 1982; Cook and Fleischfresser, 1985). It should be noted that Synthappret BAP can also be applied as a shrink resist treatment by means of an exhaust process (Allanach, 1980) or by adsorption (Fleischfresser, 1982).

2.1.2.2 Use of Synthappret BAP as a Binder

The function of Synthappret BAP as a binder is linked to its self cross-linking mechanism. Whilst there is little evidence to suggest that any cross-linking occurs with

textile fibres, Synthappret BAP’s self cross-linking mechanism allows for mechanical trapping of the colorant. Its solubility in water and its relatively low viscosity are definite advantages in terms of its suitability for an ink jet ink formulation. Synthappret BAP is reported to be very stable at ambient temperatures in neutral or slightly acidic conditions, but readily polymerises via its carbomoyl sulphonate groups when heated or in alkaline conditions (Rippon, 1985). Therefore, it is thought that Synthappret BAP could be used within an ink jet formulation for printing onto textiles and then be cured by exposure to high temperatures. The physical and chemical nature of Synthappret is detailed in Table 2.1.f (Bayer, 2000).

Table 2.1.f Physical chemical properties of Synthappret BAP

Commercial Name	Synthappret BAP
Description	Bisulphite adduct of a polyether polyisocyanate
Functionality	3 i.e. 3 active sites for cross-linking (-NHCOSO ₃ ⁻) per molecule
pH	2.5-4
Stability	Stable to organic acids and alkalis up to pH 9
Density	1g cm ⁻¹
Physical nature	Liquid
Solubility	Soluble/miscible in water in all proportions

2.1.3 Other Chemicals

During the course of this investigation a number of humectants, additives and speciality chemicals were incorporated into ink jet ink formulations. Such materials are detailed in Table 2.1.g.

Table 2.1.g Chemicals used throughout the investigation

Name	Function	Supplier
Ethylene Glycol	Humectant	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Diethylene Glycol	Humectant	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Polyethylene Glycol	Humectant	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Isopropyl alcohol	Co-solvent	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Alginate (MANUTEX RS210)	High viscosity thickener	International Speciality Products, Emil-Hoffmann-Strasse 1a, 50996 Koln, Germany
Ethanol	Co-solvent	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Sodium bicarbonate	Alkali component	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Solsperse 27000	Dispersing agent	Avecia Ltd, Hexagon House, Blackley, Manchester UK
TEGOWET 590	Wetting agent	Tego Chemie, Essen, Germany
Lubrisil CR 200	Anti slip additive	Brookstone Chemicals Ltd., Leek, Staffordshire, UK
Lubit 64	Anti slip additive	Bayer Speciality Chemicals, Leverkusen, Germany
Michem Lube 180	Anti slip additive	Michelman Inc., 9080 Shell Road, Cincinnati, Ohio, USA
Dow Corning Additive	Anti slip additive	Dow Corning Limited, Meriden Business Park, Copse Drive, Allesley, Coventry, UK
Ammonia	Alkali component	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Diethanolamine	Alkali component	Sigma-Aldrich, New Road, Gillingham, Dorset, UK

Name	Function	Supplier
Triethanolamine	Alkali component	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Ethylene diamine	Alkali component	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Sodium hydroxide	Alkali component	Sigma-Aldrich, New Road, Gillingham, Dorset, UK
Hydrochloric acid	Acid component	Sigma-Aldrich, New Road, Gillingham, Dorset, UK

2.2 Equipment

During the course of this investigation a number of pieces of equipment were used for the formulation and characterisation of inks as well as the characterisation of printed substrates. Such equipment is detailed in Table 2.2.a.

Table 2.2.a Equipment used throughout the investigation

Equipment Name	Function	Supplier
MK11 Eiger Torrance bead mill (50ml chamber)	Dispersion of the ink formulations	Eiger Torrance Ltd., Warrington, Cheshire, UK
Coulter N135 particle size analyser	Particle size analysis of inks	Beckman Coulter Ltd., High Wycombe, Buckinghamshire, UK
Mathis WT wash-fastness tester	Washfastness tests on printed substrate	Werner Mathis AG, Zurich, Switzerland
KTF 4099 Curing oven	Thermal curing of printed substrate	Werner Mathis AG, Zurich, Switzerland
Crockmeter	Rubfastness testing of printed substrate	International Ltd., Staffordshire, UK
Gretag D183 colour densitometer	Measuring colour densities of printed substrate	Colour Data Systems Ltd, Eastham Village, Wirral, UK
X-Rite SP68 spectrophotometer	Measurement of the colour properties of the printed	X-Rite Ltd., Poynton, Cheshire, UK

Equipment Name	Function	Supplier
Brookfield DV-II+ viscometer	Measurement of the viscosity of inks	Brookfield Viscometers Ltd., Harlow, Essex, UK
TBS Torsion Balance	Measurement of the surface tension of the inks	Torsion Balance Supplies, Malvern Wells, Worcestershire, UK
pH meter	Measurement of the pH of the inks	BDH Ltd., Poole, Dorset, UK
ImageXpert	Objective, repeatable and fully automatic image quality analysis	VisonJet Ltd., Lumen House, Royston, Hertfordshire, UK
DSC 2010	Differential scanning calorimetry	TA Instruments, Leatherhead, Surrey, UK
TGA 2050	Thermo gravimetical analysis	TA Instruments, Leatherhead, Surrey, UK
Apollo P-1200	Desktop inkjet printer	PC World, Leeds, UK
Apollo P-2100	Desktop inkjet printer	PC World, Leeds, UK
HP51626A	Inkjet cartridges	PC World, Leeds, UK
HP51629A	Inkjet cartridges	PC World, Leeds, UK
Jeol JSM-820	Scanning electron microscopy	JEOL(UK)Ltd. JEOL House, Silvercourt Watchmead, Welwyn Garden City, UK
Au Annular Polaron E5100	SEM gold coating unit	Emitech Ltd. South Stour Avenue, Ashford, Kent, UK
Perkin Elmer Spectrum One FT-IR Spectrophotometer	FT Infra red analysis	Perkin Elmer, Seer Green, Beaconsfield, Bucks, UK
Xenotest Alpha LM	Lightfastness	Alpas Technology Ltd., Ferry Hinksey Road, Oxford, UK

2.3 Experimental Procedures

Throughout the course of the investigation, several techniques were used in the preparation and characterisation of various ink formulations.

2.3.1 Preparation of a Fabric Sample for Ink Jet Printing

Before an ink can be printed onto a textile fabric, the fabric sample must be prepared. In this investigation two fabric types were used, a mercerized, lightly bleached poplin cotton and a standard grade polyester. In this investigation, the hardware used to print the samples was an Apollo P1200 desktop ink jet printer. A piece of fabric was cut to a size of 20 × 30cm and attached to a sheet of A4 copy paper with double sided tape. When printing, the sample was fed into the printer from the back feeder slot to avoid any unnecessary creasing of the fabric.

2.3.2 Preparation of an Ink Cartridge for Ink Jet Printing of a New Ink Formulation

A monochrome cartridge, a Hewlett Packard HP 51629A shown in Figure 2.3.a was used to print the ink formulated during the investigation. Such a cartridge has 60 ejection nozzles each having a diameter of 65 μm. The arrangement of these nozzles can be seen in Table 2.3.a, alongside a micrograph of a single nozzle orifice.

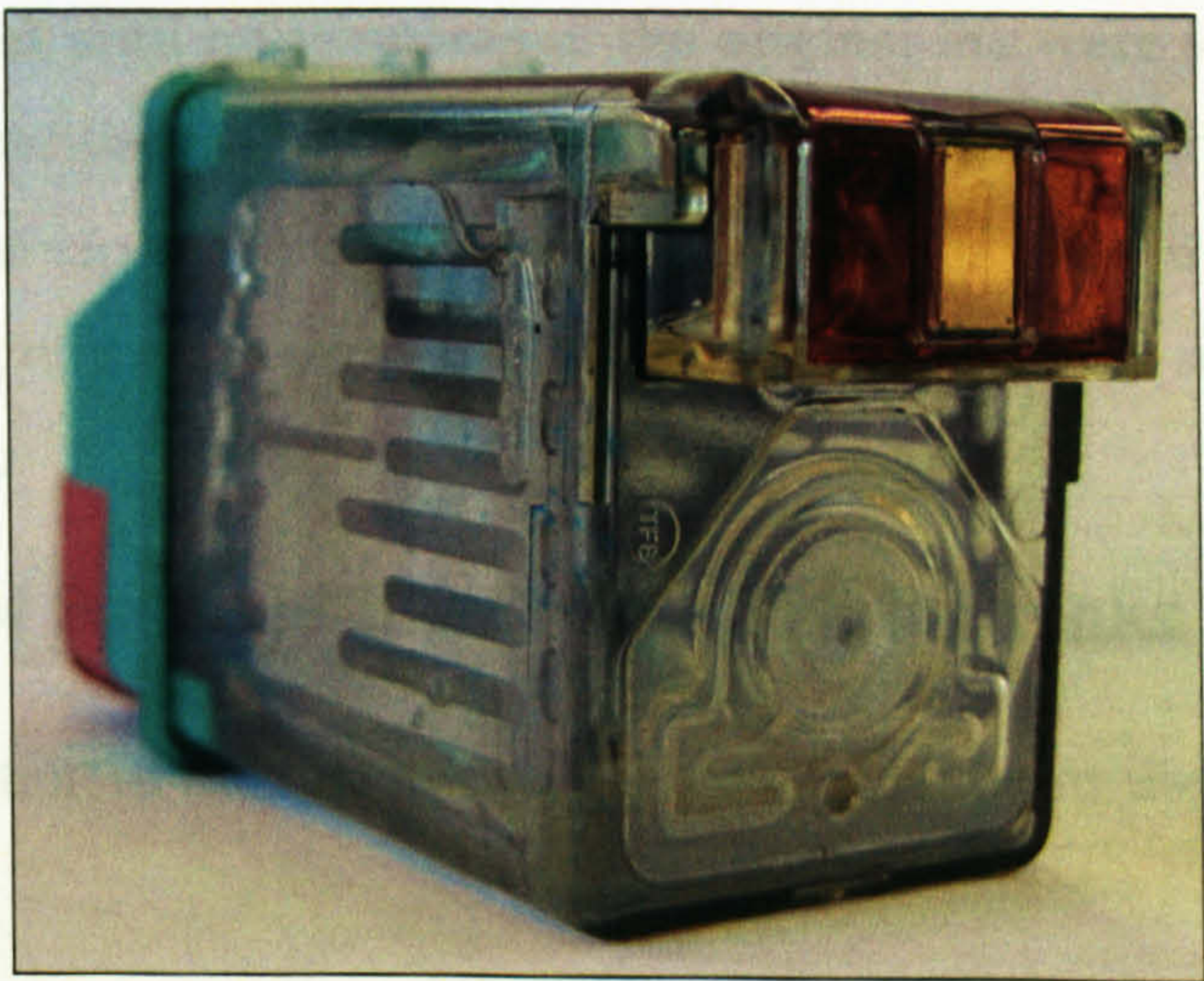
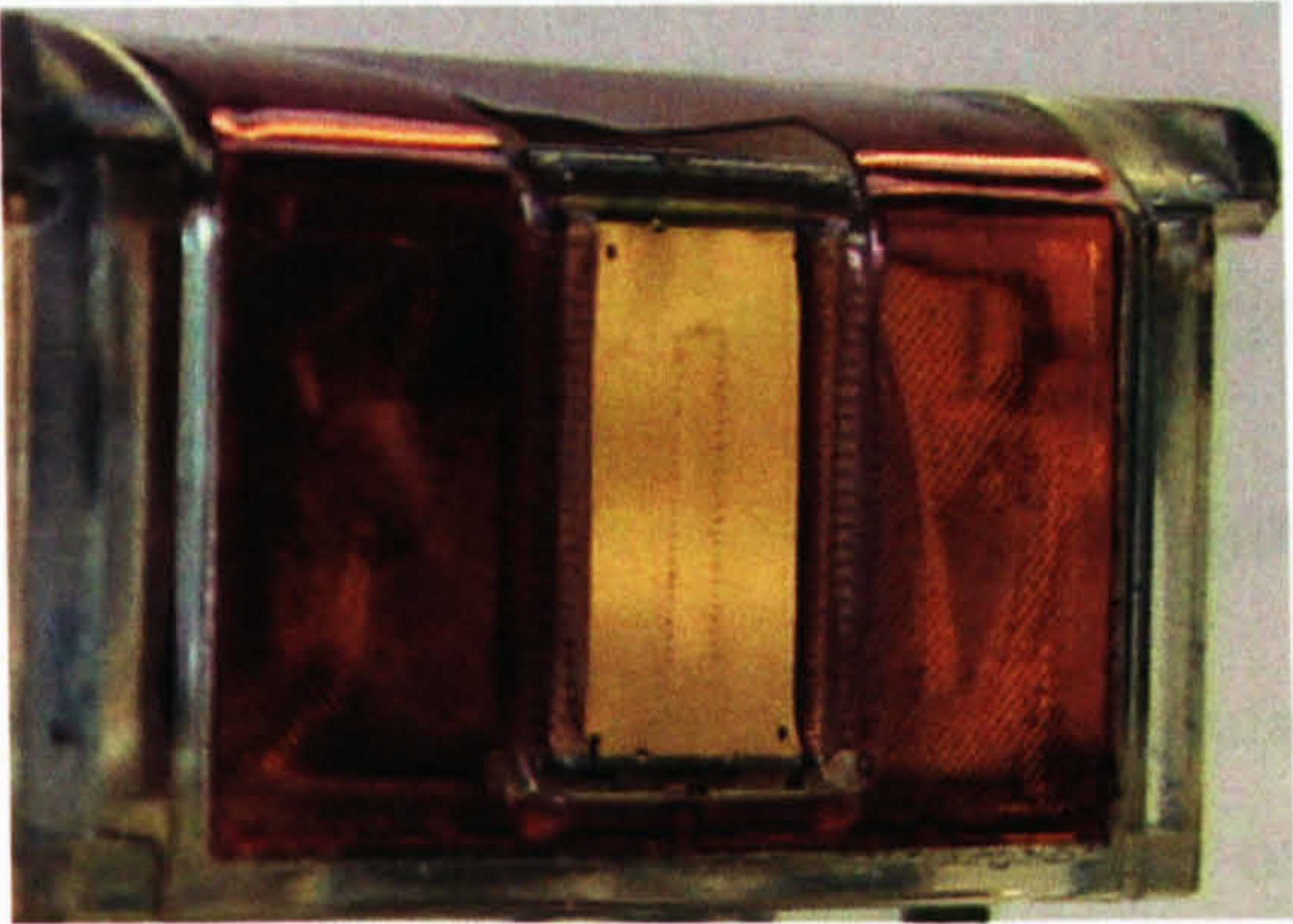
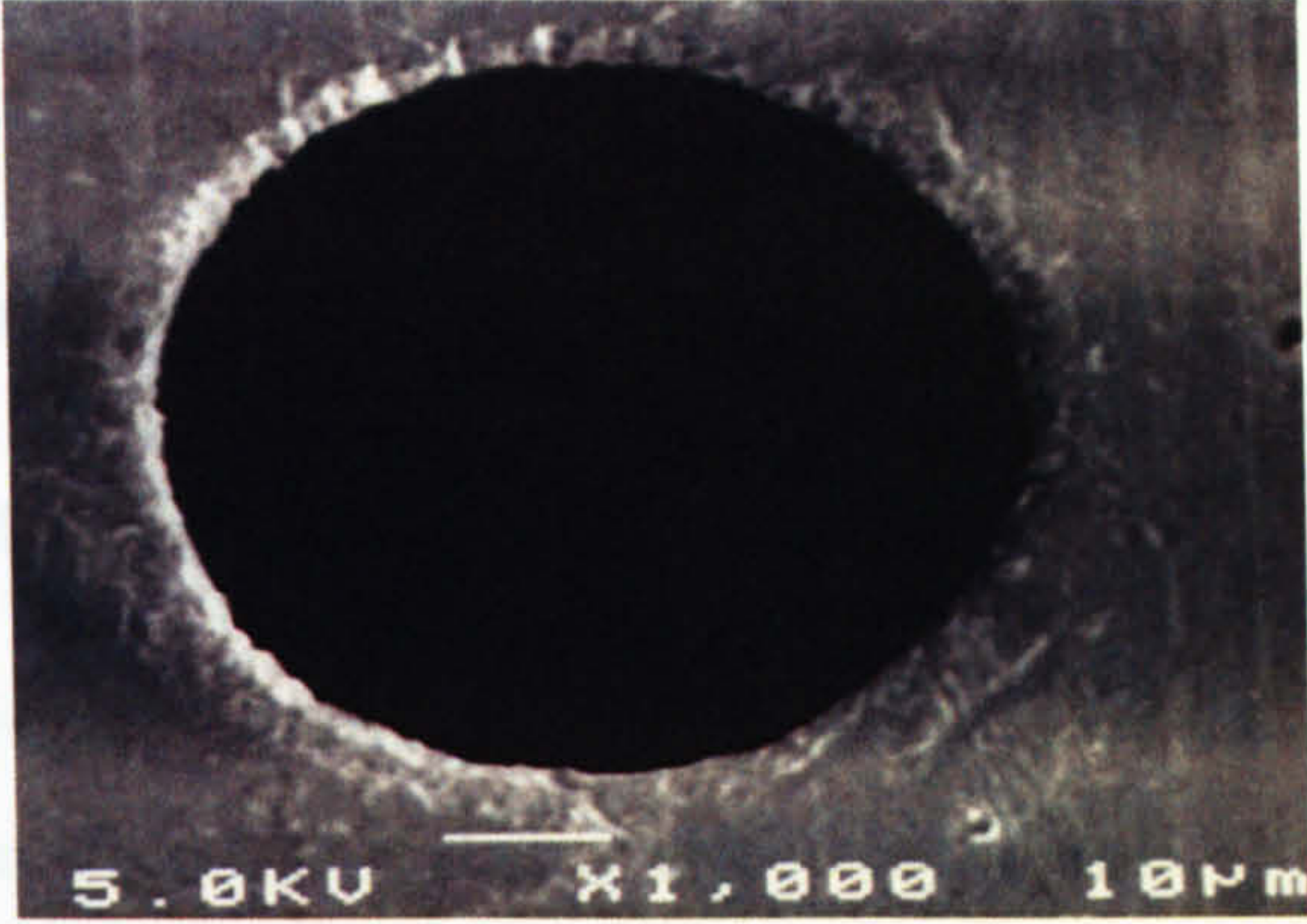


Figure 2.3.a Hewlett Packard HP 51629A ink jet cartridge

Table 2.3.a Hewlett Packard ink jet e nozzles and SEM of one nozzle

Nozzle area of a Hewlett Packard HP 51626A ink jet cartridge	Micrograph of one ink jet nozzle
	

Before a new ink could be printed, the cartridge being used had to be cleaned of any existing ink. This was done by drilling a hole in the top of the cartridge and emptying out the ink. The cartridge was then filled with water, shaken and emptied again. This process was repeated until no remnants of the original ink were left. Once clean, the cartridge was then refilled with the required experimental ink and the hole in the top sealed with electrical tape. The cartridge was then left for a few minutes to let the ink settle. Such settling of the ink was established when the ink was seen to stop dripping from the print-head.

2.3.3 Method of Formulating Screen Printing Inks

During the preparation of the screen printing ink formulations the following guideline was used:

1. Initially, the Synthappret BAP was added to the water and blended to give a homogeneous solution, using a Silverson Lab Emulsifier.
2. The Alginate (MANUTEX RS210) thickener was then gradually added to the mixture whilst it was continually agitated.
3. Any further components included within the formulation were added prior to the addition of pigment.
4. The pigment (Toner Magenta E02) was then added step-wise and the formulation mixed with emulsifier until a smooth printing paste was obtained.

5. The inks prepared were then used to print cotton samples.
6. Once printed the cotton samples were thermally cured in a Werner Mathis KTF 4099 curing oven at the required temperature.
7. Cured samples were tested for washfastness and rubfastness according to the methods detailed in Section 2.4.8 and Section 2.4.9.

2.3.4 Method of Ink Formulation of Inks using Toner Pigments

2.3.4.1 Formulation of a Pigment Concentrate

Before the preparation of an ink formulation, a pigment concentrate was produced. In order to aid the dispersion stability of the pigment a dispersant was added. The dispersant used was Solsperse 27000 supplied by Avecia Ltd. The pigment concentrate was made up according to the following recipe where the relative amounts of its constituents are given as weight for weight percentages where the total mass of the formulation was 200g:

- Pigment powder 10%
- Dispersant 2%
- DEG 5%
- PEG 3%
- EG 5%
- IPA 10%
- Water 65%

During the preparation of the ink formulations each ingredient was weighed accurately into a beaker and blended by hand until uniform in consistency. This mixture was then transferred to a bead mill and milled for 1 hour using 1-1.5mm beads. The operation of the bead mill is described in section 2.3.5. Once milled the paste was then used in the formulation of inks for ink jet printing. The process of formulating such inks was as follows:

1. Water, co-solvent and humectants were accurately weighed and blended together until homogeneous using a magnetic stirrer.
2. Synthappret BAP was added to the mixture and stirred in.

3. A dispersant and any further additives were included at this stage.
4. The pigment powder or pigment concentrate was then added gradually whilst the mixture was continually stirred.
5. The formulation was then transferred into a bead mill and milled for 1 hour at 350 rpm with 1-1.5 mm beads.
6. The final ink obtained was then measured for its viscosity, surface tension and for particle size.
7. Once completed the ink formulation was used to print the required samples via an ink jet printer.
8. The printed samples were then cured at 200°C for 2 minutes in a Werner Mathis KTF 4099 curing oven.
9. After curing, the printed sample was tested for its washfastness and rubfastness following the procedures detailed in Section 2.3.10 and Section 2.3.11.

2.3.5 Operation of a Bead Mill

The bead mill used in this investigation was an MK11 Eiger Torrance bead mill, which had a 50 ml chamber. As such at least 75 ml of liquid was required to ensure flow through the mill. Prior to milling 35 ml of beads was introduced into the chamber and all the components were tightened and joints sealed. The ink was then introduced into the milling chamber and milled for an hour at a speed of 300-400 rpm. Once milled the liquid was decanted from the chamber and the mill itself washed with water.

2.3.6 Method of Ink Formulation of Inks using Microlith™ Pigments

Use of Microlith pigments in ink formulations required the preparation of a base pigment paste prior to their inclusion in an ink jet ink. The reason for this was to include ammonia at this stage, as it is necessary for such a component to enhance the partially soluble nature of the pigments. The initial pigment paste formulation was as follows where the proportions are given as weight for weight percentages where a mass of 100g was formulated.

- Pigment 25%

- Water 54%
- IPA 20%
- Ammonia 1%

The paste was made up as follows:

1. Initially water and IPA were accurately weighed out and blended together.
2. The pigment was then weighed and added to the water/IPA mixture with the application of a magnetic stirrer to allow for continual agitation of the formulation.
3. Ammonia was then added drop-wise, whilst the mixture was continually stirred, until a smooth paste was obtained. (Process took about 30 minutes for complete mixing).

Once the pigment paste had been made it was used as the basis of the ink formulations for use in ink jet printing. Such ink formulations were made up as follows:

1. Water, co-solvent (if appropriate) and humectants were weighed out and blended together using a magnetic stirrer.
2. When a homogeneous solution was obtained, the Synthappret BAP binder was introduced and the solution mixed.
3. The pigment paste was then added and the resulting ink formulation stirred for a further 30 minutes.
4. The ink formulation was then filtered using a 1 μ m filter.
5. After filtration to remove any larger elements of the ink, the formulation was analysed for its viscosity, surface tension and particle size following the procedures detailed for Section 2.4.1, Section 2.4.2 and Section 2.4.3.
6. Once completed the ink formulation was used to print the required samples via an ink jet printer.
7. The printed samples were then cured at 200°C for 2 minutes in a Werner Mathis KTF 4099 curing oven.
8. After curing, the printed sample was tested for its washfastness and rubfastness following the procedures detailed in Section 2.4.8 and Section 2.4.9.

2.3.7 Method of Ink Formulation of Inks using Cab-O-Jet Pigment Dispersions

As mentioned in Section 2.1.1.3 Cabot produces a range of pigments tailored specifically for use in ink jet printing. These pigments were supplied as dispersions of between 10% and 30% solids and were seen to have a low viscosity and high surface tension. The pigments were modified by the addition of a diazonium ion on the surface of the pigment particle to provide dispersion stability. Due to the pigments being pre-dispersed by Cabot Corp. there was no need for the formulation of a pigment paste or any high shear mixing process. As such the pigmented ink jet inks were formulated according to the following steps:

1. The water, co-solvent and humectants were blended together until a homogeneous solution was obtained.
2. The Synthappret BAP was then added and blended as previously along with any further components required such as additives.
3. The pigment dispersion was then added and the formulation mixed by the application of a magnetic stirrer for 30 minutes.
4. Once mixing had been completed the ink formulation was measured for viscosity, surface tension and particle size following the procedures detailed in Section 2.4.1, Section 2.4.2 and Section 2.4.3.
5. Once completed the ink formulation was used to print the required samples via an ink jet printer.
6. The printed samples were then cured at 200°C for 2 minutes in a Werner Mathis KTF 4099 curing oven.
7. After curing, the printed sample was tested for its washfastness and rubfastness following the procedures detailed in Section 2.4.8 and Section 2.4.9.

2.4 Characterisation Techniques and Methods used in the Analysis of Inks and Printed Substrate

The following sub-sections detail the techniques used to characterise the ink formulations and the substrates once printed and cured.

2.4.1 Measurement of Viscosity

As previously mentioned in Section 1.4.3.2, for it to be viable for ink jet printing an ink is required to have a viscosity of less than 20 mPa.s (MacFaul, 2003). As such, it was important for every ink formulated to be tested for viscosity, to ensure its suitability for ink jet applications. Without such a measurement, it would be very difficult to prove whether or not an ink could be printed via an ink jet mechanism viscosity determines droplet formation and ejection.

In this investigation the inks were measured for their viscosity using a Brookfield DV II+ viscometer. The viscometer is designed to measure the torque required to overcome the resistance to any induced movement of the fluid being analysed. To allow for more accurate measurement, an ultra low adaptor was used. This is an additional spindle, which is designed to be used for formulations of a low viscosity, that is to say below 20 mPa.s (Kang, 1991). The ultra low adaptor also allows for easy temperature control as it has a fitted water jacket, which can be attached to a water bath. This allows every ink to be measured under the same conditions. During the course of this investigation all viscosities were measured at a temperature of 25°C.

In order to measure an ink using the Brookfield DV II+ viscometer with ultra low adaptor application, 16ml of ink was required to give an acceptable depth of immersion of the spindle. The ink was left in the chamber and allowed to reach the temperature of the heated water jacket. Once at the desired temperature, the ink was measured for its viscosity over a range of spindle rotation speeds, these being 1, 5, 10, 20 and 60 rpm corresponding to shear rates of 1.22, 6.11, 12.23, 24.46 and 73.38 s⁻¹ respectively. Pictures of the Brookfield DVII+ viscometer and the ultra low adaptor can be seen in Figure 2.3.b and Figure 2.3.c.

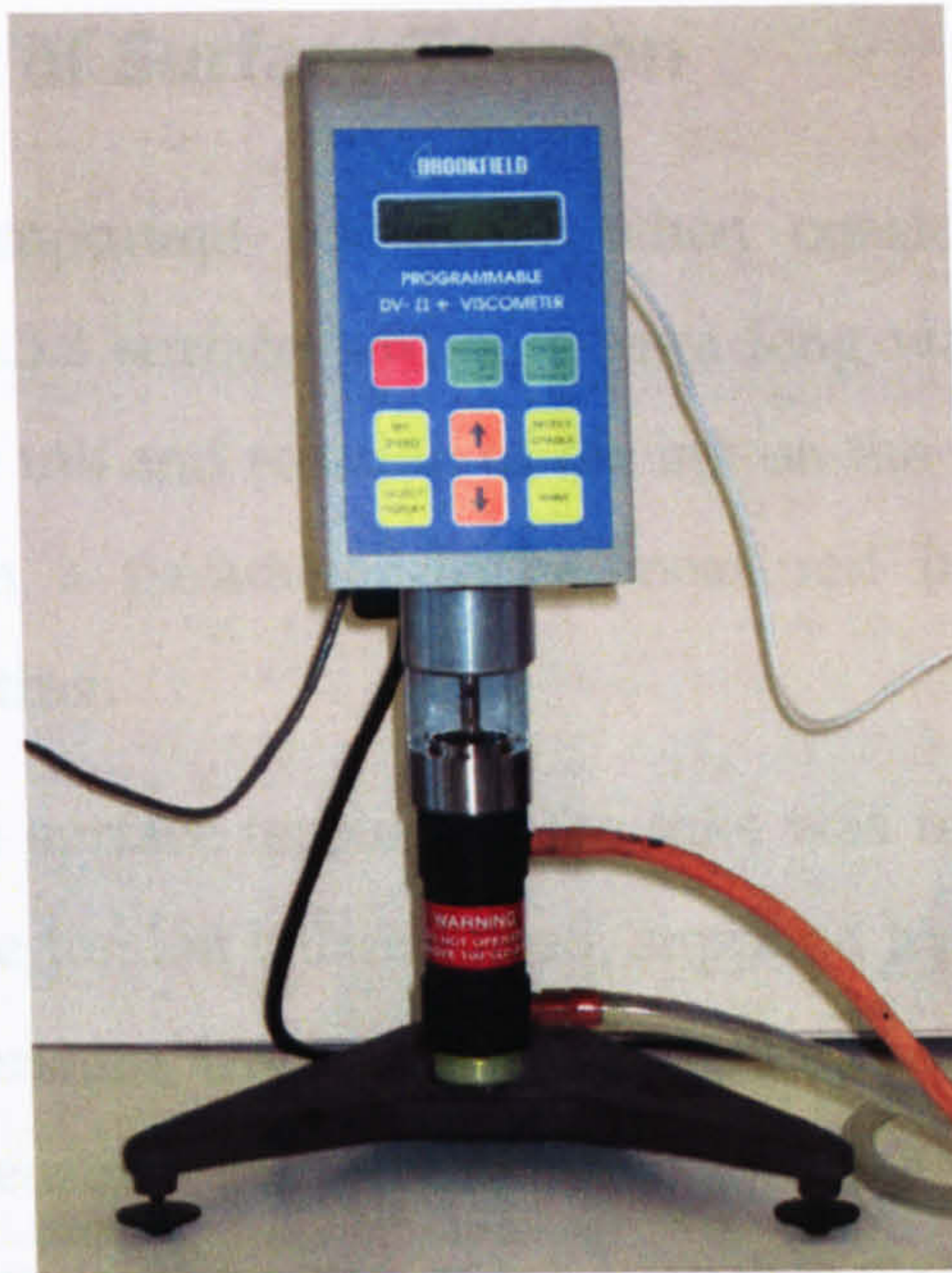


Figure 2.4.a Brookfield DV II+ viscometer with ultra-low adaptor



Figure 2.4.b Ultra-low adaptor for a Brookfield DV II+ viscometer

It should be noted that during this report whilst some viscosity profiles are shown, in general, viscosities have been quoted at 60 rpm and 25°C.

2.4.2 Measurement of Surface Tension

Surface tension is an important parameter when considering ink jet inks. As mentioned in Section 1.4.3.3 surface tension goes a long way to determining droplet formation, ejection of the ink and reaction of the ink on the substrate. As such, it was very important for such a parameter to be measured in order to assess an ink suitability for ink jet printing.

In this investigation, the surface tension of the inks was measured using a DuNuoy ring torsion balance. The torsion balance used, supplied by Torsion Balance Supplies, Malvern Wells, Worcestershire, UK, had a measurement range of 0 to 120 mNm⁻¹. The DuNuoy ring method measures the force required to pull a ring away from the surface of a liquid. For this investigation, every ink was measured for its surface tension 3 times and an average taken to give a definitive result. A picture of the DuNuoy tensiometer is shown in Figure 2.3.d.

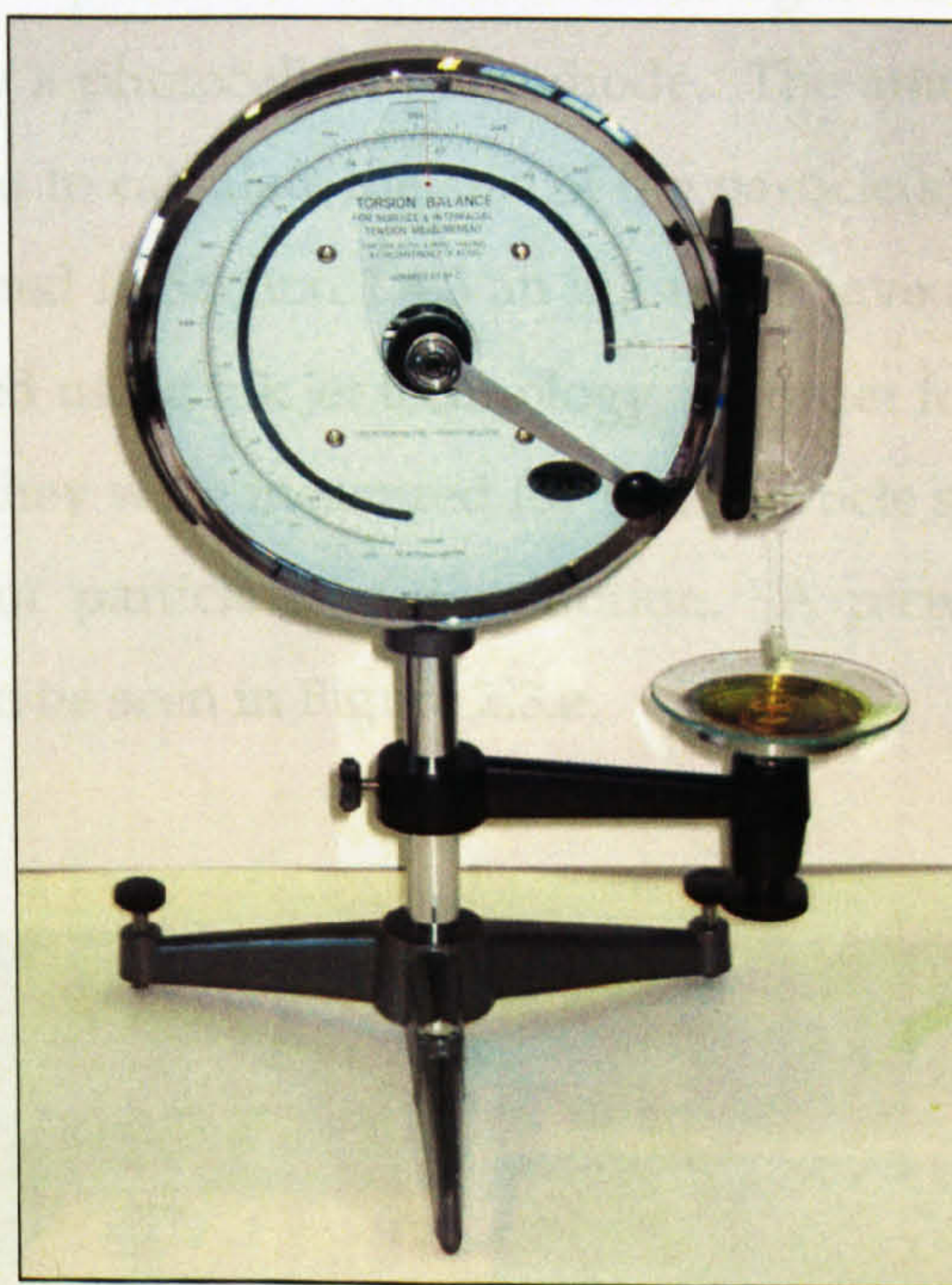


Figure 2.4.c DuNuoy tensiometer

2.4.3 Particle Size Analysis

Particle size of the pigment is critical in determining the suitability of an ink for ink jet printing. If a pigment particle is too large ($\geq 1 \mu\text{m}$) it may act to block the nozzles of

the print-head, thus, preventing the smooth ejection of the ink. Such large particles may be the result of flocculation or agglomeration and therefore stability of the pigment within the ink is vital. Therefore tests on ink stability were also carried out in terms of freeze-thaw tests, pH variation (low and high pH) and extended periods at elevated temperatures.

A particle size distribution may be measured in terms of the individual particles within a sample or by the measurement of size fractions. The actual method of measuring particle size varies. However, the most common method used is known as particle counting. There are two types of particle counting which are detailed as follows:

Coulter Counter Method: In this method, the particles are dispersed in an electrolyte solution before being passed through an aperture. Either side of this aperture are electrodes and the change in conductivity of the sample as it passes these electrodes can be measured to give a value for the size of any particles suspended therein.

Optical Method: In this method, a laser or white light is shone through the sample containing the suspended particles. The amount of light blocked or scattered by the particles is measured by a photocell or photodiode. The amount of light scattered or blocked can then be used to calculate the size of the particle(s) causing this obstruction of the light. As mentioned in Section 1.4.3 an ink must have a particle size of 1 μm or less in order to be printed using ink jet technology. In order for the ink formulations to be passed for printing, they were measured for their particle size using a Coulter N135 particle size analyser for particle size distribution. A picture of the Coulter N135 particle size analyser can be seen in Figure 2.3.e.



Figure 2.4.d Coulter N135 particle size analyser Morphological Evaluation

2.4.4 Topological Evaluation of Print Surfaces

Scanning electron microscopy (SEM) is a technique used to examine surfaces at a magnitude greater than that possible using conventional microscopy. In SEM, a beam of focused electrons (typically 10 keV) is used to scan the surface of a solid using a raster pattern. Any backscattered or secondary electrons produced by this scan form the basis of the SEM technique. The electron beam moves over the surface of the sample and back (the x direction) and then moved downwards (y direction), until the surface has been scanned fully. During this process, a signal is established above the surface (z direction). A computer then processes this signal to produce the desired image of the surface being examined (Edwards, 2003).

SEM technology was used to view the printed samples at a high magnification. A Jeol JSM-920 SEM was used for this type of analysis. A picture of the Au Annular Polaron E5100 gold coater used for the coating of the samples and the Jeol JSM-820 SEM can be seen in Figure 2.3.f and Figure 2.3.g.



Figure 2.4.e Au Annular Polaron E5100 gold coater

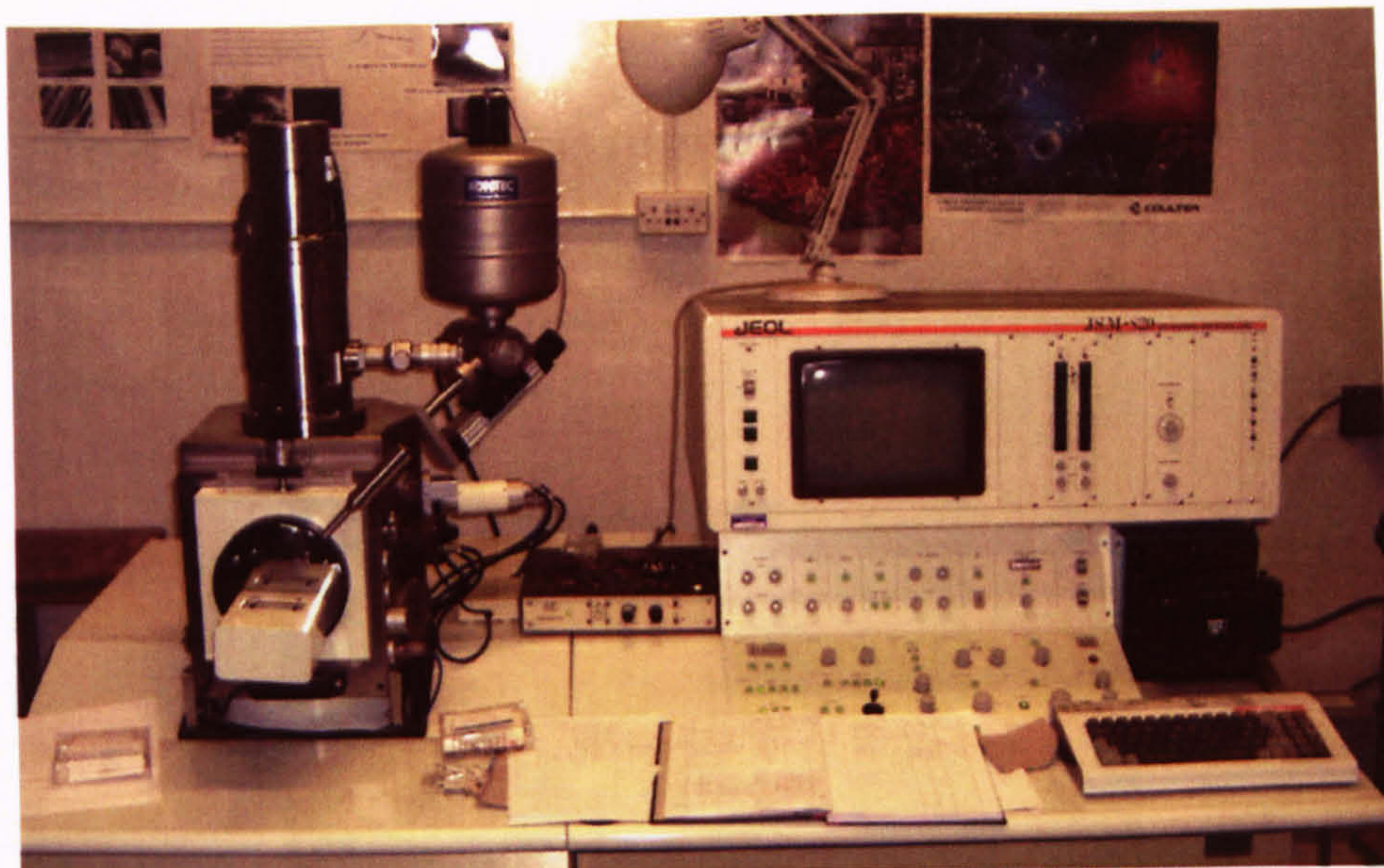


Figure 2.4.f Jeol JSM-820 SEM

2.4.5 Analysis of the Elemental Composition of Print Surfaces

Energy Dispersive x-ray analysis (EDX) is used to map the elements present within a given sample and is a technique often used alongside SEM. Similarly to SEM, in EDX a beam of electrons (typically 10-20 keV) is focused on the surface of the given sample. This causes X-rays to be emitted from the sample and on passing the electron beam across the sample an image profile of each element encountered in the sample can be attained. This technique was used to identify pigment located on printed samples in the form of copper from the copper phthalocyanine based cyan pigments.

2.4.6 Evaluation of the Thermal Properties of Ink and Substrate

Due to the extreme temperatures exerted on an ink within a thermal ink jet printing process, it was necessary to measure the thermal stability of the ink. The ink and substrate were also subjected to elevated temperatures during the curing process and so thermal profiles of the ink and substrate were required. Thermo Gravimetric Analysis (TGA) measures the change in mass of a given sample as a function of temperature as the temperature is increased. TGA can be used to analyse decomposition rates and thermal stability (Hatakeyama and Quinn, 1995; Skoog et al., 1998). The technique produces a plot of mass or percentage mass as a function of time. This plot is referred to as a thermogram or a thermal decomposition curve.

Using TGA a known quantity of sample was placed in a sample reservoir. A computer was used to set the temperature program. Any change in mass of the sample over the period of time at which it was heated was recorded.

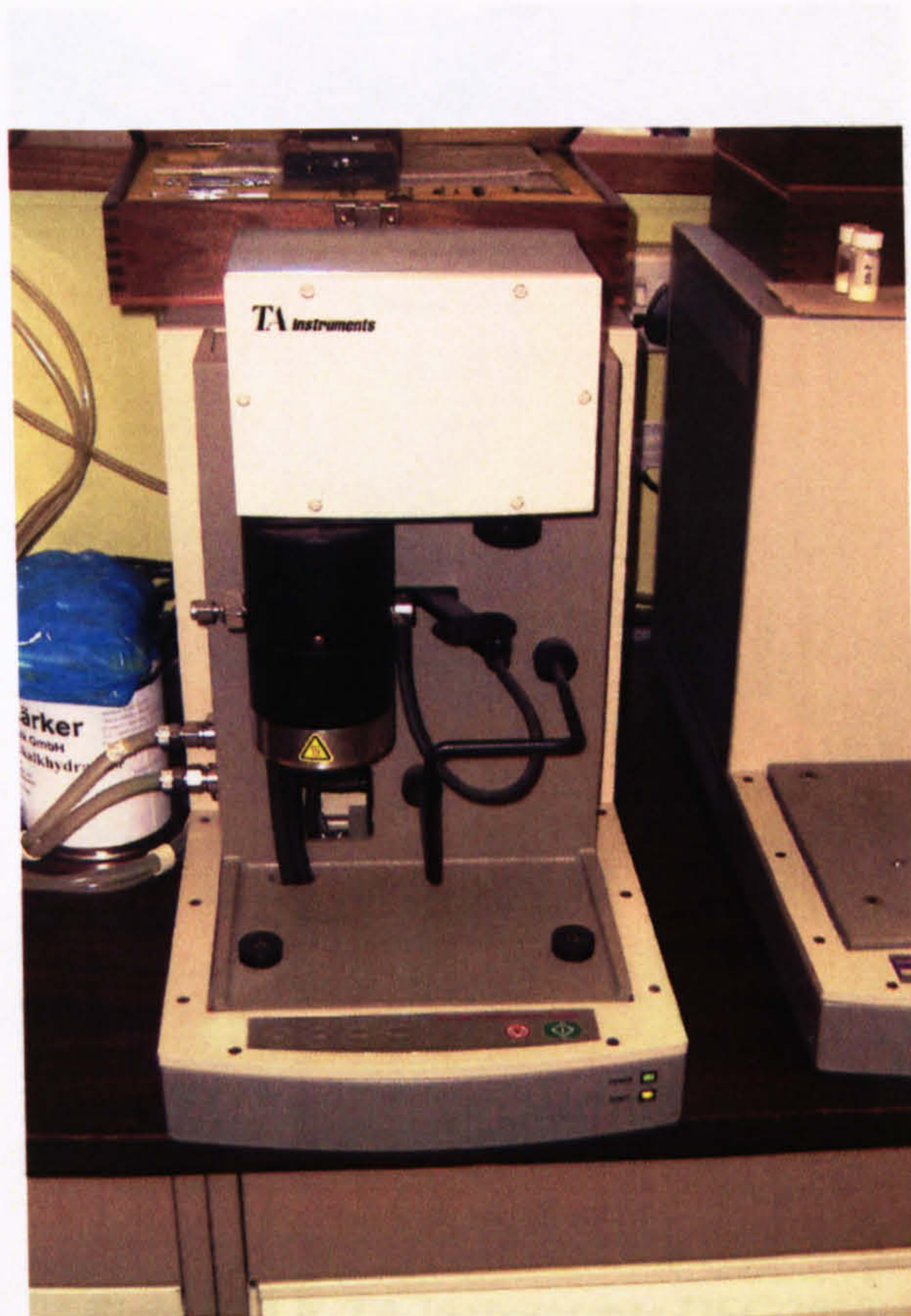


Figure 2.4.g TA Instruments TGA 2050

Differential Scanning Calorimetry (DSC) is primarily a technique used for the measurement of the thermal properties of a material. This technique measures the differences in heat flow into a sample in comparison to that of a known standard (Skoog et al., 1998). The information gathered allows for the calculation of energy changes when changes such as crystal melting occur (Campbell et al., 2000). A DSC curve plots the temperature transition within the measured sample as a function of temperature in terms of energy transfer (Hatakeyama and Quinn, 1995).

During DSC analysis, a known quantity of sample was placed in a sample reservoir. The sample was heated over a known temperature range and any endothermic or exothermic heat exchange of the sample recorded.



Figure 2.4.h TA Instruments DSC 2010

2.4.7 Evaluation of the Cross-Linking Mechanism of the Binder

A method was required in order to analyse the cross linking mechanism of the binder used within the ink formulations. Such an analysis was intended to prove the change in structure of the binder upon curing. Thus, Fourier Transform Infra Red (FTIR) analysis was used. FTIR is a measure of the amount of infra red light absorbed by a sample due to the deformation of bonds within the molecules of the measured sample when exposed to infra red radiation. The spectra produced can be used to elute structural or chemical information regarding the sample. The data produced can be used for quantitative or qualitative evaluations. The spectrum obtained shows the wave number of the light of the incident radiation versus the absorption by the sample.

In order to see changes in the structure of the binder before and after curing, infra red spectroscopy was used. This technique allowed for the analysis of both liquid and solid samples. Once a spectra was obtained, differences between the spectra could be highlighted and the relevant peaks identified using literary sources. A picture of the Spectrum One FT-IR spectrophotometer infra red spectrophotometer can be seen in Figure 2.3.j.

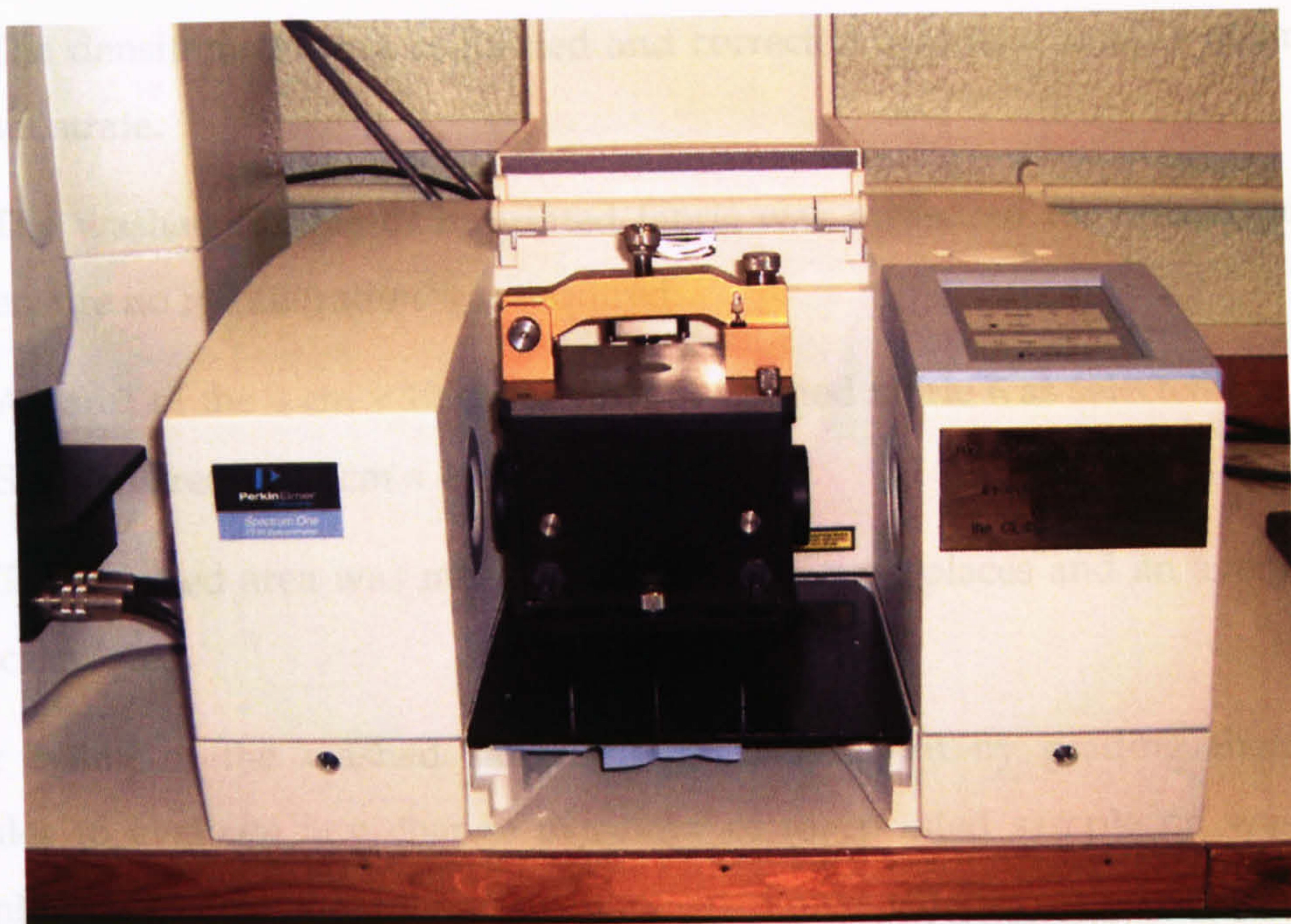


Figure 2.4.i Perkin Elmer Spectrum One FT-IR spectrophotomer

2.4.8 Washfastness Testing

Initially, crude washfastness tests were carried out to see the extent of curing that had been achieved. Thus, cured samples were stirred in cold water for 20 minutes. After this had been completed a thorough wash test was carried out according to the British Standard ISO2. Thus, samples of the cured printed cotton were cut to 4 × 10 cm and attached to a piece of multifibre strip of equivalent size. These were then washed in a Werner Mathis WT washfastness tester at 60°C for 30 minutes, in a wash-bath liquor containing 5g of SDC standard soap and 1g of sodium carbonate per litre of water, whilst being tumbled continually. It should be noted that for each wash pot containing a 4 cm × 10 cm sample, 150 ml of was-bath liquor was used. For each wash test, a piece of unprinted substrate was also washed, in order to prove that no discoloration of the fabric was seen upon washing. On completion of the washing cycle, the samples were rinsed with cold water to remove any soap and air dried. A picture of the Werner Mathis WT washfastness tester can be seen in Figure 2.3.k. In order to assess the effect of the washing process on the printed substrate, the samples were measured for their optical density before and after washing. All measurements were made on the same day of washing usually within 3 hours of each other, i.e. optical density of the print before and after washing, to ensure measurement conditions remained constant. The process of optical density measurement was carried out using the following steps:

1. The densitometer was calibrated and corrected against a sample of unprinted substrate.
2. The washed sample of unprinted fabric was measured for optical density to ensure no re-calibration was required.
3. An area of the 4 cm × 10 cm sample of washed fabric was selected for analysis. Such an area was 1 cm × 4 cm.
4. The selected area was measured in five different places and an average result calculated.

Further rating of the washed samples was carried out by grading them against greyscales to evaluate any change in colour of the printed sample on washing. A randomly selected panel of twenty people carried out such greyscale analysis. Grading was made on viewing fabric samples in a light box of neutral grey colour at an angle of 45° and using D65 illumination.



Figure 2.4.j Werner Mathis WT washfastness machine

2.4.9 Rubfastness Testing

Rub fastness was carried out using a Roaches crock meter according to the AATCC test procedure. Thus, the sample of printed textile was subjected to a standard rub fastness test of 10 rubs back and forth with both dry and wet cotton lawn rubbing fabric. A picture of the Roaches crock meter can be seen in Figure 2.3.1. In order to assess the rub

resistance of the printed substrate, the color removed from the sample and onto the cotton lawn fabric was measured for its optical density. The area of cotton lawn fabric used for the rub test was measured for its optical density in five different places and an average value recorded. Visual assessment of the cotton lawn pads was also made according to greyscales to judge the colour difference after rubbing. A randomly selected panel of twenty people carried out such greyscale analysis. Grading was made on viewing fabric samples in a light box of neutral grey colour at an angle of 45° and using D65 illumination.

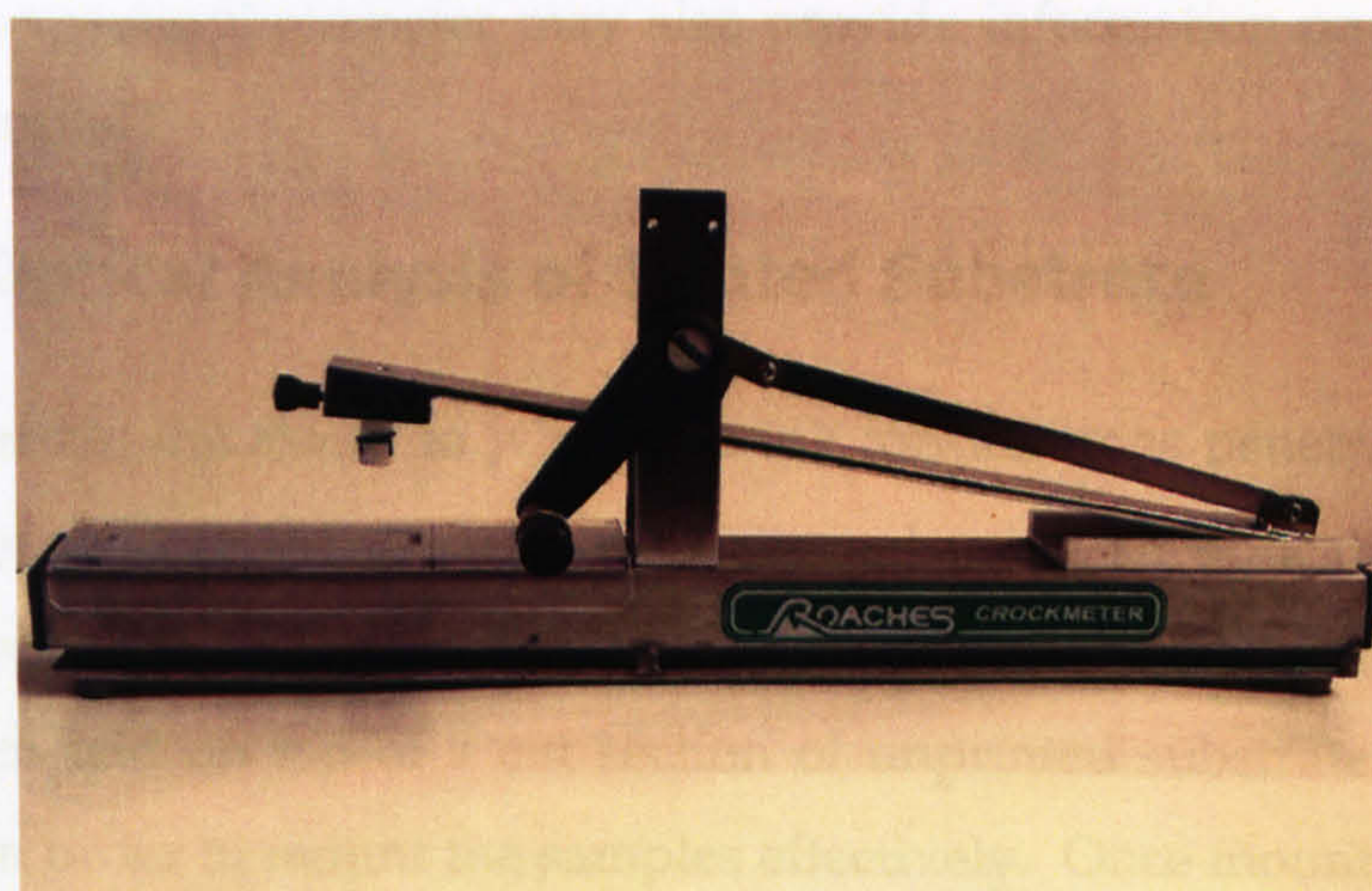


Figure 2.4.k Roaches crock meter

2.4.10 Assessment of Fabric Handle

In order to assess the change in handle of the fabric after printing, a test was required. Due to the lack of a Handle-O-Meter, a test was devised in order to make such an assessment. The test devised involved assessment of the change in the handle of the fabric by a test panel that graded any change between a printed and unprinted sample on a scale of 1 to 5 similarly to the visual assessment scales used for washfastness and rubfastness.

2.4.11 Image Quality Analysis

In order to measure the print quality of an ink on a substrate, an image analysis system can be used. The ImageXpert system supplied by ImageXpert Inc., Nashua, New Hampshire, USA, allows for the analysis of such properties as line quality and dot

roundness. This enables analysis of the effectiveness of an ink on a particular substrate in terms of wicking along the fibres.

In order to ascertain the colour properties of a printed substrate, it may be necessary to measure the $L^*a^*b^*$ values along with the colour density. A spectrophotometer is used to measure these values. L^* refers to the lightness of a sample, a^* refers to the redness/greenness of a sample where a negative value denotes green to varying intensities and a positive value indicates red and b^* refers to the yellowness/blueness of the sample where a negative value is blue and a positive value is yellow. The spectrophotometer or a colour densitometer can be used to measure the colour density of a sample. A spectrophotometer may also provide information on the chroma (C^*) and hue of a sample.

2.4.12 Optical Analysis of Printed Substrate

In order to ascertain the extent to which the ink formulations penetrate the substrate, cross-sections of the printed samples were viewed using an optical microscope. To prepare the cross-sections, a slice was cut across the width of the fabric. This small section was then laid on top of a cut section of unprinted substrate in order to give some stability in order to mount the samples effectively. Once mounted onto a slide, a colourless laquer was applied to the surface to prevent any freying of the fibres. The samples were then observed using an optical microscope and photographs taken of the observed area.

2.4.13 Lightfastness Testing of Printed Samples

As mentioned previously, it is necessary for a printed textile to have appropriate lightfastness depending on its application. In this investigation, the printed and cured substrates were assessed for their lightfastness using a Xenotest Alpha LM for the length of time required for blue wool to fade. On completion of the test, the samples were graded for their relative lightfastness according to the blue wool scale.

2.5 Investigation into the Cross-linking Mechanism of Synthappret BAP

In order to prove that cross-linking did occur when Synthappret BAP was subjected to thermal curing, samples were prepared for analysis using Fourier Transfer infrared spectroscopy.

2.5.1.1 Sample Preparation and Measurement

Due to the versatility of FTIR technology, both solid and liquid samples could be analysed. Therefore, a liquid sample of Synthappret BAP could be measured directly. To assess the cross-linking of the Synthappret BAP, a cured sample had to be produced. A film of Synthappret BAP was drawn down onto a piece of glass using a number 7 K-bar. The film was then thermally cured at 200°C for 2 minutes in a Werner Mathis KTF 4099 curing oven. Once cured, the solid layer of Synthappret BAP could be peeled from the surface of the glass and analysed using the FTIR Spectrometer following the procedures detailed for Section 2.4.7. In order to assess the extent of cross-linking at different temperatures, the same procedure was used to analyse samples of Synthappret BAP cured for 10 seconds at 100°C, 160°C and 200°C.

2.6 Methods for the Preparation of Various Ink Formulations

The following sections detail the recipes for the preparation of inks tested throughout the investigation.

2.6.1 Screen Printing Ink Formulation 1 Containing 15% Synthappret BAP

A basic screen ink was formulated using the following recipe:

- Alginate (MANUTEX RS210) 4%
- Binder (Synthappret BAP) 15% (of solution provided)
- Hostaperm pigment 5%
- Water 76%

It should be noted that all formulations are given as recipes using a weight for weight percentage value for each component with each ink having a final mass of 200g. The formulation was prepared and characterised using the method detailed in Section 2.3.3.

The substrate was then taken and thermally cured in a Werner Mathis KTF 4099 curing oven at 120°C, one piece for 20 seconds and a further piece for 2 minutes. After initial fastness tests, a further set of samples were printed and cured in a Werner Mathis KTF 4099 curing oven at 200°C for 10 seconds, 20 seconds, 30 seconds, 60 seconds, 2 minutes and 3 minutes.

2.6.2 Screen Printing Ink Formulation 2 – Addition of Ethanol to Aid Drying

In order to try and increase the drying rate of the printed samples, a second ink containing ethanol in place of some of the water was formulated. The premise was that the ethanol would evaporate at a greater rate than the water thus reducing the time required to dry the printed samples. The following recipe was formulated and characterised using the method detailed in Section 2.3.3.

- Alginate (MANUTEX RS210) 4%
- Binder (Synthappret BAP) 15%
- Hostaperm pigment 5%
- Water 71%
- Ethanol 5%

Screen Printing Ink Formulation 2 was cured in a Werner Mathis KTF 4099 curing oven at 200°C for 10 seconds, 20 seconds, 30 seconds, 60 seconds, 2 minutes and 3 minutes.

2.6.3 Screen Printing Ink Formulation 3 – Addition of Sodium Hydroxide

It is known that Synthappret BAP cross-links more readily in alkaline conditions. It was therefore decided to include a small amount of sodium hydroxide in the original ink formulation. Under normal conditions, Synthappret BAP has a pH of around 3.5. In Formulation 3, the same recipe was used as for Formulation 2 with the inclusion of a sufficient amount of sodium hydroxide (1M solution) was to ensure that the final formulation had a pH of 11, at the stage at which the Synthappret BAP was blended with the water. Screen printing Ink Formulation 3 was then taken, screen printed onto cotton and cured in a Werner Mathis KTF 4099 curing oven at 200°C for 10 seconds, 20 seconds, 30 seconds, 60 seconds and 2 minutes.

2.6.4 Screen Printing Ink Formulation 4 – Reduction of Thickener to Produce a Thinner Layer of Ink

In a further effort to increase the drying rate of the ink, it was decided to attempt to produce a thinner layer of ink on the surface of the substrate by reducing the amount of thickener in the formulation. It was thought that a thinner layer of ink would allow

for faster evaporation of water thus leaving more energy for cross-linking of the Synthappret BAP on the fabric. As a result, the amount of Alginate (MANUTEX RS210) given in Screen Printing Ink Formulation 1 was halved to 2% and the water level increased to 78% accordingly. Such a formulation was prepared and characterised according to the method outlined in Section 2.3.3.

Screen Printing Ink Formulation 4 was screen printed onto cotton and cured in a Werner Mathis KTF 4099 curing oven at 200°C for 10 seconds, 20 seconds, 30 seconds, 60 seconds, 2 minutes and 3 minutes.

2.6.5 Screen Printing Ink Formulation 5 – Increased Concentration of Synthappret BAP

The amount of binder included in the formulations to this point had remained constant. Therefore, it was decided to increase the amount of Synthappret BAP to further increase the rate of cure of the ink. The following formulation designed was prepared and characterised according to the method outlined in Section 2.3.3.

- Alginate (MANUTEX RS210) 4%
- Binder (Synthappret BAP) 30%
- Hostaperm pigment 5%
- Water 61%

Fixing of the print involved thermal curing using a Werner Mathis KTF 4099 curing oven at 200°C for 10 seconds, 20 seconds, 30 seconds, 60 seconds, 2 minutes and 3 minutes.

2.6.6 Screen Printing Ink Formulation 6 – Further Increase in Synthappret BAP

A further increase in the amount of binder was attempted. In this case, to compensate for the increased viscosity of the ink formulation as a result of the increased level of Synthappret BAP, the amount of thickener and pigment were reduced accordingly whilst maintaining the appropriate ink properties to give the following formulation prepared and characterised according to the method outlined in Section 2.3.3.

- Alginate (MANUTEX RS210) 4%
- Binder (Synthappret BAP) 50%

- Hostaperm pigment 3%
- Water 45%

Fixing of the print involved thermal curing using a Werner Mathis KTF 4099 curing oven at 200°C for 10 seconds, 20 seconds, 30 seconds, 60 seconds, 2 minutes and 3 minutes.

2.6.7 Screen Printing Ink Formulation 7 – Introduction of Sodium Bicarbonate

It has been reported Bell et al. and by Cook and Fleischfresser that sodium bicarbonate acts as an accelerator in the cross-linking mechanism of Synthappret BAP (Bell et al., 1985; Cook and Fleischfresser, 1985). It was therefore decided to incorporate 1% of sodium bicarbonate into Screen Printing Ink Formulation 6. The sodium carbonate was added along with the Alginate (MANUTEX RS210) thickener in the process outlined in Section 2.3.3. The resulting ink formulation had a pH of 8. Screen Printing Ink Formulation 7 was then printed and cured as previously detailed.

2.6.8 Preparation and Characterisation of Ink Jet Printing Inks for Application onto Textile Materials

The investigation into the use of Synthappret BAP as a binder in a screen printing ink was found to be successful. It was therefore decided to continue the investigation in terms of the use of Synthappret BAP as a binder within an ink jet ink formulation. Ink jet inks are required to require low viscosities and the ink jet process imparts less ink to the substrate and as such, the quantity of Synthappret BAP that can be applied is limited. Prior to using it within a full ink formulation it was necessary to evaluate the printability of Synthappret BAP in terms of an ink jet printing process.

2.6.9 Printing of Synthappret BAP as a Shrink Resist Treatment

Before formulating complete ink jet inks containing pigments, it was decided to ink jet print a Synthappret BAP formulation without colorant to see if the process was a viable option. As Synthappret BAP is widely used as a shrink resist treatment for wool fibres, it was decided to ink jet print wool with a Synthappret BAP formulation and then apply a shrinking treatment.

2.6.9.1 Shrinkage Treatment

Once printed and cured, the wool samples were felted using a shrinkage treatment. Such a treatment comprised of a process of milling the wool by hand for 10 minutes with a soap concentrate. After this treatment, the samples were rinsed with cold water and air dried in order to see the extent of the sculpting effect achieved.

2.6.9.2 Shrink Resist Ink Formulation 1

An initial shrink resist ink formulation was prepared according to the following recipe:

- Synthappret BAP 25%
- IPA 10%
- Ethylene Glycol 10%
- Water 55%

2.6.9.3 Method 1 of Ink Preparation

One method of ink preparation consisted of the following steps. Water, IPA and ethylene glycol were weighed out accurately and blended together using a magnetic stirrer for 5 minutes. The Synthappret BAP was then added and the formulation mixed for a further 10 minutes to ensure homogeneity. The formulation was tested for viscosity and surface tension following the procedures detailed in Section 2.4.1 and Section 2.4.2. The resulting ink formulation was then introduced into an ink jet cartridge and printed onto wool using an Apollo P1200 ink jet printer. Once printed, the wool sample was cured at 150°C for 3 minutes in a Werner Mathis KTF 4099 curing oven.

2.6.9.4 Shrink Resist Ink Formulation 2 – Increased amount of Synthappret BAP

A further ink formulation was formulated in the same way as Shrink Resist Formulation 1 except that 30% Synthappret BAP was incorporated and the amount of water reduced accordingly. The ink was printed onto wool and cured following the procedures detailed in Method 1.

2.6.9.5 Method 2 of Ink Preparation

The shrink resist ink formulations were prepared and tested for their viscosity and surface tension following the procedures detailed in Method 1. In a further method,

the formulations were printed onto wool twice. Thus, after the initial print the samples were fed through the printer again in order for a second layer of the ink to be printed on top of the first to deliver a greater amount of Synthappret BAP onto the wool surface. The process of felting was repeated following the procedures detailed in Section 2.6.9.1.

2.6.9.6 Shrink Resist Ink Formulation 3 – Incorporation of Colorant

It was considered necessary to introduce a colorant into Shrink Resist Ink Formulation 1 so that the sculpted area was a coloured design. Such a procedure would aid to prove the printability of Synthappret BAP within a pigmented ink formulation. The colorant chosen was a pigment pre-dispersion Cab-O-Jet Magenta 260 M supplied by Cabot Corp. The ink formulation was made up as follows:

- Synthappret BAP 25%
- Ethylene Glycol 5%
- Pigment dispersion 5%
- Water 65%

The formulation was printed onto wool and cured following the procedures detailed for Method 2.

2.6.10 Toner Ink Formulation 1

The formulation was made up using the following recipe where the amounts of each component are given as weight for weight percentages in a total mass of 200g. The formulation was made up via a pigment concentrate and prepared and characterized according to the methods outlined in Section 2.3.4.

- Pigment concentrate 20%
- Dispersant 1%
- DEG 5%
- EG 5%
- IPA 5%
- Synthappret BAP 10%
- TEGOWET 590 1 drop

- Water 54%

The ink was used to ink jet print cotton samples, which were cured and characterized according to the method detailed in Section 2.3.4.

2.6.10.1 Calculation of the Amount of Ink Deposited

In order to assess the success of the printing, the amount of ink deposited was calculated. This was achieved by weighing an A4 size transparency before and after printing and calculating the difference. The difference in weight could then be determined to be the weight of the ink printed. The samples were weighed on a four decimal point balance to ensure accuracy. To achieve accurate results, the printing and weighing were repeated three times and an average taken for each print setting.

2.6.11 Toner Ink Formulation 2 – Increased Concentration of Pigment

In an attempt to increase the colour strength of Toner Ink Formulation 1, a second ink with an increased amount of pigment concentrate and binder was prepared. The new formulation prepared and characterised using the following recipe according to the method detailed in Section 2.3.4.

- Pigment concentrate 25%
- Dispersant 1%
- DEG 5%
- EG 5%
- IPA 5%
- Synthappret BAP 12.5%
- TEGOWET 590 1 drop
- Water 46.5%

Toner Ink Formulation 2 was then printed onto cotton and onto polyester, cured and tested for its fastness properties following the procedures detailed in Section 2.3.4.

2.6.12 Toner Ink Formulation 3 – One Step Process

A further ink was prepared using Toner pigments. In this case, instead of basing the formulation on a pigment concentrate, the ink was made in a one step formulation according to the method outlined in Section 2.3.4 using the following recipe:

- Pigment 4%
- Synthappret BAP 10%
- DEG 3%
- EG 3%
- IPA 5%
- Dispersant 2%
- TEGOWET 590 1 drop
- Water 73%

This characterisation of the ink was repeated after 3 weeks to ascertain whether the physical properties of the ink changed over a period of time.

2.6.13 Toner Ink Formulation 4 – Incorporation of a Slip Additive

In an attempt to improve the rubfastness of the inks, a further ink was created which incorporated an anti slip additive. The additive chosen, in this case was Lubrisil CR 200 supplied by Brookstone Chemicals Ltd. Lubrisil CR 200 was a silicon based emulsion (Brookstone Chemicals, 1999). The ink was prepared and characterized according to the methods outlined in Section 2.3.4.

- Pigment concentrate 20%
- Lubrisil CR 200 1%
- DEG 5%
- EG 5%
- IPA 5%
- Synthappret BAP 10%
- Dispersant 1%

- Water 53%

The resulting samples were tested for their washfastness and rubfastness following the procedures detailed in Section 2.3.4.

2.6.14 Microlith Formulation 1 - Initial Ink

For the preliminary investigation into the suitability of Microlith pigments for inclusion in ink jet formulations, Microlith Magenta B-WA was predominantly used. SEM was used to analyse the pigment in its crystalline form and in the pigment paste containing water, IPA and ammonia to see the extent of the dispersibility of the Microlith pigment.

Microlith Formulation 1 was prepared and characterised using the following recipe according to the method outlined in Section 2.3.5.

- Pigment paste 6%
- DEG 10%
- PEG 10%
- Binder 10%
- Water 64%

The ink was printed onto cotton, cured and the printed fabric characterised according to the method outlined in Section 2.3.6.

2.6.15 Microlith Formulation 2 – Replacement of Ammonia with Sodium Hydroxide

In this formulation, a different pigment paste was used in which the ammonia was replaced by sodium hydroxide as the alkaline constituent helping to achieve the partial solubility of the pigment. The amount of binder (Synthappret BAP) was also increased to 15% and made up to the following recipe according to the method outlined in Section 2.3.6.

- Pigment Paste 5%
- Binder 15%
- PEG 10%

- DEG 10%
- Water 60%

Once complete the ink was printed onto cotton, cured and the printed fabric characterised according to the method outlined in Section 2.3.6.

2.6.16 Cabot Ink Formulation 1 – Initial Ink

As mentioned in Section 2.1.1.3 Cabot produces a range of pigments tailored specifically for use in ink jet printing. These pigments were supplied as dispersions of between 10% and 30% solids and were seen to have a low viscosity and high surface tension.

An initial formulation was made using Cab-O-Jet Magenta 260 M. This particular pigment was supplied as a dispersion containing 10% solids. Cabot Formulation 1 was prepared to the following recipe according to the method outlined in Section 2.3.7.

- Pigment dispersion 30%
- DEG 5%
- EG 5%
- IPA 5%
- Synthappret BAP 5%
- Water 45%

Once complete the ink was printed onto cotton and polyester, cured and the printed fabric characterised according to the method outlined in Section 2.3.7.

2.6.17 Cabot Ink Formulation 2 – Incorporation of a Slip Additive

In an attempt to improve the rubfastness of the printed textile, a slip additive commonly used in the dyeing industry was incorporated into the ink formulation. The additive chosen was Lubrisil CR 200 supplied by Brookstone Chemicals Ltd. Lubrisil CR 200 was supplied as a non-ionic silicone based emulsion (Brookstone Chemicals, 1999). The aim of incorporating this product was to aid the slip properties of the print and discourage the removal of colour when rubbed. Thus, Cabot Ink Formulation 2 was prepared to the following recipe according to the method outlined in Section 2.3.7.

- Pigment dispersion 20%
- Lubrisil CR 200 2.5%
- Synthappret BAP 10%
- IPA 5%
- EG 5%
- DEG 5%
- Deionised water 52.5%

Once complete Cabot Ink Formulation 2 was printed onto cotton and polyester, cured and the printed fabric characterised according to the method outlined in Section 2.3.7.

2.6.18 Cabot Ink Formulation 3 – Pre-Treatment of the Substrate

As it was known that the cross-linking reaction of Synthappret BAP was enhanced by the presence of sodium bicarbonate (Fleischfresser, 1982; Bell et al. 1985). As such, a sample of cotton was pre-treated with sodium bicarbonate with the intention of catalysing the cross-linking reaction of the Synthappret BAP during the curing process. During the investigation into screen printing inks, it was discovered that the presence of sodium bicarbonate within the actual ink formulation caused premature cross-linking of the Synthappret BAP at ambient temperatures prior to any printing process. Thus, this option was disregarded for ink jet inks.

A 1 molar solution of sodium bicarbonate in water was prepared. Cotton fabric was soaked in this solution for 30 minutes and then air dried prior to being prepared for printing following the procedures detailed in Section 2.3.1. Cabot Ink Formulation 3 was formulated according to the following guideline:

- Synthappret BAP 10%
- EG 5%
- IPA 5%
- Pigment dispersion 10%
- Water 70%

Once complete Cabot Ink Formulation 3 was printed onto cotton and polyester, cured

and the printed fabric characterised according to the method outlined in Section 2.3.7.

In a further attempt to increase the rub resistance of the printed substrate, a number of slip agents and anti mar additives were tested within an ink jet ink made with Cab-O-Jet pigment dispersions. These are discussed in the following sections.

2.6.19 Cabot Ink Formulation 4 – Incorporation of Lubit 64

It was decided to incorporate a commercially available dye bath lubricant within an ink. Lubit 64 was a dye bath lubricant supplied by Bayer specifically for cellulosic, synthetic fibres and blends (Bayer, 2001). Cabot Ink Formulation 4 was prepared containing a concentration of 2% by weight of Lubit 64 according method outlined in Section 2.3.7.

- Synthappret BAP 10%
- EG 5%
- IPA 5%
- Lubit 64 2%
- Pigment dispersion 10%
- Water 68%

Once complete Cabot Ink Formulation 4 was printed onto cotton and polyester, cured and the printed fabric characterised according to the method outlined in Section 2.3.7.

2.6.20 Cabot Ink Formulation 5 – Incorporation of Dow Corning 51 Additive

An additive designed to impart slip and mar resistance in flexographic and gravure inks was obtained from Dow Corning. Dow Corning 51 Additive was a high molecular weight polydimethyl silicone dispersion and was water dispersible (Dow Corning, 2000). Its intended use was within water based flexographic and gravure inks at concentrations of 0.05-0.2%. Thus, it was decided to incorporate such an additive within Cabot Ink Formulation 5 at a concentration of 0.05%. Due to its high viscosity, even low levels may adversely affect the balance of the ink. Thus, Cabot Ink Formulation 5 was prepared according to the method outlined in Section 2.3.7.

- Synthappret BAP 10%
- EG 5%

- IPA 5%
- Dow Corning 51 Additive 0.05%
- Pigment dispersion 10%
- Water 69.95%

Once complete Cabot Ink Formulation 5 was printed onto cotton and polyester, cured and the printed fabric characterised according to the method outlined in Section 2.3.7.

2.6.21 Cabot Ink Formulation 6 – Incorporation of Michem Lube 182

A third slip additive identified was Michem Lube 182. Michem Lube 182 was supplied by Michelman Inc. in the form of an anionic co-emulsion of carnauba and paraffin waxes (Michelman Inc., 2001). A 2% by weight concentration of Michem Lube 182 was incorporated into Cabot Ink Formulation 6 according to method outlined in Section 2.3.7.

- Synthappret BAP 10%
- EG 5%
- IPA 5%
- Michem Lube 182 2%
- Pigment dispersion 10%
- Water 68%

Once complete Cabot Ink Formulation 6 was printed onto cotton and polyester, cured and the printed fabric characterised according to the method outlined in Section 2.3.7.

2.7 Investigation into the effect of Increased Amounts of Synthappret BAP within an Ink Jet Ink

The formulations made up for application via screen printing were found to have improved fastness properties and cure rates when the amount of Synthappret BAP within the formulation was increased. It was therefore decided to increase the amount of Synthappret BAP within the ink jet formulations and to assess the suitability of the resulting inks for ink jet printing.

In order to ascertain the effect of binder on the physical properties of an ink jet ink, a set of inks was prepared and characterised using the following generic formulation according to the method outlined in Section 2.3.7.

- Synthappret BAP (5%)
- IPA 5%
- DEG 5%
- EG 5%
- Pigment dispersion 10%
- Water (70%)

Formulations were made up containing 5%, 10%, 15%, 20%, 25% and 40% Synthappret BAP respectively with the amount of water contained in each varied accordingly.

If the formulations were seen to comply with the guidelines acceptable for ink jet printing via a desktop printer, i.e. $<10 \text{ mPa.s}$ and between 30 and 60 mNm^{-1} , they were printed onto cotton and characterized according to the method outlined in Section 2.3.7. Each of the ink formulations was also tested for pH and particle size to ascertain the effect of increased amounts of Synthappret BAP on these parameters and the stability of each subsequent ink.

2.8 Evaluation of Pigments for Their Suitability for Ink Jet Printing

As mentioned in Section 1.4.3, it was necessary for an ink to have certain physical properties in order for it to be a long term option for ink jet printing. The stability of an ink is vital in whether or not it will be acceptable for such a process. In order to assess the suitability of the three chosen pigments for ink jet inks, a series of tests was devised.

Pigment concentrates/dispersions were prepared and their jettability evaluated. This was followed by blending the pigment dispersions with other suitable ingredients to give ink formulations. The printability of such ink formulations and the quality of the printed and cured images on textile fabrics were assessed. It should be noted that the term “jettability” was used to refer to the ease at which printing occurred and how well the ink jetted onto the substrate.

2.8.1 Preparation of Pigment Dispersions

All percentages concerned are percentages by weight. Each of the pigments was dispersed in deionised water to give a 1 % formulation. In particular,

The Toner Magenta E02 dispersion was prepared by mixing the pigment (1%) with 2% of dispersing agent (Solsperse 27000) and 97% of deionised water and milled for 1 hour using the Eiger-Torence bead mill.

The Microlith Magenta B-WA dispersion was prepared by initially making a paste following the procedures detailed for Section 2.3.6. Such a paste was then used to make a dispersion containing 1% pigment and 99% deionised water which was mechanically stirred for 1 hour to achieve uniformity.

The Cab-O-Jet Magenta 260 M dispersion was prepared by blending 1% of the pigment pre-dispersion in 99% of deionised water followed by mechanical stirring for 1 hour.

2.8.2 Preparation of Ink Jet inks

For the purpose of the current investigation, a general formulation was employed. Thus, each of the pigments was used in the formulation of an ink jet ink to the following specification using the same methods as for the preparation of the pigment dispersions:

- Pigment 2%
- Binder 15%
- Ethylene Glycol 5%
- IPA 5%
- Water 73%

It should be noted that the ink formulation containing Toner Magenta E02 included 2% Solsperse 27000 as a dispersing agent, thus reducing the content of the deionised water to 71%.

2.8.3 Characterisation of particle size and particle size distribution

Particle size and particle size distribution of the pigment dispersions prepared were measured using the Coulter N135 particle size analyser immediately after preparation,

1 week and 4 weeks after the preparation of the dispersion following the procedures detailed in Section 2.4.2. Freeze/thaw cycling was carried out as described by Bugner and Bermel. (Bugner and Bermel, 1997). Thus, the dispersions were held for 24 hours at -20°C followed by 24 hours at 60°C. This process formed one cycle and was repeated for 4 cycles. The dispersions were also monitored visually for any signs of pigment sedimentation.

2.8.4 Characterisation of inkjet parameters and stability

As mentioned previously in Section 1.4.4, the stability of the pigment dispersion was of significant importance for inkjet printing inks. A widely accepted method for the evaluation of the stability of a pigment dispersion is the monitoring of the relevant properties of the pigment dispersion over a period of time. In this study, the viscosity, the surface tension and the pH stability of the pigment dispersions prepared were monitored over a period of 4 weeks.

2.8.5 Effect of pH on the Dispersions

The pH of the pigment dispersion was varied at 2, 3, 7 and 12, by the addition of either diluted hydrochloric acid solution (1 molar solution) or diluted sodium hydroxide solution (1%). Visual assessments of the subsequent effect of the pH variation on the pigment suspension were made.

2.8.6 Measurement of Viscosity

The pigment dispersions and ink formulations were measured for their viscosity following the procedures detailed for Section 2.4.1. These measurements were carried out over a period of 4 weeks in order to determine the effect of any pigment settling on the viscosity of the inks.

2.8.7 Measurement of Surface Tension

The pigment dispersions and the ink formulations were measured for their surface tension following the procedures detailed for Section 2.4.2. Such measurements were carried out over a period of 4 weeks in order to determine the effect of any pigment settling on the surface tension of the inks.

2.8.8 Printing of the Ink Formulations – Assessment of Jettability

The ink formulations were printed onto cotton and polyester fabrics using an Apollo P2100 ink jet printer. All preparation of the cartridges and fabric samples for printing was carried out following the procedures detailed in Section 2.3.1 and Section 2.3.2. Once printed, the fabric samples were cured at 200°C for 2 minutes in a Werner Mathis KTF 4099 curing oven.

2.8.9 Assessment of the Fastness Properties

Both the wash-fastness and the rub-fastness of the printed and cured fabric (cotton and polyester) samples were assessed. These tests were carried out following the procedures detailed in Section 2.4.8 and Section 2.4.9.

2.8.10 Assessment of Colour Characteristics of the Pigments

The colour characteristics of both the pigment dispersions and the ink formulations were assessed. For the pigment dispersions, optical density of the drawdown samples, prepared using a No. 2 K-bar and standard white photocopy paper, was measured. For the ink formulations, optical density of the prints on both cotton and polyester fabrics was measured. All measurements of optical density were taken using both the Gretag D183 optical densitometer and the X-Rite SP68 Spectrophotometer.

2.8.11 Assessment of Jettability through Print Image Quality

The printed samples were visually assessed for their print quality and graded poor, average or good accordingly. Image qualities such as the dot quality, the dot position, the line quality, the mottle, the text quality and the registration all make a significant contribution to the visual effect of the image. All these image qualities could be measured using the ImageXpert image analysis system. For the purposes of this investigation, dot qualities such as the dot area, the dot roundness, the centre-to-left distance, the centre-to-right distance, the centre-to-top distance and the centre-to-bottom distance were obtained through the ImageXpert system (KDY Inc., 1999). The marked area, shown in Figure 2.16, was chosen for analysis, this being a solid circle of colour. The same image printed on standard copy paper using the HP LaserJet 4P printer was used as standard for purpose of comparison. The ImageXpert software was then used to measure the area of the circle, its roundness and its dimensions from

the centre of the circle to its extremities at the left, the right, the top and at bottom. It should be noted that that the area of the image being analysed referred to the total area of the “dot” including any joined satellites, the roundness referred to the roundness of the blob and the centre was the geometric centre of the “dot”.

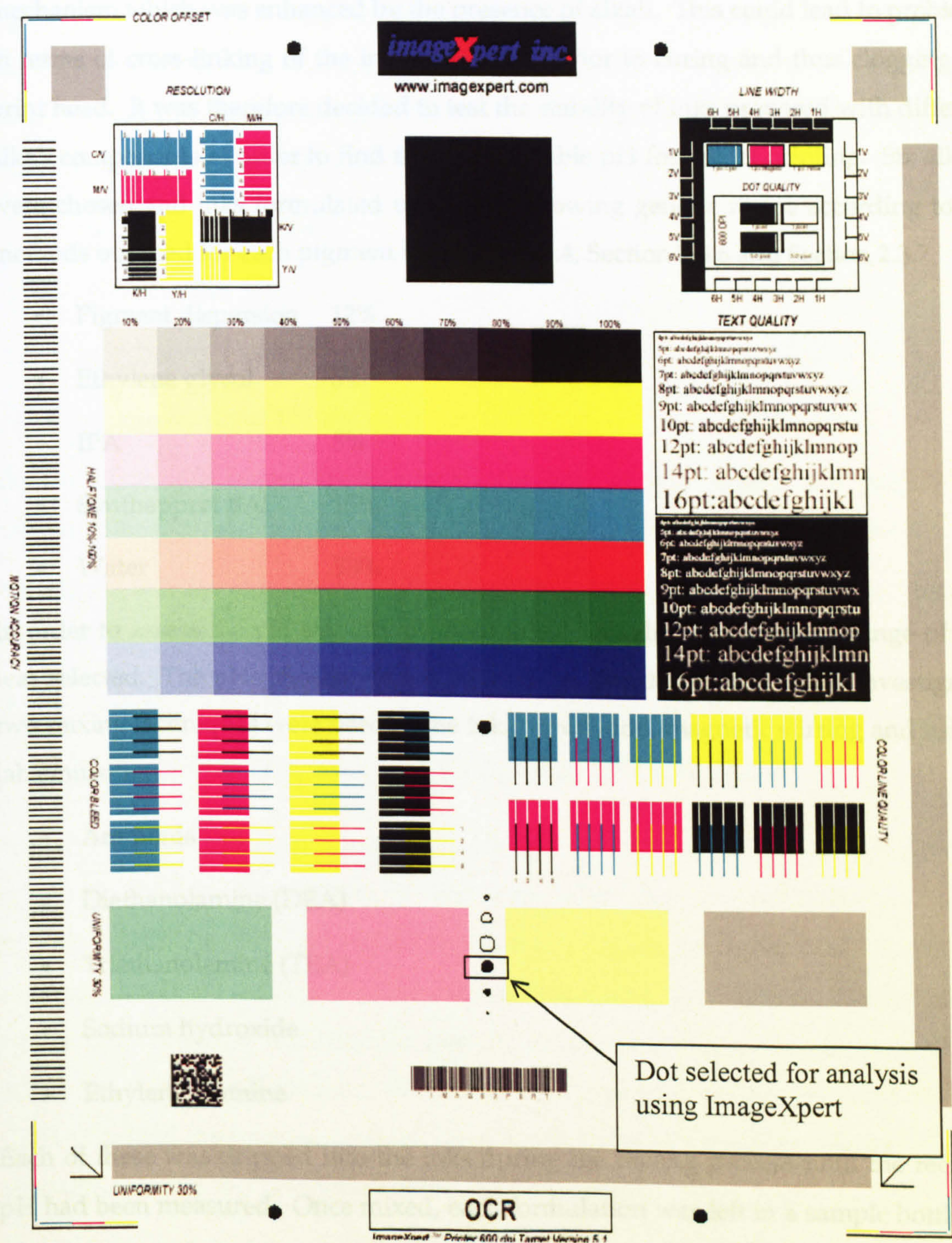


Figure 2.8.a ImageXpert test pattern detailing the area selected for image analysis

2.9 Investigation into the pH Stability of Synthappret BAP

As mentioned in Section 2.1.1.2, Microlith pigments were partially soluble under alkaline conditions. Other pigments may require the presence of slightly alkaline conditions in order to remain well dispersed within a formulation. The binder used within this investigation, Synthappret BAP, was seen to have a cross-linking mechanism which was enhanced by the presence of alkali. This could lead to problems in terms of cross-linking of the ink formulation prior to curing and thus clogging the print head. It was therefore decided to test the stability of inks prepared with different alkali components in order to find the most suitable pH for ink jet printing. Six alkalis were chosen and inks formulated using the following generic recipe according to the methods outlined for each pigment in Section 2.3.4, Section 2.3.6 and Section 2.3.7.

- Pigment dispersion 12%
- Ethylene glycol 5%
- IPA 5%
- Synthappret BAP 15%
- Water 53%

In order to assess the pH stability of these inks to alkaline conditions a range of pHs was selected. The pHs chosen were 8, 11, and 14. For this section of the investigation two mixing techniques were used in the ink formulation, magnetic stirring and using a lab emulsifier.

- Ammonia
- Diethanolamine (DEA)
- Triethanolamine (TEA)
- Sodium hydroxide
- Ethylene diamine

Each of these was dripped into the inks during the mixing process until the required pH had been measured. Once mixed, each formulation was left in a sample bottle and any changes in their appearance over a period of 2 weeks were noted.

2.10 Assessment of Cabot Ink Formulation in Comparison to an Alternative Commercially Available Set of Inks

In order to obtain an idea of the relative ink performance, it was decided to compare the inks prepared with a commercially available alternative. A set of water-based pigmented ink jet inks produced by Ciba Speciality Chemicals was obtained. The Irgaphor ranges of inks were optimised pigmented systems which could be printed directly onto the required substrate without any pre-treatment. The inks must be fixed with dry heat for 3 to 5 minutes at between 160 and 180°C. It was decided to choose four colours equivalent to those formulated, these being:

- Irgaphor Black TBI 800
- Irgaphor Blue TBI 500
- Irgaphor Red TBI 300
- Irgaphor Yellow TBI 100

Each of these inks was assessed for its viscosity, surface tension and particle size following the procedures detailed in Section 2.4.1, Section 2.4.2 and Section 2.4.3.

An attempt was made to obtain further commercially available inks, however, this was unsuccessful due to the commercial sensitivity of such products.

2.11 Formulation and Characterisation of a Four Colour Set of Inks for the Ink Jet Printing of Textiles

From the previous investigation into the effect of the concentration of Synthappret BAP within an ink jet formulation, it was concluded that the optimum amount of Synthappret BAP to be used within an ink was 15%. As such, this concentration was used to provide the basis of a set of inks encompassing the colorants required for ink jet printing. From the investigation into the long term stability of pigments within an ink jet ink, it was concluded that the Cab-O-Jet pigment dispersions provided by Cabot Corp. provided the greatest stability. As a result, Cab-O-Jet pigments were used as the colorants forming the base colour of the ink formulations.

The ink formulations were prepared to the following specifications and then characterized according to the method detailed in Section 2.3.7.

Cyan

- Synthappret BAP 15%
- Cab-O-Jet Cyan 250 C 15%
- EG 5%
- IPA 5%
- Water 60%

Magenta

- Synthappret BAP 15%
- Cab-O-Jet Magenta 260 M 15%
- EG 5%
- IPA 5%
- Water 60%

Yellow

- Synthappret BAP 15%
- Cab-O-Jet Yellow 270 Y 20%
- EG 5%
- IPA 5%
- Water 55%

Black

- Synthappret BAP 15%
- Cab-O-Jet Black 300 20%
- EG 5%
- IPA 5%
- Water 55%

The yellow and the black inks required the incorporation of extra pigment dispersion in order to attain the required colour strength on application to the substrate. It should also be noted that the incorporation of humectants was kept to a minimum in order to reduce the chances of any instability within the ink whilst still maintaining essential ingredients to aid the jetting process and the overall balance of the formulation.

Each ink was printed onto both cotton and polyester substrates, cured and characterized according to the method outlined in Section 2.3.7. The printed cotton and polyester were also assessed for any change in handle after printing following the procedures detailed in Section 2.4.10.

2.11.1.1 Thermal Stability of the Four Colour Set of Inks

In order to gauge the thermal stability of the ink formulations, each ink was held at 40°C over a period of 5 months. The physical properties of the inks i.e. the viscosity, the surface tension and the particle size of the inks were assessed over this period immediately after ink preparation, after 4 weeks and after 5 months. These tests were carried out to assess the thermal stability of the pigment within the ink at an extended period of time at elevated temperature and also the stability of the Synthappret BAP within the ink system at the given temperature.

3 Results and Discussion

The following chapter outlines the results obtained from the various printing and characterisation experiments carried out along with discussion of the findings.

3.1 Investigation into the Cross-linking Mechanism of Synthappret BAP

In an attempt to prove that the Synthappret BAP used as a binder within the ink formulations cross-linked on application of a high temperature, FTIR analysis was carried out on samples of cured and uncured Synthappret BAP. The findings of this analysis are detailed in this section.

In order to assess the cross-linking mechanism of the Synthappret BAP binder used within the investigation FTIR analysis was carried out. The spectra obtained for an uncured sample of Synthappret BAP and a fully cured sample of Synthappret BAP can be seen in Figure 3.3.a and Figure 3.3.b.

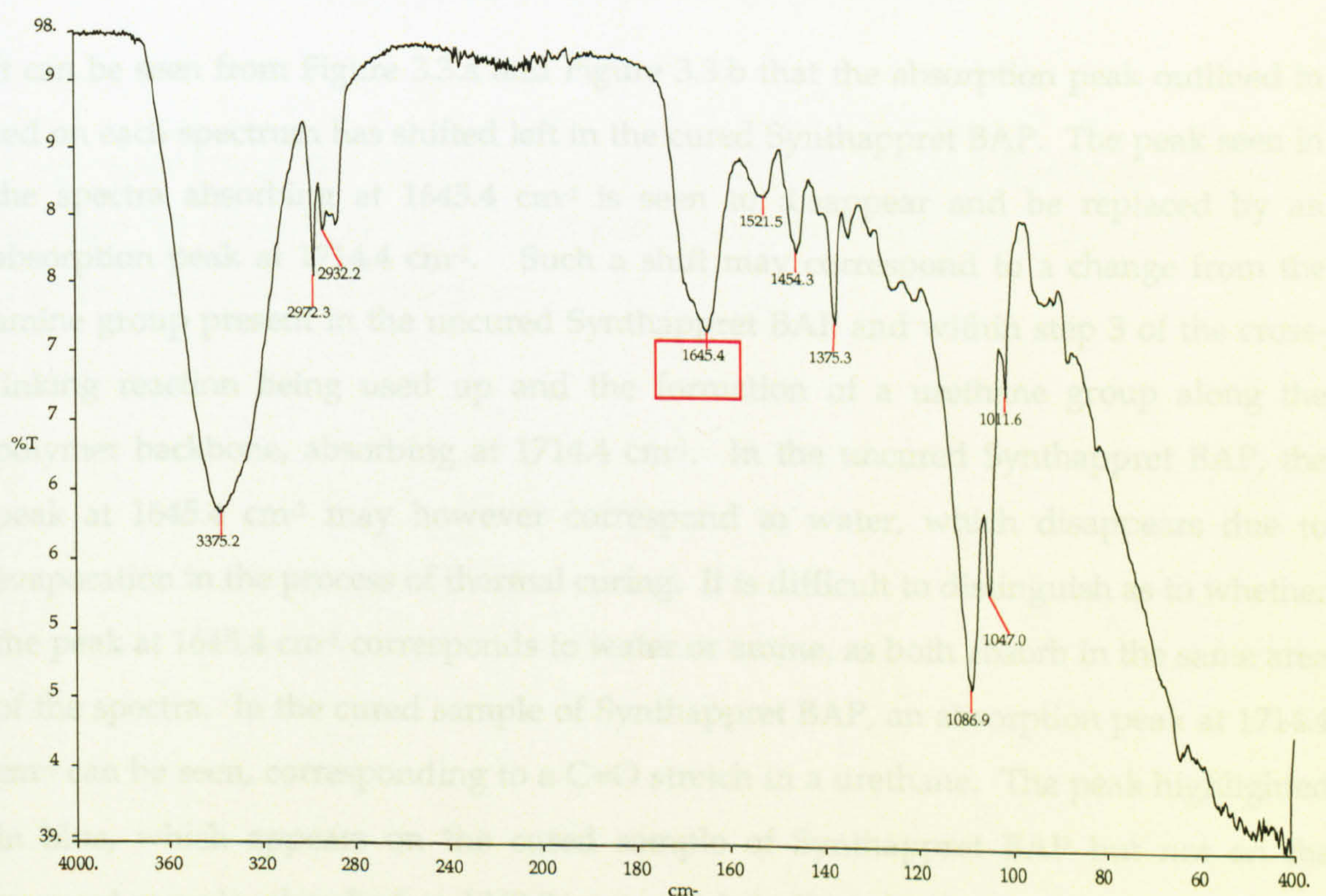


Figure 3.1.a FTIR spectrum of Synthappret BAP

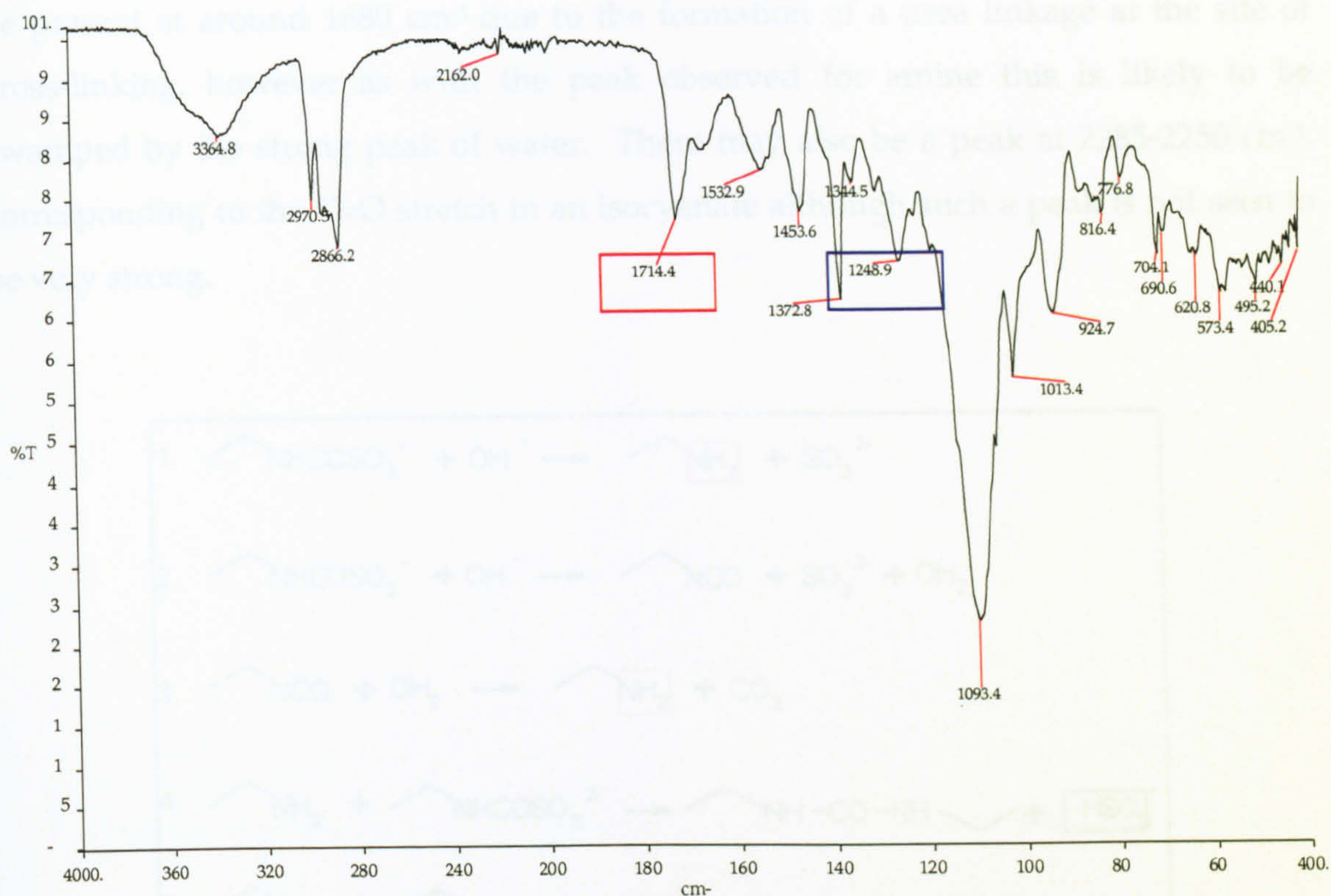


Figure 3.1.b FTIR spectrum of cross-linked Synthappret BAP

It can be seen from Figure 3.3.a and Figure 3.3.b that the absorption peak outlined in red on each spectrum has shifted left in the cured Synthappret BAP. The peak seen in the spectra absorbing at 1645.4 cm^{-1} is seen to disappear and be replaced by an absorption peak at 1714.4 cm^{-1} . Such a shift may correspond to a change from the amine group present in the uncured Synthappret BAP and within step 3 of the cross-linking reaction being used up and the formation of a urethane group along the polymer backbone, absorbing at 1714.4 cm^{-1} . In the uncured Synthappret BAP, the peak at 1645.4 cm^{-1} may however correspond to water, which disappears due to evaporation in the process of thermal curing. It is difficult to distinguish as to whether the peak at 1645.4 cm^{-1} corresponds to water or amine, as both absorb in the same area of the spectra. In the cured sample of Synthappret BAP, an absorption peak at 1714.4 cm^{-1} can be seen, corresponding to a C=O stretch in a urethane. The peak highlighted in blue, which appears on the cured sample of Synthappret BAP but not on the uncured sample, absorbed at 1243.9 cm^{-1} which indicated a S=O stretch within SO_3H which is formed during the cross-linking of the Synthappret BAP. The equations for the cross-linking reaction are given in Figure 3.3.c with the bonds of interest highlighted to correspond to their absorption peaks in the FTIR spectra. A Peak may

be present at around 1680 cm^{-1} due to the formation of a urea linkage at the site of cross-linking, however as with the peak observed for amine this is likely to be swamped by the strong peak of water. There may also be a peak at $2285\text{--}2250\text{ cm}^{-1}$, corresponding to the $\text{C}=\text{O}$ stretch in an isocyanate although such a peak is not seen to be very strong.

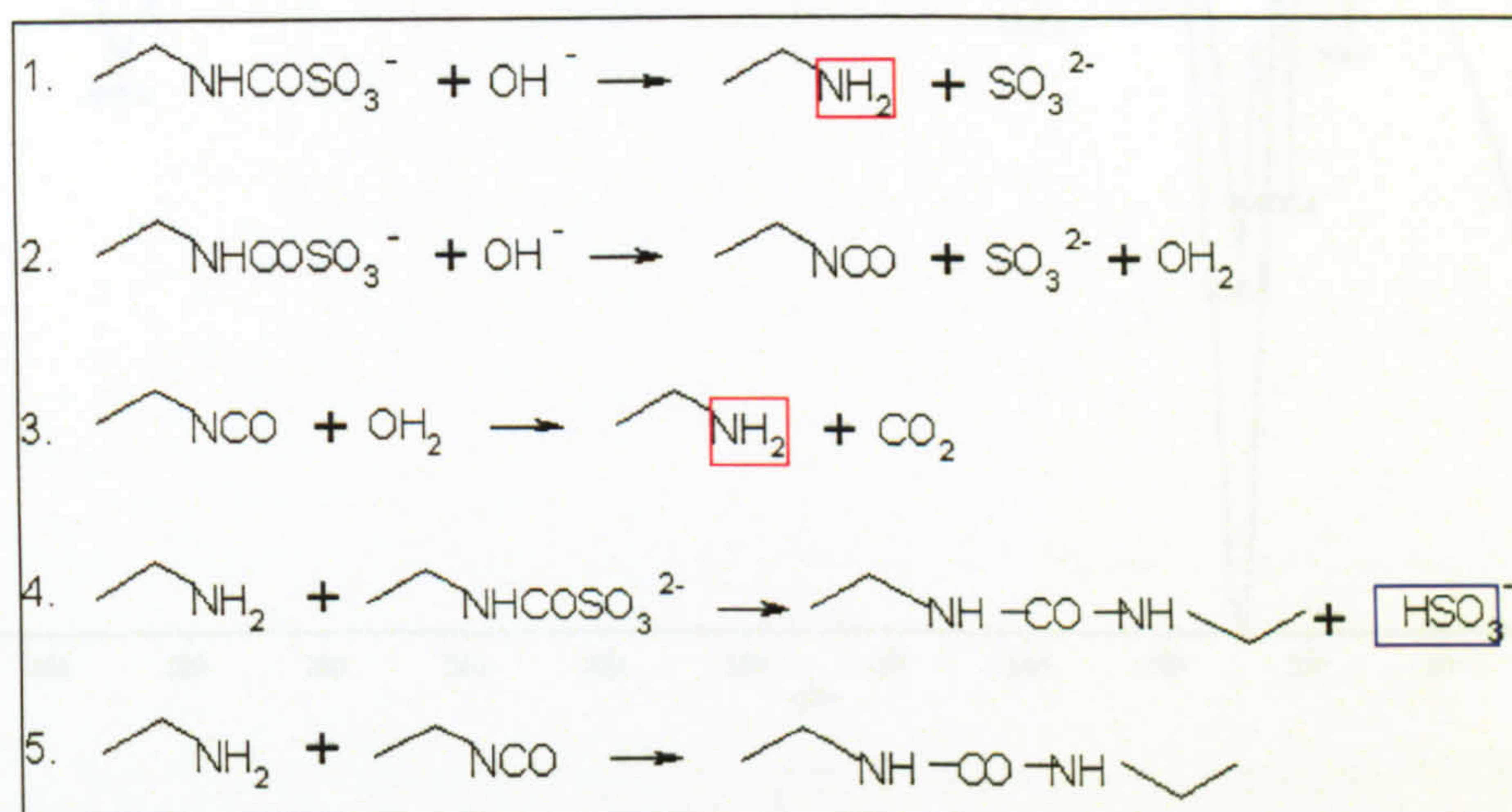


Figure 3.1.c Equations detailing the cross-linking mechanism of Synthappret BAP and highlighting the groups analysed using FTIR

In order to assess the extent of cure, samples of Synthappret BAP cured for 10 s at 150°C were analysed. A spectrum containing an overlap of the cured and uncured Synthappret BAP to highlight the changes can be seen in Figure 3.3.d. The cured sample is the black curve with the uncured sample being blue.

It can be seen from Figure 3.3.e that there is some evidence for splitting of the $\text{C}=\text{O}$ absorption peak observed for the formation of a urethane. However, for the sample cured at 150°C for 10 s the strongest peaking is at 1680.0 cm^{-1} , which indicates that the cross-linking mechanism has not occurred and that either water or amine was present.

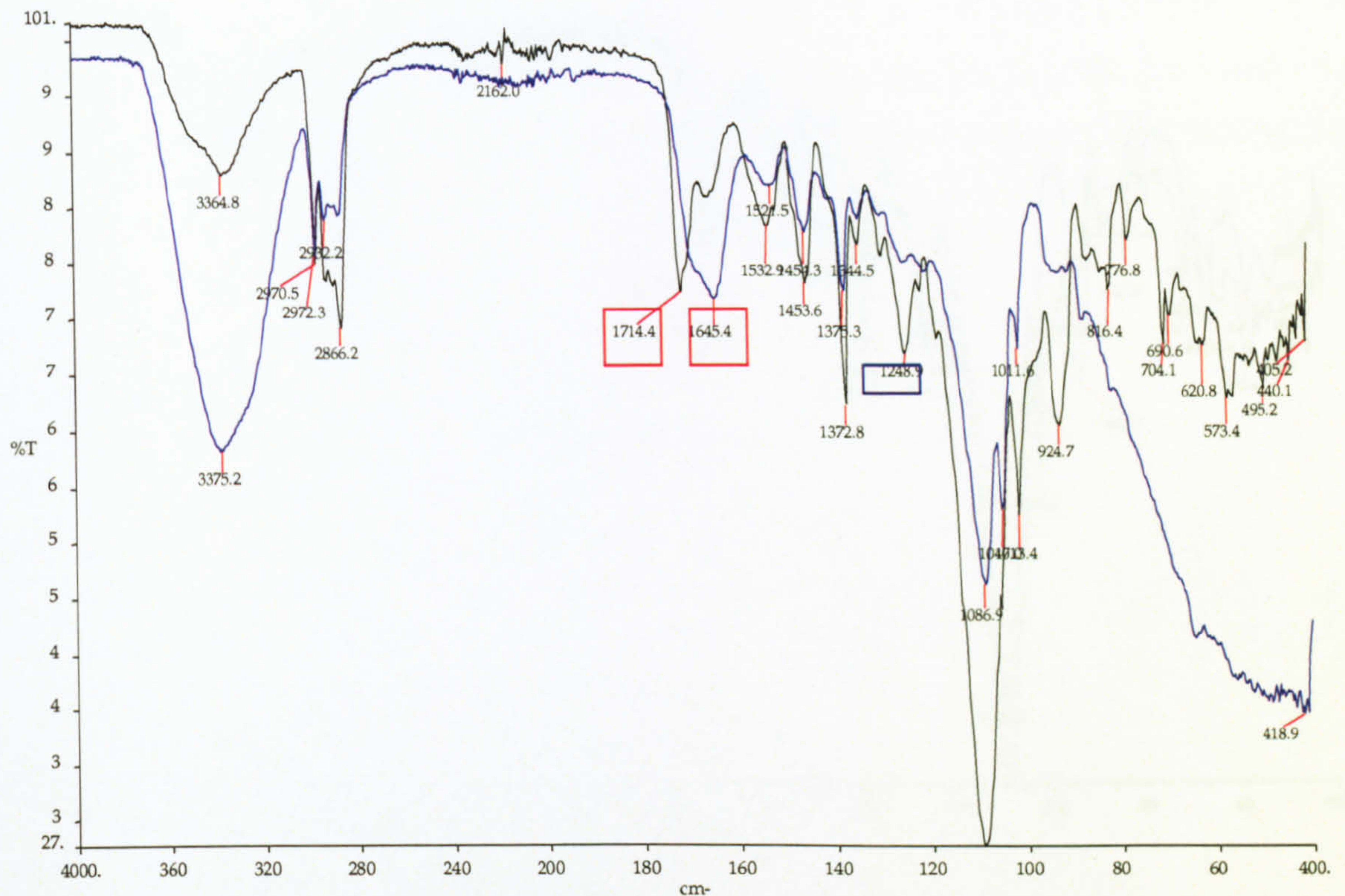


Figure 3.1.d FTIR spectra showing the change in absorbance of Synthappret BAP after cross-linking

In order to assess the extent of cure, samples of Synthappret BAP cured for 10 s at 100°C, 160°C and 200°C were analysed and compared to the fully cured sample of Synthappret BAP. The spectra obtained from the FTIR analysis of these samples can be seen in Figure 3.3.e to Figure 3.3.g. In each spectrum the black line is the fully cured sample of Synthappret BAP.

It can be seen from Figure 3.3.e that there is some evidence for splitting of the C=O absorbance peak observed for the formation of a urethane. However, for the sample cured at 100°C for 10 s the strongest peaking is at 1695.0 cm⁻¹, which indicates that the cross-linking mechanism has not occurred and that either water or amine was present.

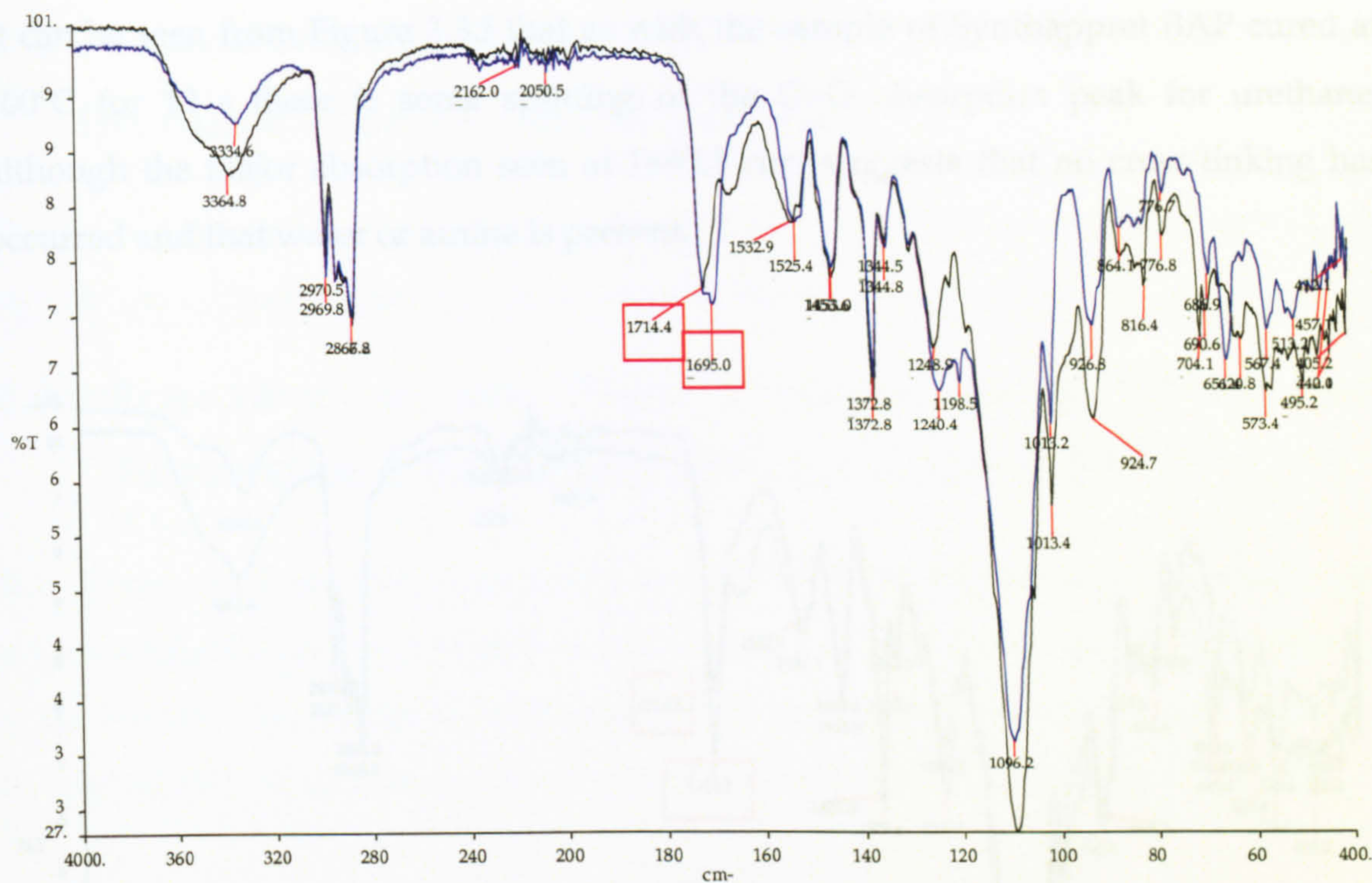


Figure 3.1.e FTIR spectra highlighting the effect of curing of Synthappret BAP at 100 °C for 10 s against a fully cross-linked sample of Synthappret BAP

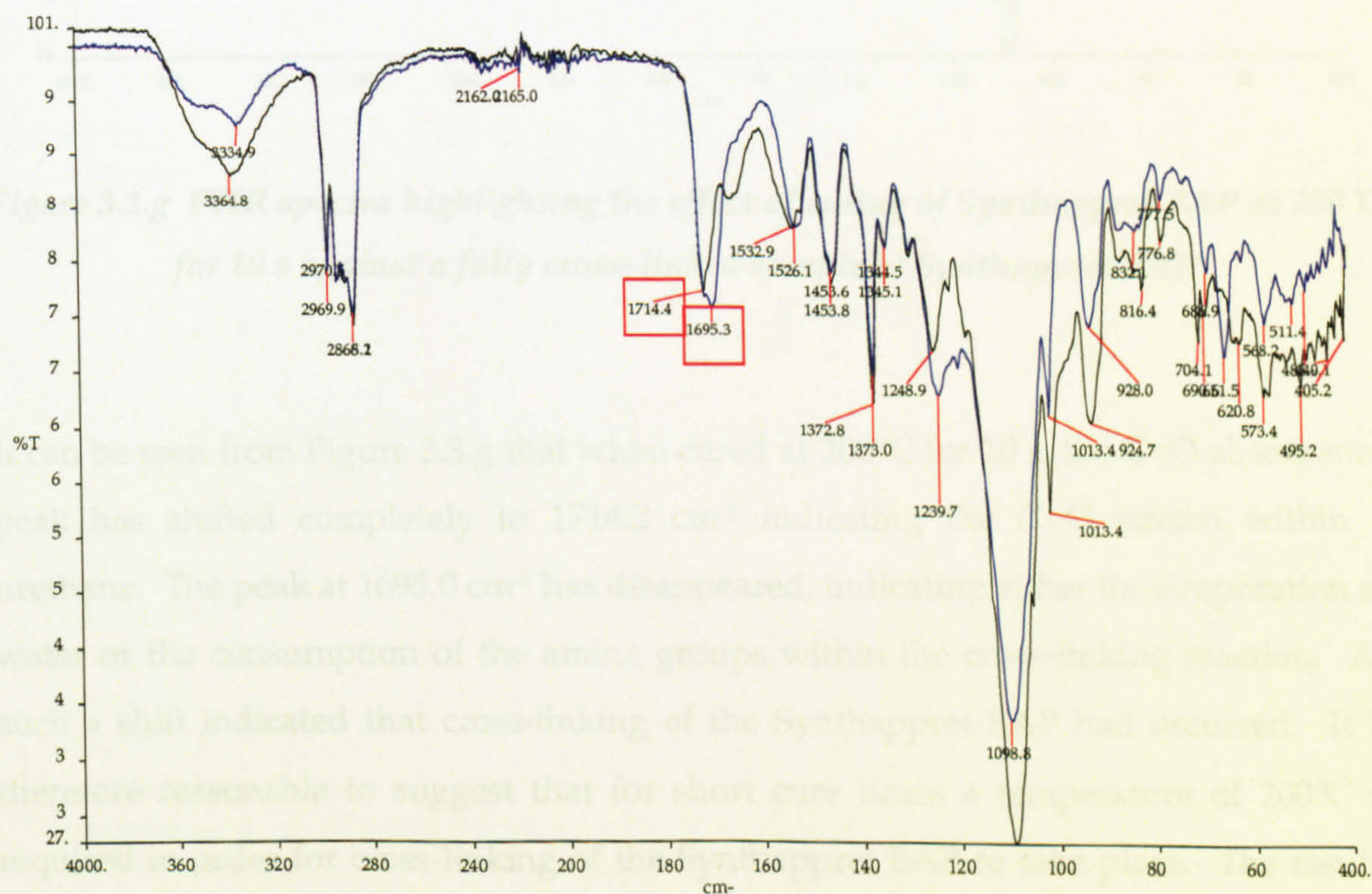


Figure 3.1.f FTIR spectra highlighting the effect of curing of Synthappret BAP at 160 °C for 10 s against a fully cross-linked sample of Synthappret BAP

It can be seen from Figure 3.3.f that as with the sample of Synthappret BAP cured at 100°C for 10 s there is some splitting of the C=O absorption peak for urethane, although the major absorption seen at 1695.3 cm⁻¹ suggests that no cross-linking has occurred and that water or amine is present.

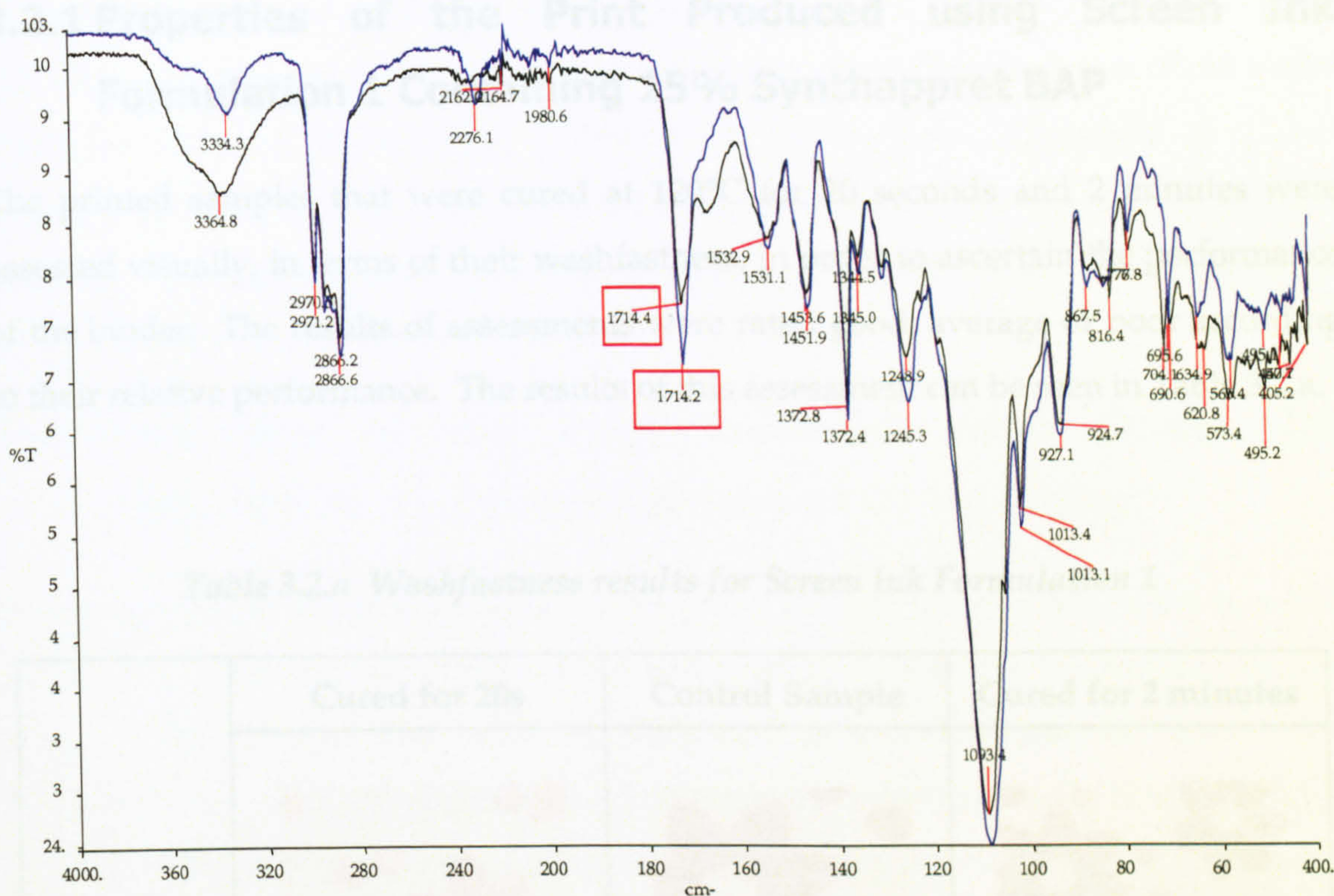


Figure 3.1.g FTIR spectra highlighting the effect of curing of Synthappret BAP at 200 °C for 10 s against a fully cross-linked sample of Synthappret BAP

It can be seen from Figure 3.3.g that when cured at 200°C for 10 s, the C=O absorbance peak has shifted completely to 1714.2 cm⁻¹ indicating the C=O stretch within a urethane. The peak at 1695.0 cm⁻¹ has disappeared, indicating either the evaporation of water or the consumption of the amine groups within the cross-linking reaction. As such a shift indicated that cross-linking of the Synthappret BAP had occurred. It is therefore reasonable to suggest that for short cure times a temperature of 200°C is required in order for cross-linking of the Synthappret BAP to take place. The results obtained from the FTIR analysis of Synthappret proved that a cross-linking mechanism occurred on application of high temperatures. As such, there was a possibility of using Synthappret BAP as the binder system in inks for ink jet printing of textiles without an alkaline component.




3.2 Preparation and Charaterisation of Screen Printing Inks for Application to Textile Materials

The following section details the results obtained from the investigation carried out into the use of Synthappret BAP as a binder in screen printing inks.

3.2.1 Properties of the Print Produced using Screen Ink Formulation 1 Containing 15% Synthappret BAP

The printed samples that were cured at 120°C for 20 seconds and 2 minutes were assessed visually, in terms of their washfastness, in order to ascertain the performance of the binder. The results of assessments were rated good, average or poor according to their relative performance. The results of this assessment can be seen in Table 3.1.a.

Table 3.2.a Washfastness results for Screen Ink Formulation 1

	Cured for 20s	Control Sample	Cured for 2 minutes
Printed sample			
Visual assessment of samples before and after printing according to greyscales	1	N/A	5

It can be seen from Table 3.1.a that the majority of the print was removed from the sample that had been cured for 20 seconds whereas the sample cured for 2 minutes retained all of the ink applied. It could, therefore, be concluded that a temperature of

120°C was sufficiently high to cure the binder enough, resulting in good adherence of the pigment to the substrate. However, in order to achieve, this a cure time of 2 minutes was required.

The samples printed with Screen Ink Formulation 1 and cured at 200°C to produce similar results to the samples cured at 120°C required a cure time of 2 minutes in order for acceptable fastness properties to be obtained. It should be noted that an extended cure time of 3 minutes at this elevated temperature caused discolouration of the cotton fabric in terms of it becoming yellowed on the surface. Therefore, at a cure temperature of 200°C, with a binder level of 15%, the cured time required should be 2 minutes. As a result, further investigation into screen printing inks was carried out using a maximum cure time of 2 minutes.

3.2.2 Properties of the Print Produced using Screen Ink Formulation 2 – Containing Ethanol to Aid Drying

The incorporation of ethanol into the formulation in an attempt to reduce the cure time resulted in a detrimental effect on the print quality. The ink formulation became lumpy. When printed and cured, no significant difference in fastness properties to those achieved when using Screen Ink Formulation 1 was observed. It was therefore concluded that the incorporation of ethanol as a drying aid had no effect on the cure time required in order to achieve acceptable prints.

3.2.3 Properties of the Print Produced using Screen Ink Formulation 3 – Containing of Sodium Hydroxide

The incorporation of sodium hydroxide (1M solution) to give a pH of 11 as an inducing aid to cross-linking was seen to reduce the print quality of the ink. Prints had grainy and streaky appearance in places as is highlighted in Figure 3.1.a. This was thought to be due to some of the Synthappret BAP cross-linking, thus providing some resistance to the process of screen printing. That is to say that the alkaline conditions caused some cross-linking of the Synthappret BAP resulting in larger polymers within the ink which provided resistance to being forced through the screen mesh.

Figure 3.2.b Picture of cotton printed with Screen Ink Formulation 4



Figure 3.2.a Picture of cotton printed with Screen Ink Formulation 3

The cure time was not significantly improved over that found for Screen Ink Formulation 1. After a period of 4 weeks, the ink formulation was found to have formed a sponge like structure whilst stored, indicating a possibility that the binder may have cross-linked upon itself. This led to the conclusion that the incorporation of sodium hydroxide at the concentration investigated, i.e. a 1M solution to give a pH 11, within the ink formulation had an overall negative impact.

3.2.4 Properties of the Print Produced using Screen Ink Formulation 4 – Containing a Reduced Level of Thickener to Produce a Thinner Layer of Ink

The reduction in thickener level within this formulation acted to reduce the print quality. The ink was seen to bleed once on the substrate giving a distorted image. An example demonstrating this problem can be seen in Figure 3.1.b.

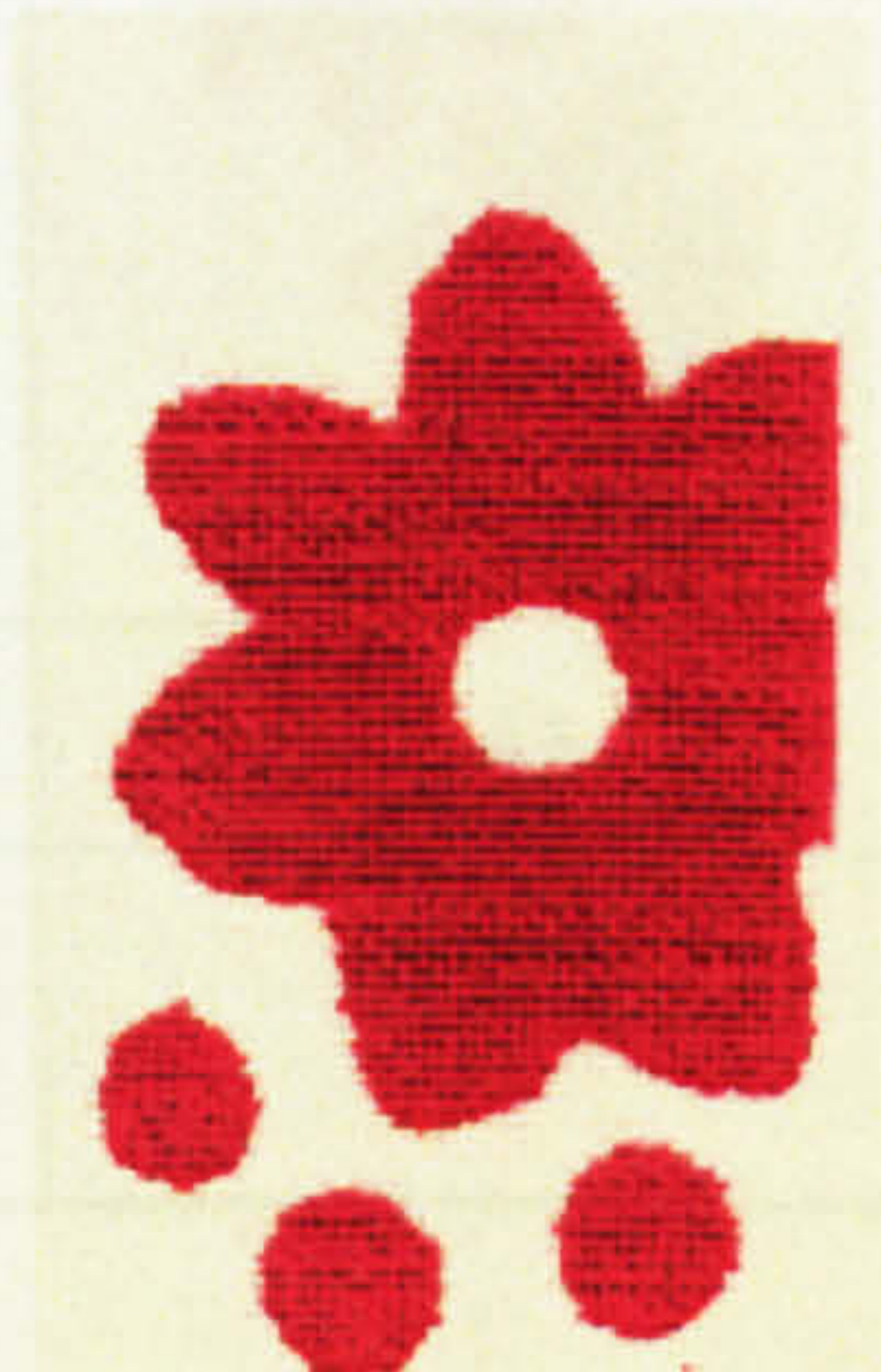


Figure 3.2.b Picture of cotton printed with Screen Ink Formulation 4

However, the cure time required was not hindered by the reduction in thickener level. Prints with the required resistance properties were obtained using cure conditions of 200°C for 2 minutes. The increase of water within the formulation did not act lengthen the cure time required to give acceptable fastness properties. It was therefore concluded, from the results obtained for Screen Ink Formulations 2 and 4, that the limiting factor when considering the cure speed of a screen ink formulation was not the film thickness of the ink on the substrate.

3.2.5 Properties of the Print Produced using Screen Ink Formulation 5 – Containing an Increased Concentration of Synthappret BAP

The increased level of binder within the formulation to a level of 30% by weight was found to have a significant effect on the performance of the ink in terms of its fastness properties. A cure time of 200°C was chosen as after consultation with professional screen printers the most important factor was to sufficiently cure the print in the shortest time possible. The results of washfastness and rubfastness testing of prints cured at 200°C for 60 seconds can be seen in Table 3.1.b and Table 3.1.c.

Table 3.2.b Washfastness results of cotton printed with Screen Ink Formulation 5



	Before Washing	After Washing
Printed samples		
Optical density	1.45	1.45
Rating according to greyscale	5	5

Table 3.2.c Rubfastness results of cotton printed with Screen Ink Formulation 5

Optical Density of Cotton Lawn Rubbing Fabric after Rubbing of the Substrate	
Dry rub	Wet rub
0.00	0.01

The fact that acceptable fastness properties were obtained after a cure time of 60 seconds indicates that the limiting factor, in terms of the rate at which the required level of cure is achieved, of the ink formulation is the amount of binder incorporated. It should be noted that when cured at a lower temperature of 120°C for the same time, i.e. 60 seconds, the same resistance properties were not observed. It was not thought that the presence of water was a determining factor as similar results to those for dry heat curing were achieved when the prints were steam cured at 200°C for 60 seconds. Such results are not reported here as steaming of the prints requires not only a greater layout cost for equipment and resources but also requires an extra drying stage to the process. Results of SEM analysis carried out on samples cured at 200°C for 60 seconds and then washed can be seen in Figure 3.1.c and Figure 3.1.d.

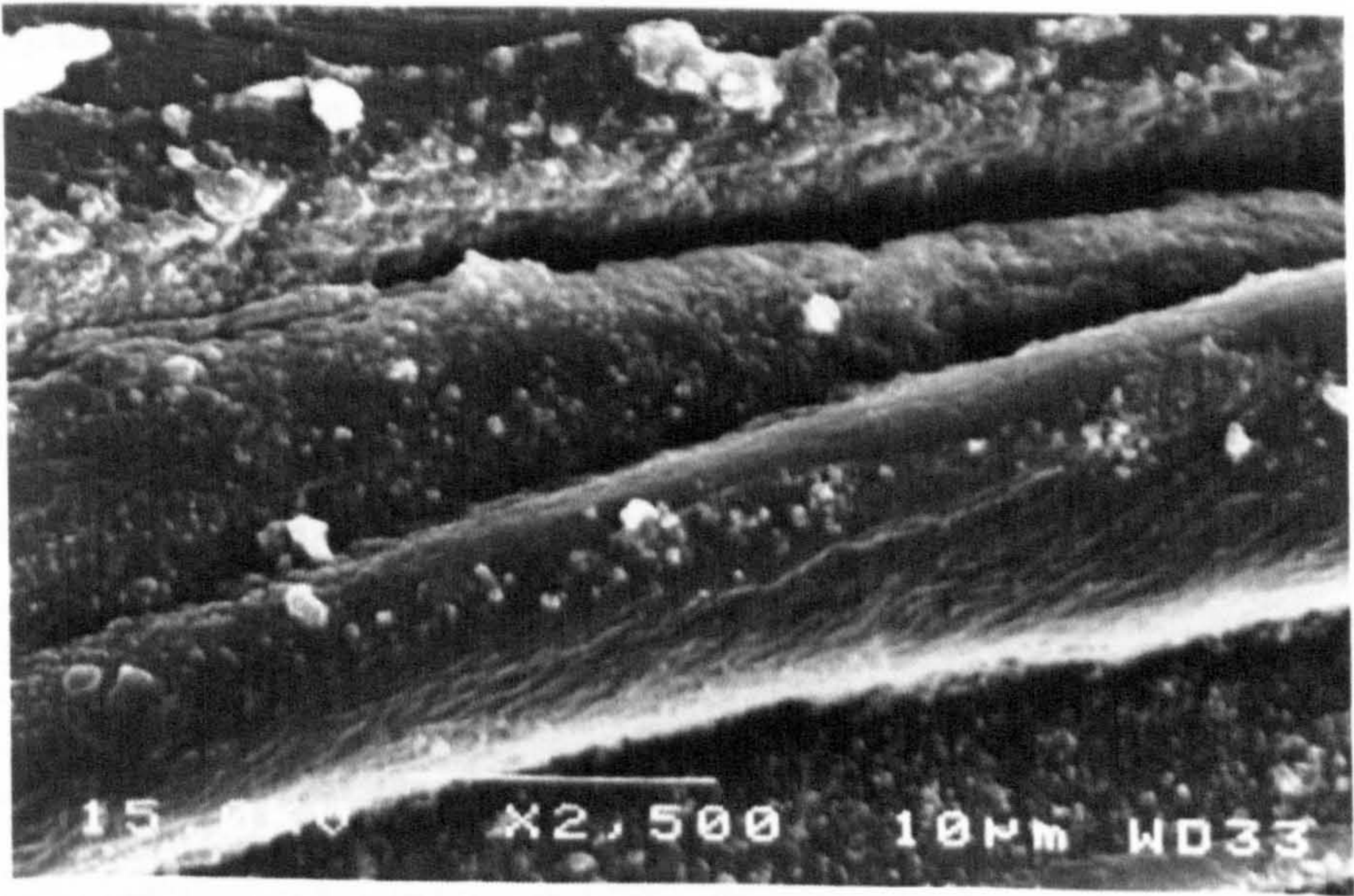


Figure 3.2.c SEM of cotton printed with Screen Ink Formulation 5 before washing (× 2500)

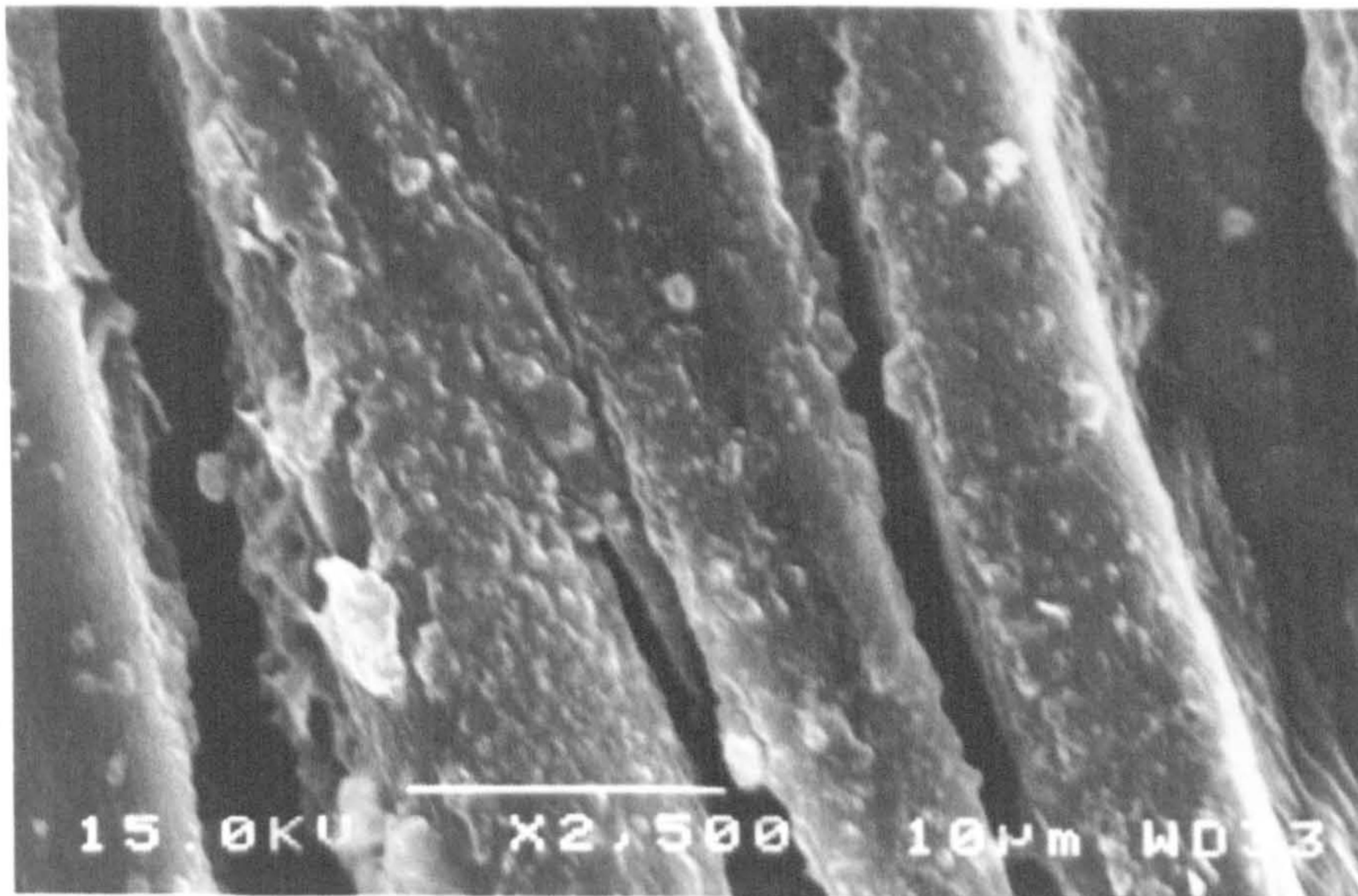


Figure 3.2.d SEM of cotton printed with Screen Ink Formulation 5 after washing (× 2500)

It can be seen from Figure 3.1.c and Figure 3.1.d that there is little or no difference between the micrographs of washed and unwashed printed substrate. There is strong evidence for the presence of both binder and pigment in both samples. Such evidence obtained from the application of SEM acts to confirm the results of the washfastness testing seen in Table 3.1.b.

3.2.6 Properties of the Print Produced using Screen Ink Formulation 6 – Containing a Further Increase in Synthappret BAP

Increasing the level of Synthappret BAP within the formulation to 50% reduced the time required for acceptable cure to 30 seconds. This acted to confirm the thought that, as the level of binder within the ink formulation was increased, the time needed for cross-linking of the Synthappret BAP and thus the cure time required lowered. As previously discussed in Section 3.1.5 the reduction in the amount of water was not thought to have a great effect on the cure rate of the ink formulation.

3.2.7 Properties of the Print Produced using Screen Ink Formulation 7 – Containing Sodium Bicarbonate to Promote Cross-Linking

Addition of 1% sodium bicarbonate within Screen Ink Formulation 6 was seen to

promote cross-linking of the Synthappret BAP within the ink at ambient temperatures over a period of 2 days. On consultation with screen printers it was decided to incorporate sodium bicarbonate within the formulation at the very last moment prior to the printing of the substrate. This is an acceptable option as often a screen ink is made up for a specific job to a required amount in order to reduce waste and save on storage space.

The incorporation of the sodium bicarbonate prior to printing reduced the cure time required to give acceptable fastness properties to 20 seconds. The results of fastness tests carried out on samples cured at 200°C for 20 seconds can be seen in Table 3.1.d and Table 3.1.e.

Table 3.2.d Washfastness results of cotton printed with Screen Ink Formulation 7



	Before washing	After washing
Printed sample		
Optical density	1.48	1.48

Table 3.2.e Rubfastness results of cotton printed with Screen Ink Formulation 7

Optical Density of Cotton Lawn Rubbing Fabric after Rubbing of the Substrate	
Dry rub	Wet rub
0.00	0.01

Therefore, for the fastness properties of the print to be acceptable, a formulation containing 50% Synthappret BAP with 1% sodium bicarbonate catalyst allowed a cure time of 20 seconds at 200°C. SEM analysis of the sample cured at 200°C for 20 seconds and then a washed sample was carried out. The micrographs obtained can be seen in Figure 3.1.e and Figure 3.1.f.

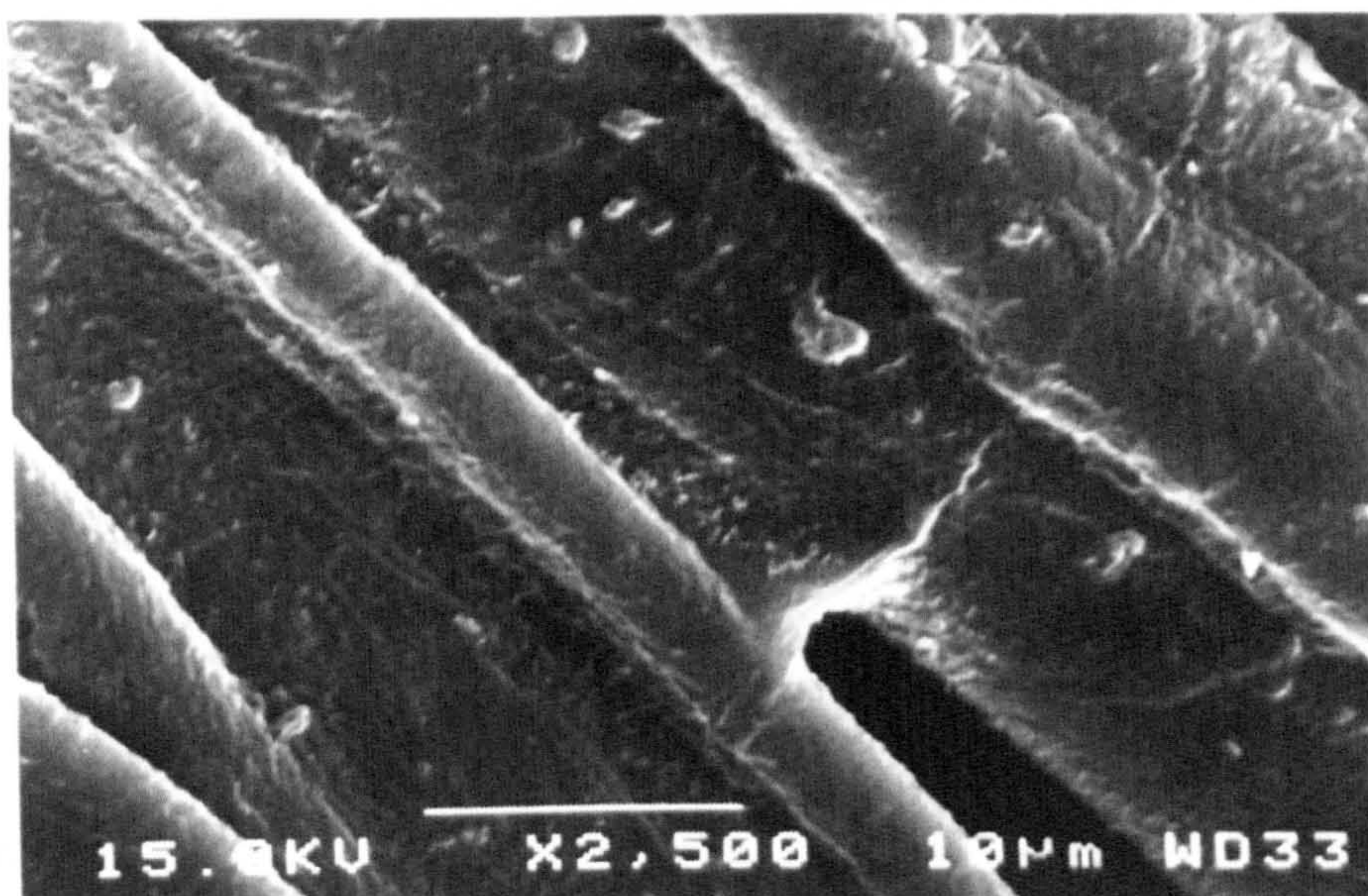


Figure 3.2.e SEM of cotton printed with Screen Ink Formulation 7 before washing (× 2500)

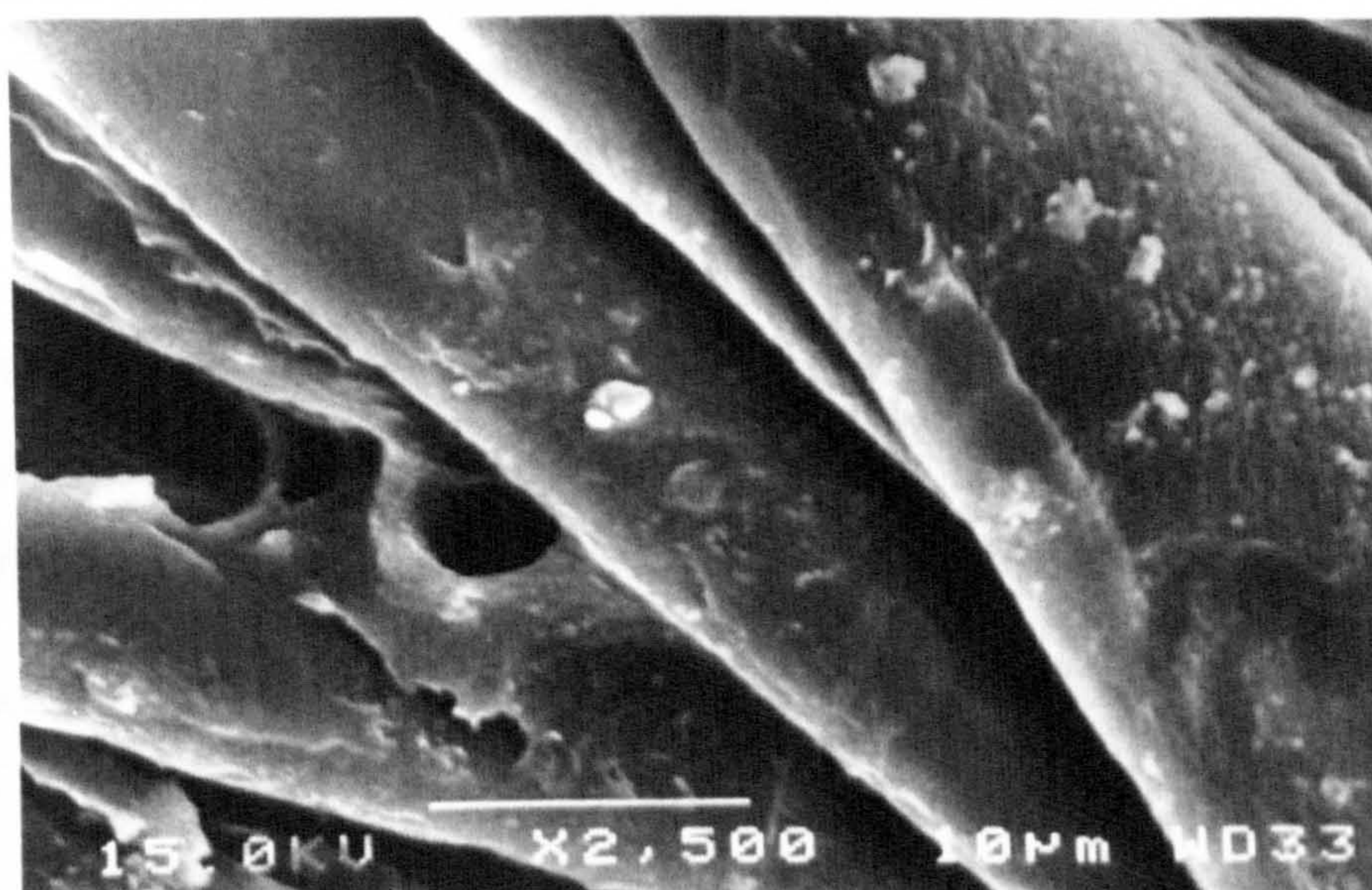


Figure 3.2.f SEM of cotton printed with Screen Ink Formulation 7 after washing (× 2500)

It can be seen from Figure 3.1.e and Figure 3.1.f that the change in the appearance of the printed and cured substrate after washing is unnoticeable even at a magnification of 2500. The micrograph depicted in Figure 3.1.e and Figure 3.1.f show strong evidence for the presence of both binder and pigment in each case. The micrographs therefore

act to confirm the likely validity of the values obtained in Table 3.1.d for the wash resistance of the printed substrate.

3.3 Properties of Ink Jet Printing Inks for Application onto Textile Materials

This section details results relevant to the effect of Synthappret BAP within an ink jet ink formulation on print properties. Due to the successful screen printing of Synthappret BAP and its success as a binder, Synthappret was used to formulate inks for ink jet printing of shrink resist treatments.

3.3.1 Properties of the Prints using Shrink Resist Ink Formulation 1

The cured and felted wool sample was seen to “puff up” in the unprinted areas. This effect was seen to a lesser extent where the ink formulation had been applied. Some sculpting effect was noticed, however, such an effect was marginal. Such a phenomena indicated that an amount of Synthappret BAP was successfully jetted although a greater amount was needed to produce a distinct sculpting effect on the wool substrate.

3.3.2 Properties of the Prints using Shrink Resist Ink Formulation 2 – Containing an Increased amount of Synthappret BAP

As was seen for Shrink Resist Ink Formulation 1, when printed and cured using Method 1 (outlined in Section 2.5.1.3) a sculpting effect was observed on the wool. However, this time the increased amount of Synthappret BAP within the formulation allowed for this effect to be more apparent. When a second layer of the formulation was applied prior to curing, as described in Method 2 (Section 2.5.1.5), the sculpting effect on the wool became even more apparent and a distinct design area could be seen. Figure 3.2.a shows a micrograph of the difference between the treated and untreated areas after felting.

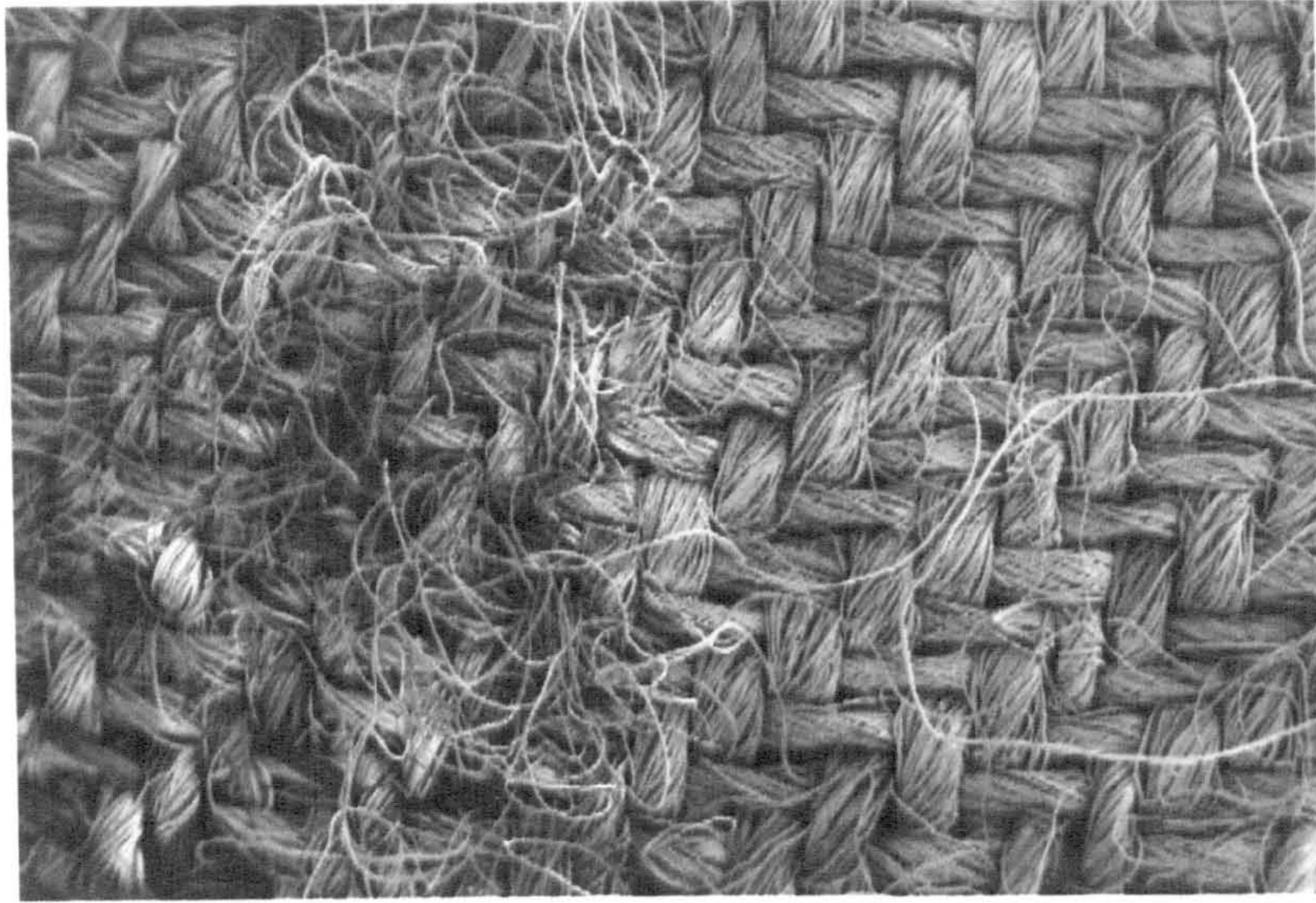


Figure 3.3.a SEM showing the border of a felted and treated area of wool ($\times 15$)

The area on the right of the micrograph seen in Figure 3.2.a shows where Shrink Resist Ink Formulation 2 had been printed. The wool appeared relatively unspoiled by the action of the shrinkage treatment applied. This is the area that forms the image. The left hand side of the micrograph shows how the untreated area of the wool became loose “felting up” when the shrinkage treatment was applied.

The effect of the application of the shrink resist treatment is further detailed in Figure 3.2.b and Figure 3.2.c where micrographs of treated and untreated area can be seen at a higher magnification.

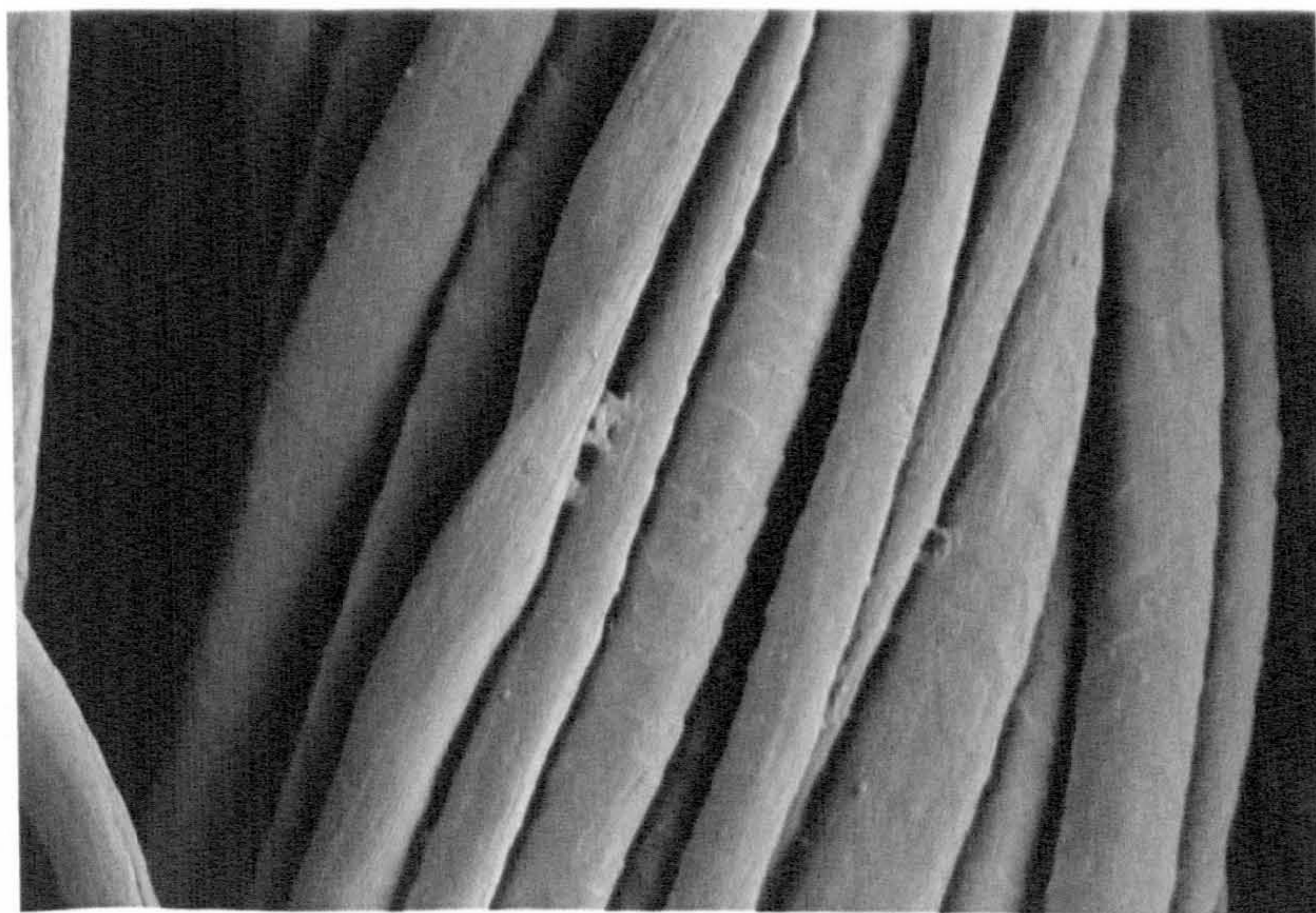


Figure 3.3.b SEM of a felted sample of wool treated with Synthappret BAP ($\times 500$)

Figure 3.2.b shows an area of the wool that had Shrink Resist Treatment 2 printed onto it after application of the shrinkage treatment. The micrograph shows that the normally rough textured wool fibres appear smooth. This is likely to be due to them being coated with the Synthappret BAP. There is also some evidence of the Synthappret BAP acting to bind the wool fibres together.

Figure 3.2.c shows an untreated area of the wool sample after application of the shrinkage treatment. When compared to the treated area, it can be seen that the wool fibres have a rougher and more textured appearance. It is also noticeable that the fibres are more loosely arranged in relation to each other indicating their reaction to the shrinkage treatment applied.

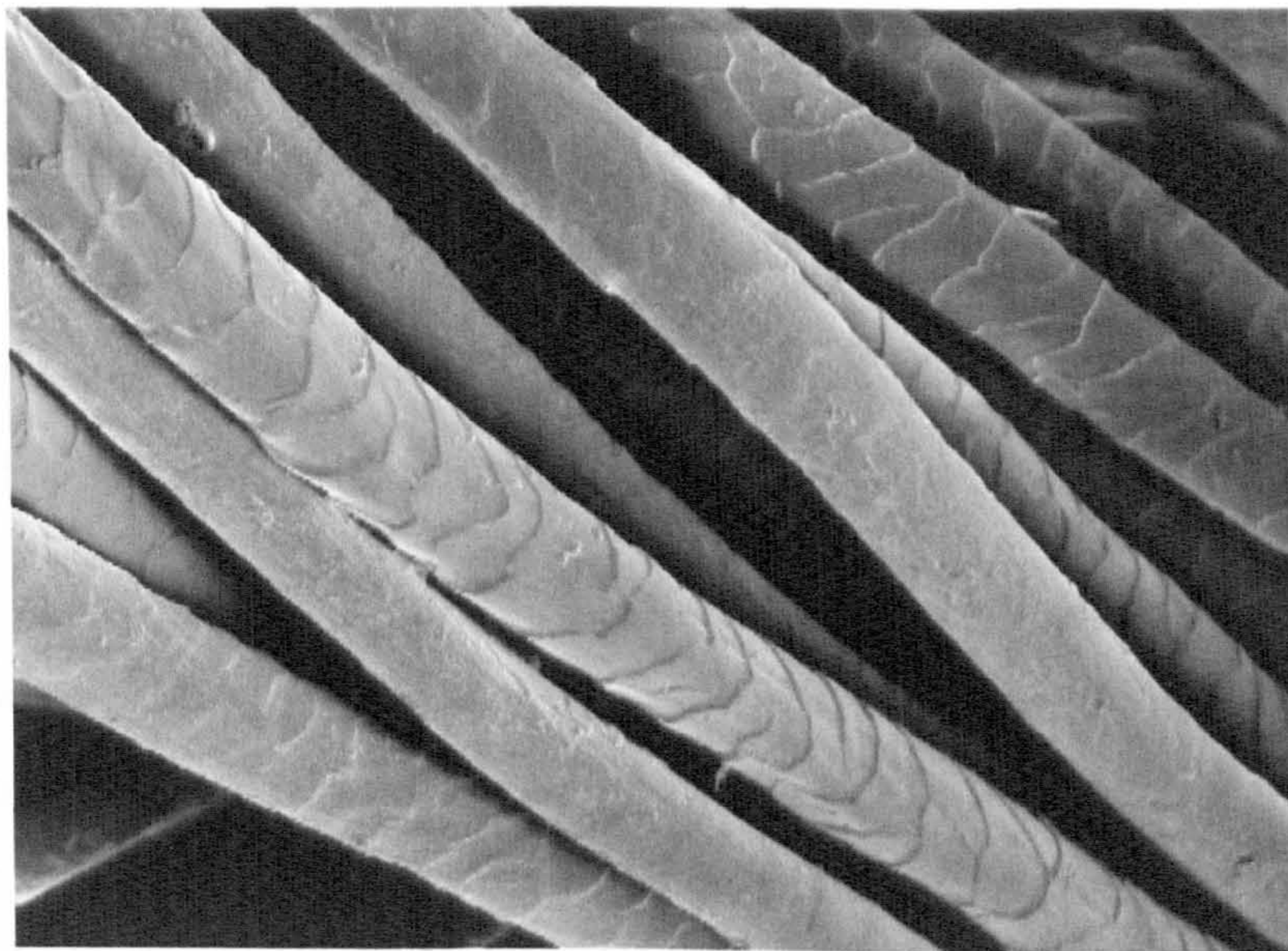


Figure 3.3.c SEM of felted sample of untreated wool ($\times 500$)

A photograph of a treated and then felted piece of wool can be seen in Figure 3.2.d.

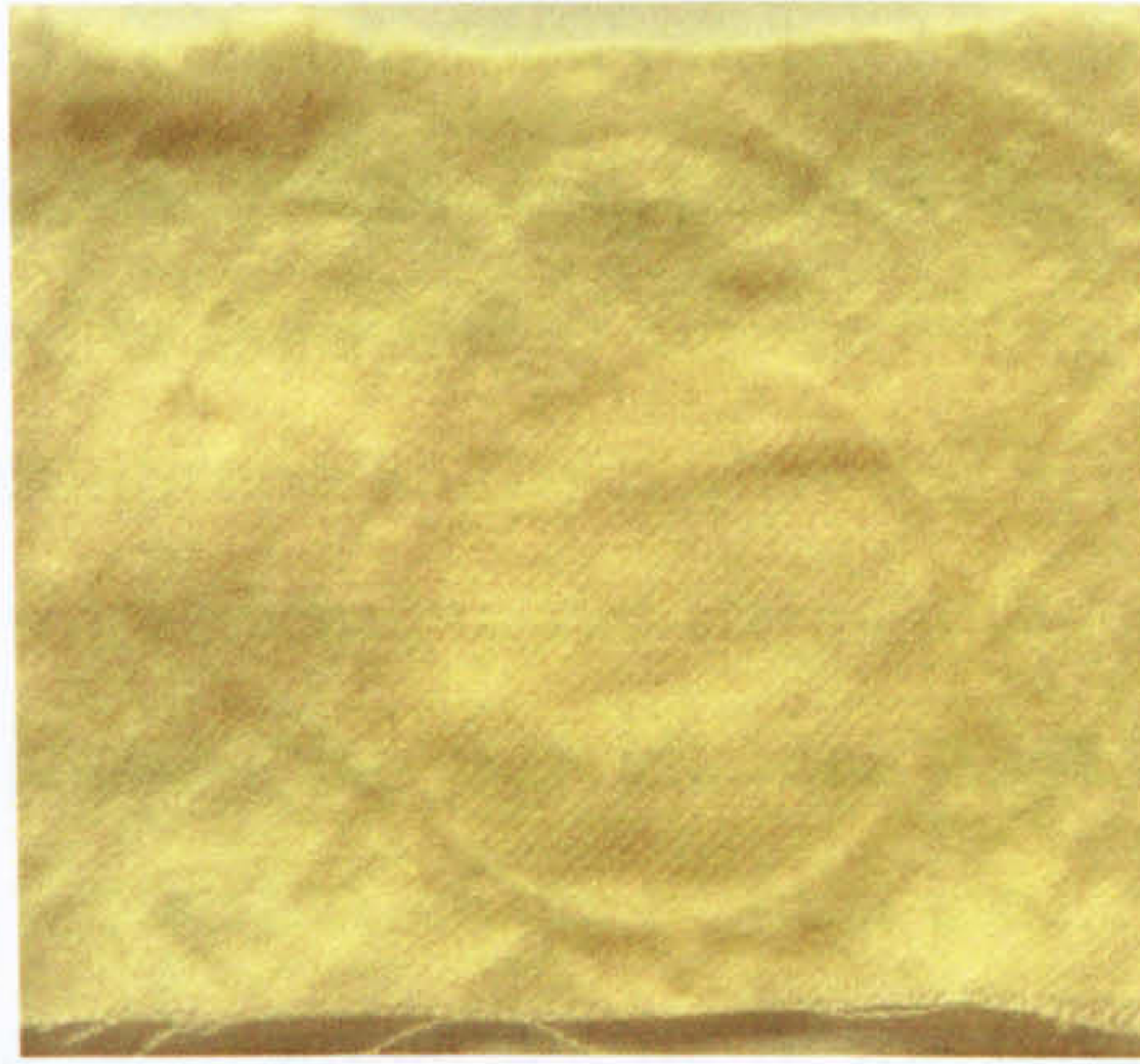


Figure 3.3.d Photograph of a felted sample of wool printed with Shrink Resist Ink Formulation 2

It can be seen from Figure 3.2.d that the felting treatment has caused the wool to shrink and felt up leaving a circle of un-felted wool where the ink formulation had been applied.

3.3.3 Properties of the Prints using Shrink Resist Ink Formulation 3 – Containing a Colorant

The incorporation of pigment into Shrink Resist Ink Formulation 3 acted to make the printed area more apparent. The sculpting effect noticed was similar to that for Shrink Resist Treatment 2 when printed using Method 2. It should be noted that on application of the Shrinkage Treatment, no colour was visibly removed from the printed area, indicating that the Synthappret BAP was also acting to bind the pigment to the wool fibres. A picture of the wool sample printed with Shrink Resist Ink Formulation 3 and felted can be seen in Figure 3.2.e.



Figure 3.3.e Photograph of a felted wool sample printed with Shrink Resist Ink Formulation 3

It can be seen from Figure 3.2.e that the non-printed area felted up whereas the printed area remained unspoiled as before the felting process. It should also be noted that after the harsh treatment applied to the wool to induce felting, the colour remained in the printed area. Such a phenomenon suggests that the Synthappret BAP has not only coated and protected the wool fibres but has trapped the pigment applied. It appears that such trapping of the pigment has provided the print with a fastness to the felting process thus maintaining the colour of the printed area. It should be noted that the hand milling process used to promote felting of the wool is as severe if not harsher than a standard washfastness test applied to textile prints.

It can be seen from the evidence presented in this section that the printing of Synthappret BAP using thermal ink jet technology was successful. The previous section proved the use of Synthappret BAP as a binder within a textile printing ink was also successful. As such, it can be said that it is likely that an ink jet ink for the printing of textile materials, containing Synthappret BAP as the binder may be possible. Following sections detail results relevant to the use of Synthappret BAP within an ink jet formulation and its application to textile materials.

3.4 Characterisation of Pigmented Ink Jet Inks for Printing Textile Materials

The following section details the findings of the investigation into the use of pigmented inks containing Synthappret BAP as a binder for the ink jet printing of textiles. It should be noted that a number of other binder systems were also investigated. However, the inks containing such binders formulated were found to be un-jettable using the available facilities and as such no relevant analysis was possible. As a result, the formulation and characterization of these inks has not been reported.

3.4.1 Properties of Ink Jet Inks containing Toner Pigments

The following section details the results of the investigation into the use of ink jet printing inks containing Synthappret BAP as the binder and Toner pigments as the colorant.

3.4.1.1 Properties of Toner Ink Formulation 1 (Yellow)

Toner Ink Formulation 1 had physical properties as shown in Table 3.4.a

Table 3.4.a Physical properties of Toner Ink Formulation 1

Physical property tested	Data obtained for Toner Ink Formulation 1
Viscosity at 60 rpm and 25°C (mPas)	4.73
Surface tension (mNm ⁻¹)	52
Particle size at a 95% limit (nm)	331

It can be seen from the data presented in Table 3.4.a that Toner Ink Formulation 1 possessed the physical properties required of an ink for ink jet printing. It should be noted however, that whilst the particle size of 331 nm obtained was below 0.5 μm , satisfying the general requirements, it was still higher than preferred. Such a particle size, suggested that should any agglomeration of particles occur, the required particle size limit of 0.5 μm would be exceeded, assuming the pigment was milled down to its primary particles. Any such agglomeration may lead to the blocking of the print-head nozzles of a desktop ink jet printer over a period of time.

However, in order to ascertain the effects of the ink formulation when printed onto a textile substrate, it was necessary for the ink to be printed. Initially, it was decided to calculate the amount of ink deposited onto the substrate and the quality of any print obtained. A square of ink measuring 153mm \times 200mm was printed onto a transparency using the "normal" and the "best" functions available on the Apollo P1200 desktop ink jet printer. The weight of ink deposited to the transparency was measured and the data presented in Table 3.4.b.

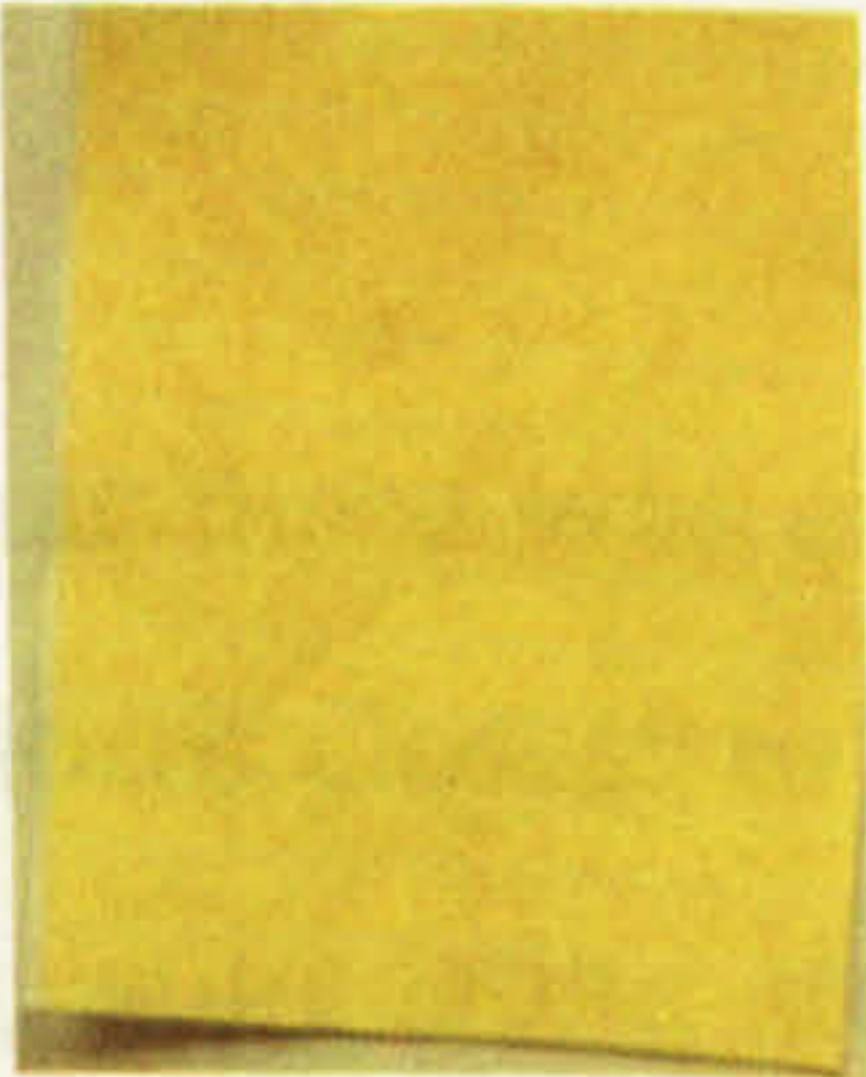

Table 3.4.b Amount of ink transferred to the substrate using different print settings

	Print Setting Used	
	Normal	Best
Initial weight of transparency (g)	12.3121	12.4325
Weight of transparency after printing (g)	12.5659	12.7991
Weight of ink deposited (g)	0.2538	0.3665

It can be seen from Table 3.4.b, that a greater amount of ink was deposited using the “best” print function, transferring more pigment and more binder to the substrate. It should be noted that within Toner Ink Formulation 1, there was 10% by weight of Synthappret BAP. As such, within a solid block of printed colour measuring 153mm×200mm, only 0.03665 g of Synthappret BAP was likely to have been applied to the substrate.

The difference in print quality of the two print settings when Toner Ink Formulation 1 was applied to paper can be seen in Table 3.4.c.

Table 3.4.c Comparison of prints printed using different print settings

	Print setting used	
	Normal	Best
		
Optical density of print	0.39	0.50
Print quality	Average	Good

It can be seen from the images and data presented in Table 3.4.c that the visual and the measured colour strength of the prints showed that the “best” print function gave better results. The “best” print function also gave a greater consistency of print allowing for an enhanced print quality. As a result of these findings all further prints were prepared using the “best” print setting.

Subsequently, Toner Ink Formulation 1 was printed onto cotton and polyester fabrics using a Hewlett Packard HP 51626A print cartridge and an Apollo P1200 ink jet printer. On completion of the required number of prints, the ink was removed from the cartridge to avoid any possible blocking of the print-head nozzles.

A scanning electron micrograph of the printed cotton can be seen in Figure 3.4.a.

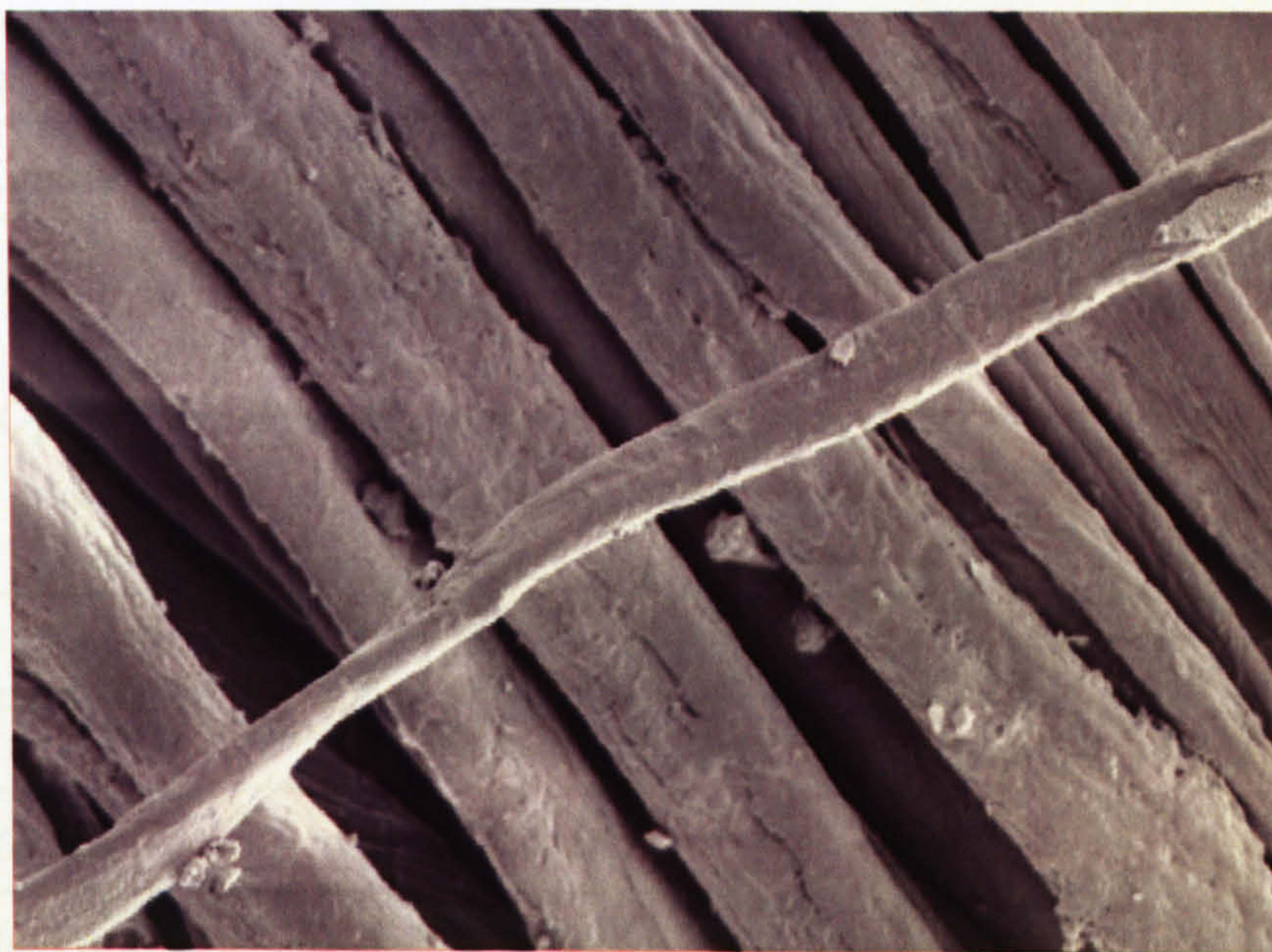


Figure 3.4.a SEM of a cotton sample printed using Toner Ink Formulation 1 ($\times 1500$)

It can be seen from Figure 3.4.a that there was evidence of particles attached to the surface of the cotton fibres. The fibres closest to the surface also appeared to be far rougher than the unprinted fibres, suggesting that these fibres were coated with a substance containing particulates. It is likely that the fibres had been coated with the ink formulation and that the Synthappret BAP was acting to bind pigment particles to the surface of the cotton fibres.

Once printed and cured, the cotton and the polyester samples were tested for their wash and rub resistance. The results of the fastness tests carried out can be seen in Table 3.4.d and Table 3.4.e, in terms of the optical densities of the printed samples before and after washing. Results of the visual assessment of the difference in colour of the samples before and after washing in terms of greyscale can be seen in Table 3.4.f. The tests were carried out using Toner Ink Formulation 1 for yellow, cyan and magenta pigments.

Table 3.4.d Optical densities of cotton printed using Toner Ink Formulation 1 before and after washfastness tests

Ink formulation	Optical density on cotton		
	Before washing	After washing	Difference
Yellow	0.50	0.49	0.01
Magenta	0.83	0.81	0.02
Cyan	0.79	0.78	0.01

Table 3.4.e Optical densities of polyester printed using Toner Ink Formulation 1 before and after washfastness tests

Ink formulation	Optical density on polyester		
	Before washing	After washing	Difference
Yellow	0.48	0.45	0.03
Magenta	0.79	0.76	0.03
Cyan	0.77	0.75	0.02

Table 3.4.f Greyscale evaluation of the change in colour of cotton and polyester fabrics printed with Toner Ink Formulation 1 after washing

Ink formulation	Value of colour difference according to greyscale	
	Cotton	Polyester
	Assessment of colour difference between printed samples before and after washing	Assessment of colour difference between printed samples before and after washing
Yellow	4/5	4/5
Magenta	4/5	4/5
Cyan	4/5	4/5

It can be seen from Table 3.4.d and Table 3.4.e that the change in optical density of the printed samples after application of the washfastness test was minimal. This was supported by the greyscale evaluations made to determine the visual change in colour of the printed samples after washing seen in Table 3.4.f. No staining of the multifibre strip was apparent however, this was as expected due to the colorant involved being a pigment. No colour was removed from the printed samples and into the wash-bath liquor.

The results obtained for the rubfastness tests carried out on the printed cotton and polyester fabrics can be seen in Table 3.4.g and Table 3.4.h, where Table 3.4.g shows the optical density of colour removed from the printed substrate onto the cotton lawn pad and Table 3.4.h shows the results of the visual assessment of colour difference between rubbed and unrubbed samples.

Table 3.4.g Optical density of colour transferred to cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed using Toner Ink Formulation 1

Pigmented ink formulation	Optical density of cotton lawn rubbing fabric after rub test			
	Cotton		Polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	0.12	0.14	0.14	0.18
Magenta	0.11	0.16	0.12	0.16
Cyan	0.11	0.15	0.13	0.16

Table 3.4.h Greyscale evaluation of the change in colour of cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed using Toner Ink Formulation

1

Pigmented ink formulation	Value of colour difference according to greyscale			
	Cotton		Polyester	
	Assessment of colour difference between printed samples before and after washing		Assessment of colour difference between printed samples before and after washing	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	4	3/4	3/4	3
Magenta	4	3/4	3/4	3
Cyan	4	3/4	3/4	3

It can be seen from Table 3.4.g and Table 3.4.h that a small amount of colour was removed from the printed cotton and polyester fabrics after rubfastness tests. It should be noted that the colour stain of the cotton lawn pads was not significant. Such results would be acceptable for a range of applications in the field of textile printing.

3.4.1.2 Properties of Toner Ink Formulation 2 – Containing an Increased Concentration of Pigment

The physical properties of Toner Ink Formulation 2 were measured to determine whether the increased amount of pigment in the ink affected the viscosity, surface tension or particle size in any way. It should be noted that as the pigment was added as part of the initial pigment dispersion formulated, the levels of the other components such as DEG, IPA and dispersant were also slightly increased. The level of Synthappret BAP was raised to 12.5% within Toner Ink Formulation 2. The results of relevant tests can be seen in Table 3.4.i.

Table 3.4.i Physical properties of Toner Ink Formulation 2

Physical property tested	Data obtained for Toner Ink Formulation 1
Viscosity at 60 rpm and 25°C (mPas)	5.97
Surface tension (mNm ⁻¹)	51
Particle size at a 95% limit (nm)	378

It can be seen from Table 3.4.i that when compared to the data obtained for Toner Ink Formulation 1 (seen in Table 3.4.a), that the viscosity and mean particle size of the pigment were significantly higher in Toner Ink Formulation 2. The higher viscosity may be explained, to an extent, by the increased level of Synthappret BAP contained within the ink. However, the greater amount of pigment and humectants was also likely to contribute to this phenomenon. The increased mean particle size was likely to be due to the increased amount of pigment within the ink. The greater the amount of pigment solids contained within the formulation, the greater chance of agglomeration between pigment particles to form larger particles. Such larger particles were more likely to provide resistance to the flow of the liquid in which they were dispersed thus have the effect of increasing the viscosity.

It was decided that, in order to compare the colour characteristics and fastness properties of Toner Ink Formulation 2 to those achieved for Toner Ink Formulation 1, it was necessary to print the ink onto cotton and polyester fabrics. Toner Ink Formulation 2 was thus printed onto the required substrates through a Hewlett

Packard HP 51626A print cartridge via an Apollo P1200 ink jet printer. On completion of the required number of prints, the ink was removed from the cartridge to avoid any possible blocking of the print-head nozzles. Once printed and cured, the cotton and polyester samples were tested for their wash and rub resistance. The results of the washfastness tests carried out on the printed cotton and polyester fabrics in terms of the optical density of the prints before and after washing can be seen in Table 3.4.j and Table 3.4.k. The results of the visual assessment carried out in terms of the colour difference between washed and unwashed prints according to greyscales can be seen in Table 3.4.l.

Table 3.4.j Optical densities of cotton printed using Toner Ink Formulation 2 before and after washfastness tests

Ink formulation	Optical density on cotton		
	Before washing	After washing	Difference
Yellow	0.49	0.48	0.01
Magenta	0.77	0.76	0.01
Cyan	0.78	0.77	0.01

Table 3.4.k Optical densities of polyester printed using Toner Ink Formulation 1 before and after washfastness tests

Ink formulation	Optical density on polyester		
	Before washing	After washing	Difference
Yellow	0.48	0.46	0.02
Magenta	0.75	0.73	0.02
Cyan	0.77	0.76	0.01

Table 3.4.l Greyscale evaluation of the change in colour of cotton and polyester fabrics printed with Toner Ink Formulation 2 after washing

Ink formulation	Value of colour difference according to greyscale	
	Cotton	Polyester
	Assessment of colour difference between printed samples before and after washing	Assessment of colour difference between printed samples before and after washing
Yellow	4/5	4/5
Magenta	4/5	4/5
Cyan	4/5	4/5

It can be seen form Table 3.4.j and Table 3.4.k that the optical density of the prints obtained using Toner Ink Formulation 2 was greater than that achieved using Toner Ink Formulation 1 (Table 3.4.d and Table 3.4.e). The actual washfastness results however, showed very little difference, as the change in optical density of the printed samples after the washfastness tests was minimal. The greyscale assessments of the colour difference between washed and unwashed samples seen in Table 3.4.l also show that the washfastness of the printed cotton and polyester fabrics were very good. No staining of the multifibre strip was apparent and no colour was removed from the printed samples and into the wash-bath liquor.

The rub resistance of the printed cotton and polyester fabrics was assessed and the results obtained can be seen in Table 3.4.m and Table 3.4.n.

Table 3.4.m Optical density of colour transferred to cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed with Toner Ink Formulation 2

Pigmented ink formulation	Optical density of cotton lawn rubbing fabric after rub test			
	Cotton		Polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	0.11	0.13	0.12	0.14
Magenta	0.12	0.15	0.13	0.15
Cyan	0.12	0.14	0.11	0.14

Table 3.4.n Greyscale evaluation of the change in colour of cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed with Toner Ink Formulation 2

Pigmented ink formulation	Value of colour difference according to greyscale			
	Cotton		Polyester	
	Assessment of colour difference between printed samples before and after washing		Assessment of colour difference between printed samples before and after washing	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	3/4	3	3/4	3
Magenta	3/4	3	3/4	3
Cyan	3/4	3	3/4	3

It can be seen from Table 3.4.m and Table 3.4.n that a small amount of colour was removed from the printed cotton and polyester fabrics after rubfastness tests. It should be noted that the colour stain of the cotton lawn pads was not significant. Such results would be acceptable for a range of applications in the field of textile printing.

It should be noted that after 2 days, there was noticeable pigment sediment on the bottom of the storage vessels. This effect was seen for both Toner Ink Formulation 1 and Toner Ink Formulation 2. After a week, there was a marked separation of the pigment from the solvent carrier. A schematic diagram of such a phenomena can be seen in Figure 3.4.b.

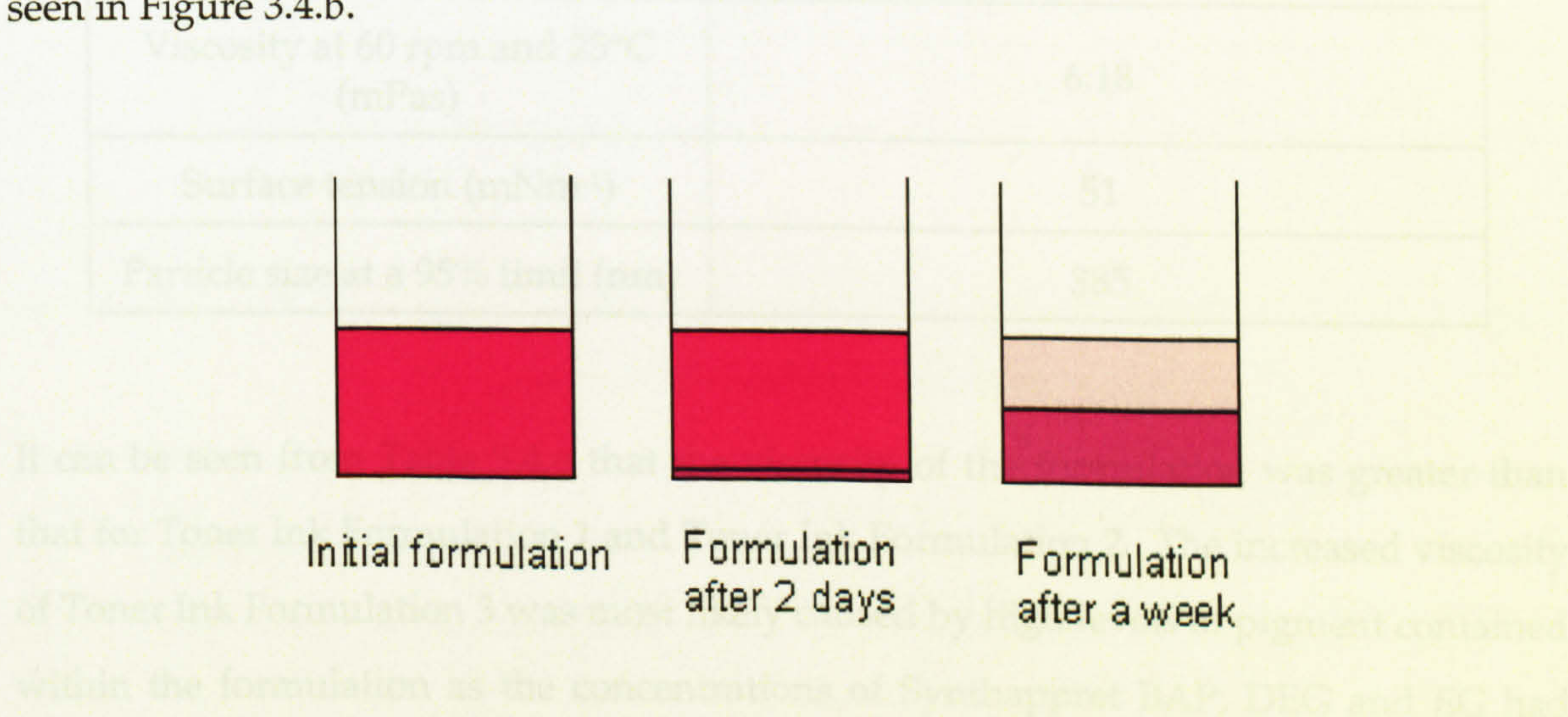


Figure 3.4.b Schematic diagram of the phenomenon of pigment settling seen in Toner Ink Formulation 2

Such settlement of the pigment suggested aggregation of the pigment particles, thus forming larger clusters of pigment that subsequently fell out of dispersion forming a layer of pigment at the bottom of the storage vessel. Should such settlement of larger pigment particle occur within an ink jet cartridge it would lead to the possible blocking of the print-head nozzles. Therefore, whilst some samples were successfully printed immediately after formulation of the ink, such prints may not be achievable over subsequent days. However, as the results of printing and fastness trials were seen to be successful, such an ink formulation may have a future in a printing process where large amounts of substrate are printed daily, allowing for frequent replenishment of the ink within the cartridge.

3.4.1.3 Properties of Toner Ink Formulation 3 – for One Step Preparations

Toner Ink Formulation 3 was made up as a one-pack preparation, i.e. there was no creation of an initial pigment concentrate prior to the formulation of the ink. Once milled, the ink was tested for its physical properties and the results of such tests can be seen in Table 3.4.o.

Table 3.4.o Physical properties of Toner Ink Formulation 3

Physical property tested	Data obtained for Toner Ink Formulation 3
Viscosity at 60 rpm and 25°C (mPas)	6.18
Surface tension (mNm ⁻¹)	51
Particle size at a 95% limit (nm)	385

It can be seen from Table 3.4.o that the viscosity of the formulation was greater than that for Toner Ink Formulation 1 and Toner Ink Formulation 2. The increased viscosity of Toner Ink Formulation 3 was most likely caused by high levels of pigment contained within the formulation as the concentrations of Synthappret BAP, DEG and EG had been reduced from those contained within Toner Ink Formulation 2. The pigment levels were increased from 2% actual weight of pigment solids in Toner Ink Formulation 2 to 4% pigment solids in Toner Ink Formulation. However, the observed

particle size of the pigment within the ink after milling was very similar to that obtained for Toner Ink Formulation 2. This effect was likely due to there being an equal percentage of active dispersant on solids contained in each formulation. Thus, for a formulation containing a pigment content of 2%, 1% dispersant was incorporated and for the formulation containing 4% pigment solids, 2% dispersant was used.

Toner Ink Formulation 3 was introduced into a Hewlett Packard HP 51626A print cartridge and printed onto cotton and polyester fabrics using an Apollo P1200 ink jet printer. On completion of the required number of prints, the ink was removed from the cartridge to avoid any possible blocking of the print-head nozzles. The prints were then tested for their fastness properties.

The results obtained for the washfastness testing carried out on the cotton and polyester samples printed using Toner Ink Formulation 3 can be seen in Table 3.4.p, Table 3.4.q and Table 3.4.r.

Table 3.4.p Optical densities of cotton printed using Toner Ink Formulation 3 before and after washfastness tests

Ink formulation	Optical density on cotton		
	Before washing	After washing	Difference
Yellow	0.50	0.48	0.02
Magenta	0.78	0.77	0.01
Cyan	0.76	0.75	0.01

Table 3.4.q Optical densities of polyester printed using Toner Ink Formulation 2 before and after washfastness tests

Ink formulation	Optical density on polyester		
	Before washing	After washing	Difference
Yellow	0.48	0.47	0.01
Magenta	0.77	0.75	0.02
Cyan	0.75	0.74	0.01

Table 3.4.r Greyscale evaluation of the change in colour of cotton and polyester fabrics printed with Toner Ink Formulation 3 after washing

Ink formulation	Value of colour difference according to greyscale	
	Cotton	Polyester
	Assessment of colour difference between printed samples before and after washing	Assessment of colour difference between printed samples before and after washing
Yellow	5	5
Magenta	5	5
Cyan	5	5

It can be seen from Table 3.4.p to Table 3.4.r that the washfastness obtained for the samples printed using Toner Ink Formulation 3 were excellent. Very minor changes in the optical density of the samples were measured, no staining of the multifibre strip was observed and no colour was removed from the printed samples and into the wash-bath liquor.

The rub resistance of the cotton and polyester fabrics printed using Toner Ink Formulation 3 was assessed and the results obtained can be seen in Table 3.4.s and Table 3.4.t.

Table 3.4.s Optical density of colour transferred to cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed with Toner Ink Formulation 3

Pigmented ink formulation	Optical density of cotton lawn rubbing fabric after rub test			
	Cotton		Polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	0.12	0.15	0.13	0.15
Magenta	0.11	0.15	0.13	0.18
Cyan	0.12	0.15	0.13	0.19

Table 3.4.t Greyscale evaluation of the change in colour of cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed with Toner Ink Formulation 3

Pigmented ink formulation	Value of colour difference according to greyscale			
	Cotton		Polyester	
	Assessment of colour difference between printed samples before and after washing		Assessment of colour difference between printed samples before and after washing	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	3/4	3	3/4	3
Magenta	3/4	3	3/4	3
Cyan	3/4	3	3/4	3

It can be seen from Table 3.4.s and Table 3.4.t that a small amount of colour was removed from the printed cotton and polyester fabrics after rubfastness tests. It should be noted that the colour stain of the cotton lawn pads was not significant. Such results would be acceptable for a range of applications in the field of textile printing.

As with the previous Toner Ink Formulations, settlement of the pigment was seen to occur after 2 days and this settling effect became pronounced over the course of a week. Thus, as mentioned for the previous formulations, whilst it printed in the first few hours after milling, the ink is likely to show deterioration in print quality over a period of time. As such, Toner Ink Formulation 3 was left for three weeks and the physical properties re-measured to ascertain the effect of pigment settling thereon. Results of the tests carried out on the three week old Toner Ink Formulation 3 can be seen in Table 3.4.u.

Table 3.4.u Physical properties of Toner Ink Formulation after a settling period of 2 weeks

Physical property tested	Data obtained for Toner Ink Formulation 3
Viscosity at 60 rpm (mPas)	7.87
Surface tension (mNm ⁻¹)	51
Particle size at a 95% limit (nm)	427

It can be seen from Table 3.4.u that the viscosity and particle size of the pigment within the formulation increased markedly over the settlement period of 3 weeks. It is likely that the pigment particles had formed larger aggregates and as such acted to resist flow within the ink to a greater extent. It should be noted that, whilst the average particle size at a 95% limit of the pigment within the formulation was 427 nm, there was a noticeable tail of much larger fragments, some greater than 1 µm in diameter.

In an attempt to show that such a particle size had detrimental effect of the quality of a printed image, the Toner Ink Formulation 3 that had been left to settle over a period of 3 weeks was used to print cotton and polyester fabrics in the same way as previously described. The resultant prints, along with those obtained for the initial prints using freshly prepared Toner Ink Formulation 3, can be seen in Figure 3.4.c.



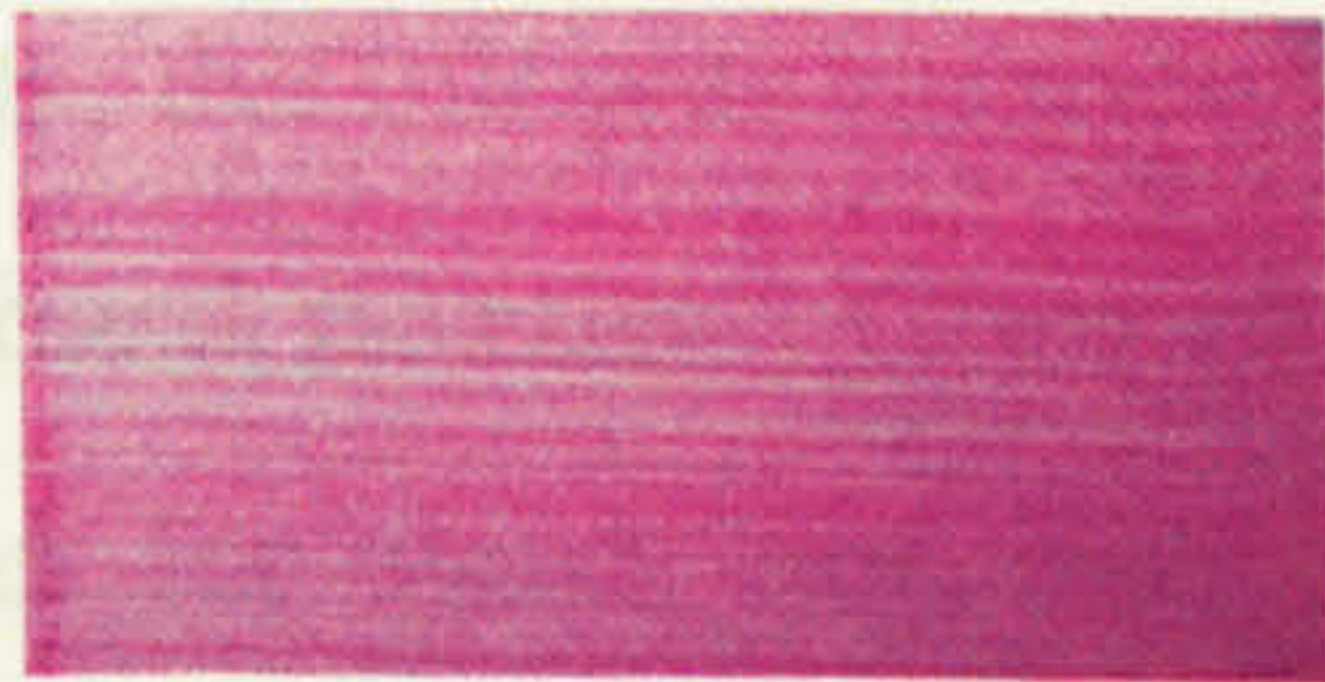

	Samples printed	
	Cotton	Polyester
Freshly prepared Toner Ink Formulation 3		
Toner Ink Formulation 3 aged for 3 weeks		

Figure 3.4.c Assessment of settling on print quality of Toner Ink Formulation 3

It can be seen from the images presented in Figure 3.4.c that the samples printed using the Toner Ink Formulation 3 aged for 3 weeks were significantly poorer in quality to

those printed with the freshly milled Toner Ink Formulation 3. The print became scratchy and deteriorated as printing continued. Such deterioration was likely to be due to the larger pigment aggregates causing a blockage of the print-head nozzles. Such blocking of the nozzles would act to reduce the amount of ink that could be ejected from the print-head onto the substrate.

3.4.1.4 Properties of Toner Ink Formulation 4 – Containing a Slip Additive

Toner Ink Formulation 4, which contained a silicone, based anti slip agent was produced in an attempt to improve the rubfastness of the printed samples. Once milled, the ink was tested for its physical properties and the results of such tests can be seen in Table 3.4.v.

Table 3.4.v Physical properties of Tone Ink Formulation 4

Physical property tested	Data obtained for Toner Ink Formulation 3
Viscosity at 60 rpm and 25°C (mPas)	4.84
Surface tension (mNm ⁻¹)	52
Particle size at a 95% limit (nm)	338

As with the data obtained for Toner Ink Formulation 1, it can be seen from Table 3.4.v that Toner Ink Formulation 4 adheres to the physical requirements of a typical ink jet ink.

Toner Ink Formulation 4 was printed onto cotton and polyester fabrics using a Hewlett Packard HP 51626A print cartridge and an Apollo P1200 ink jet printer. On completion of the required number of prints, the ink was removed from the cartridge to avoid any possible blocking of the print-head nozzles. Once printed and cured, the cotton and polyester samples were tested for wash and rub resistance. The results of the washfastness tests carried out can be seen in Table 3.4.w, Table 3.4.x and Table 3.4.y.

Table 3.4.w Optical densities of cotton printed using Toner Ink Formulation 4 before and after washfastness tests

Ink formulation	Optical density on cotton		
	Before washing	After washing	Difference
Yellow	0.50	0.49	0.01
Magenta	0.78	0.77	0.01
Cyan	0.77	0.76	0.01

Table 3.4.x Optical densities of polyester printed using Toner Ink Formulation 4 before and after washfastness tests

Ink formulation	Optical density on polyester		
	Before washing	After washing	Difference
Yellow	0.47	0.45	0.02
Magenta	0.75	0.74	0.01
Cyan	0.74	0.72	0.02

Table 3.4.y Greyscale evaluation of the change in colour of cotton and polyester fabrics printed with Toner Ink Formulation 4 after washing

Ink formulation	Value of colour difference according to greyscale	
	Cotton	Polyester
	Assessment of colour difference between printed samples before and after washing	Assessment of colour difference between printed samples before and after washing
Yellow	4/5	4/5
Magenta	4/5	4/5
Cyan	4/5	4/5

It can be seen from Table 3.4.w to Table 3.4.y that the washfastness for the samples printed using Toner Ink Formulation 4 were excellent. Very minor changes in the

optical density of the samples were measured, no staining of the multifibre strip was observed and no colour was seen to be removed from the printed samples and into the wash-bath liquor.

The rub resistance of the cotton and polyester fabrics printed using Toner Ink Formulation 3 was assessed and the results obtained can be seen in Table 3.4.z and Table 3.4.aa.

Table 3.4.z Optical density of colour transferred to cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed with Toner Ink Formulation 4

Pigmented ink formulation	Optical density of cotton lawn rubbing fabric after rub test			
	Cotton		Polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	0.12	0.15	0.14	0.17
Magenta	0.11	0.14	0.14	0.18
Cyan	0.12	0.16	0.15	0.20

Table 3.4.aa Greyscale evaluation of the change in colour of cotton lawn pads after rubfastness tests on cotton and polyester fabrics printed with Toner Ink Formulation

Pigmented ink formulation	Value of colour difference according to greyscale			
	Cotton		Polyester	
	Assessment of colour difference between printed samples before and after washing		Assessment of colour difference between printed samples before and after washing	
	Dry rub	Wet rub	Dry rub	Wet rub
Yellow	3/4	3	3/4	3
Magenta	3/4	3	3/4	3
Cyan	3/4	3	3/4	3

It can be seen from Table 3.4.z and Table 3.4.aa that some colour was removed from the printed cotton and polyester fabrics after rubfastness tests. It should be noted that the colour stain of the cotton lawn pads was not significant. Such results would be acceptable for a range of applications in the field of textile printing.

As with previous formulations a possible negative effect in settling of the pigment was noticed. This problem was again attributed to the possibility of aggregation of pigment particles within the formulation although the surfactant and glycols may contribute to this problem. Toner Formulation 4 was also seen to form a white layer on the surface of the ink. It was thought that the white separation was likely to be the silicone based emulsion falling out of dispersion and forming on the surface due to it having a lower molar mass.

As mentioned previously however, despite some long-term stability issues, the inks produced using the Toner pigments were seen to perform well. The initial physical properties measured for each ink adhered to the requirements of an ink suitable for ink jet printing. The fastness results obtained were good and the print quality was good several hours after formulation. As such, there is a possibility for such ink formulations to be used within the textile printing industry where high volumes of textiles are ink jet printed in a short period of time. Such high production rate would allow for consistent replenishment of ink thus negating any problems associated with pigment aggregation. Printing of the formulated ink with a desktop printer designed for printing paper may not show the full extent of printing offered by an industrial ink jet unit. As such any problems encountered on a desktop scale printer are likely to be greater than would be encountered on industrial scale printers due to the size of nozzles used. It should be noted, that whilst carbon black pigment is used for the standard black ink within a desktop printer, the majority of coloured inks are seen to be dye based. As such, pigmented inks are likely to encounter problems, whereas on an industrial printer designed to print pigmented inks, such pigmented inks are likely to cause far fewer disruptions to the printing process. Should stability problems still remain an issue, the addition of thickener would provide a successful transition to a screen ink formulation.

3.5 Characterisation of Ink Jet Inks Containing Microlith Pigments

The following section details the results of the investigation into the use of ink jet

printing inks containing Synthappret BAP as the binder and Microlith WA pigments as the colorant.

3.5.1 Evaluation of Microlith Pigment Paste

In order for Microlith pigments to be incorporated into an ink formulation it was necessary to produce a pigment paste. Surface modification of Microlith pigments ensures excellent dispersibility of the pigment particles in the presence of alkaline conditions. It is thought that such a surface modification allows for the pigment particles to become partially soluble in the presence of a reasonably strong alkali. In order to assess the extent of such dispersibility SEM was used to analyse the pigment in its crystalline form and then the pigment combined with water, IPA and ammonia within a pigment paste. The micrographs obtained can be seen in Figure 3.5.a and Figure 3.5.b.

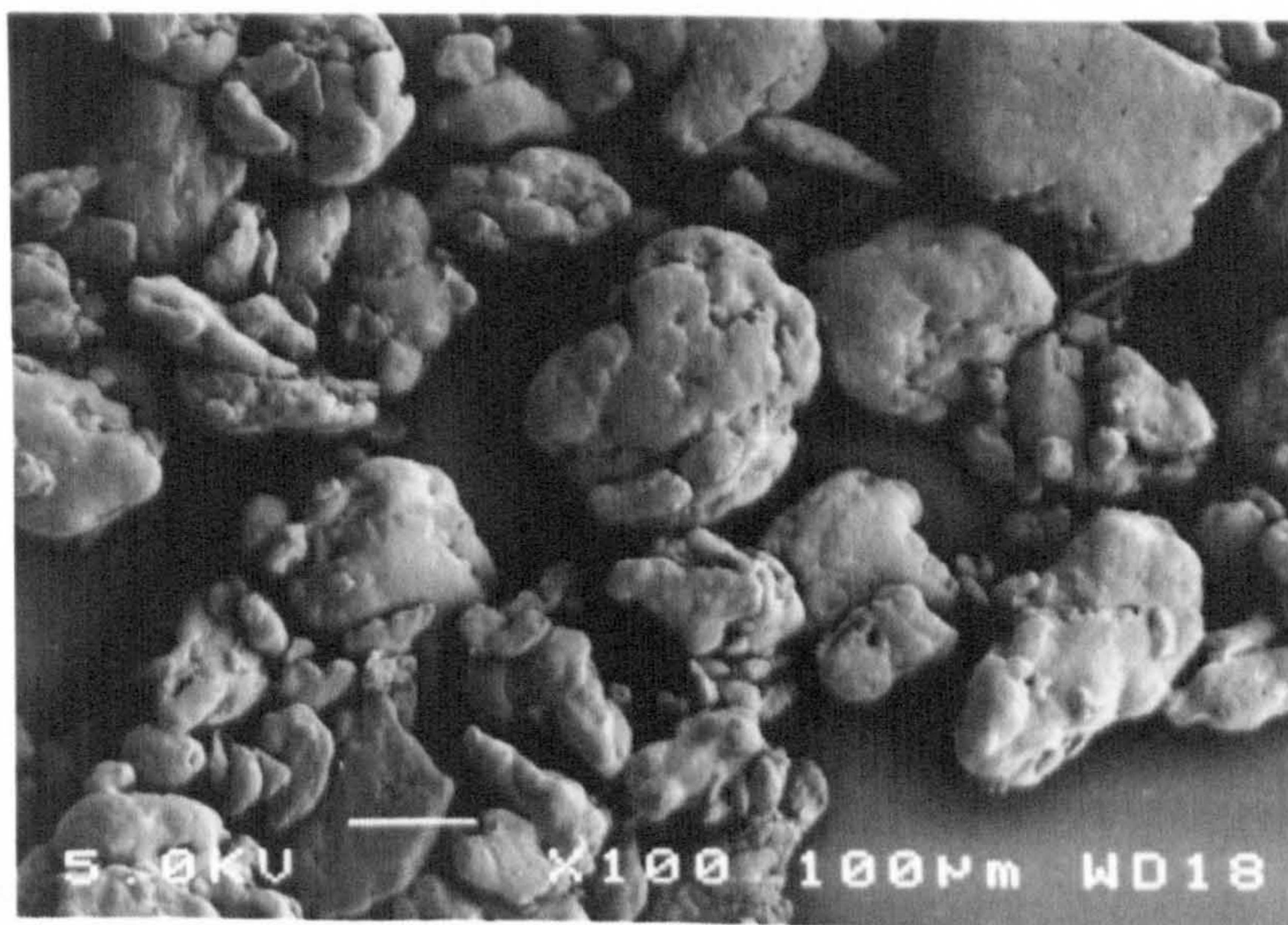


Figure 3.5.a Micrograph of Microlith Magenta BWA prior to dispersing ($\times 100$)

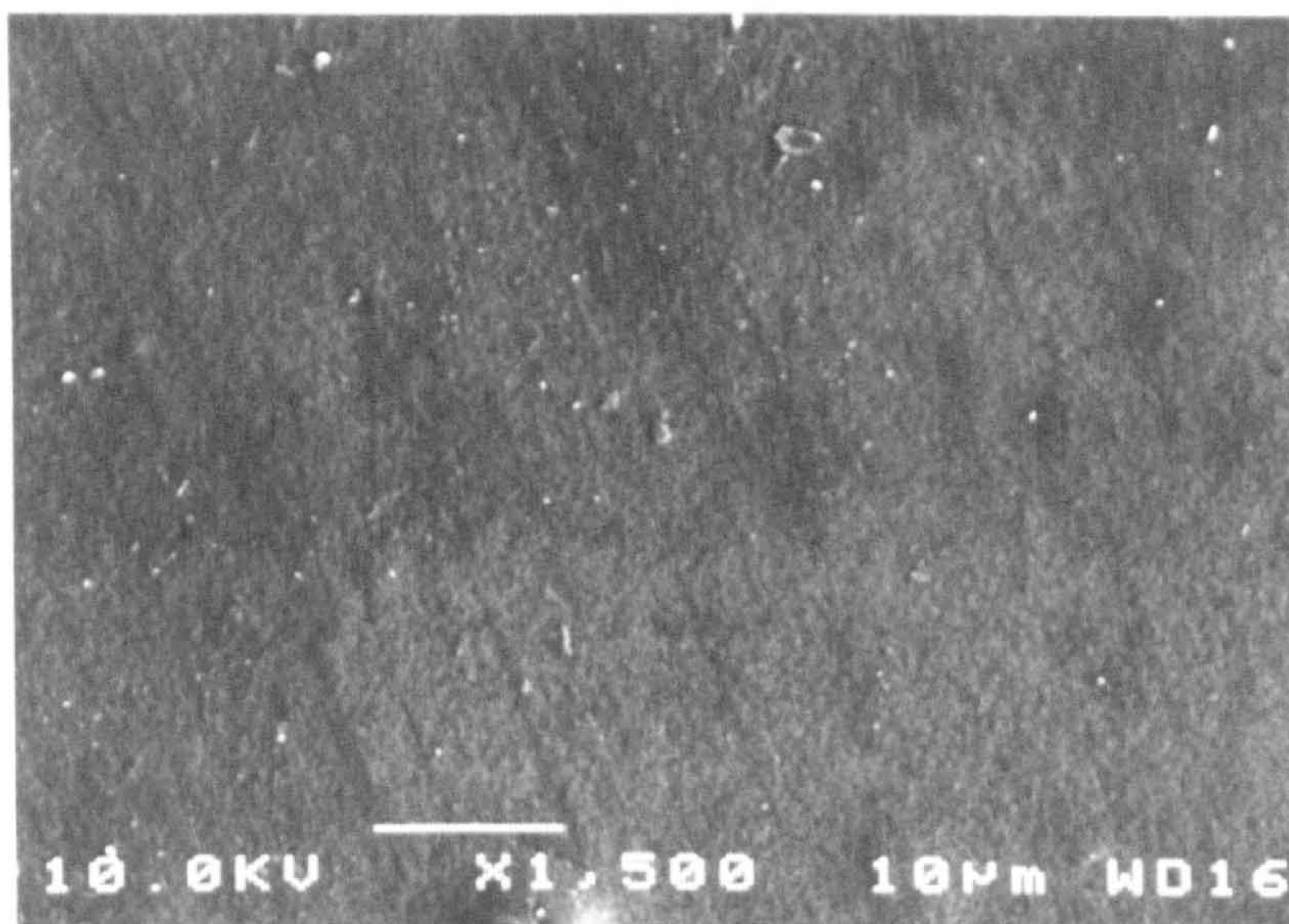


Figure 3.5.b Micrograph of dispersed Microlith Magenta BWA ($\times 1500$)

It can be seen from Figure 3.5.a that at a low magnification ($\times 100$), the pigment existed as large clusters. It is likely that these clusters were composed of aggregated pigment particles. In contrast, it can be seen from Figure 3.5.b that at a far greater magnification ($\times 1500$) that, once combined within the paste, the pigment particles were very different. There was no real evidence for pigmented aggregates and the layer of paste appeared relatively smooth. It was apparent that the pigment particles within the paste were highly dispersed and had a significantly smaller particle size than the original crystalline pigment. It should be noted that the dramatic change in the visual dispersibility and particle size of the pigment particles was noticed for a pigment paste that had very low shear forces applied. There was no application of a bead mill or other severe mixing processes, the pigment paste was stirred magnetically over a period of 30 minutes. As such, it was apparent that such dispersibility of the Microlith pigment was due to the presence of the alkali component of the paste in this case ammonia. Pigment pastes made up without the presence of an alkali constituent showed the Microlith pigment to remain in its original crystalline form within the aqueous solvent when mixed under the same conditions. The pigment did not disperse at all with the solvent and pigment particles separated out.

3.5.2 Properties of Microlith Ink Formulation 1 - Initial Ink Composition

After formulation and filtration of Microlith Ink Formulation 1, the resulting ink was tested for its physical properties to ascertain its suitability for ink jet printing. The results of the tests carried out to determine the viscosity, surface tension and particle size of Microlith Ink Formulation 1 can be seen in Table 3.5.a.

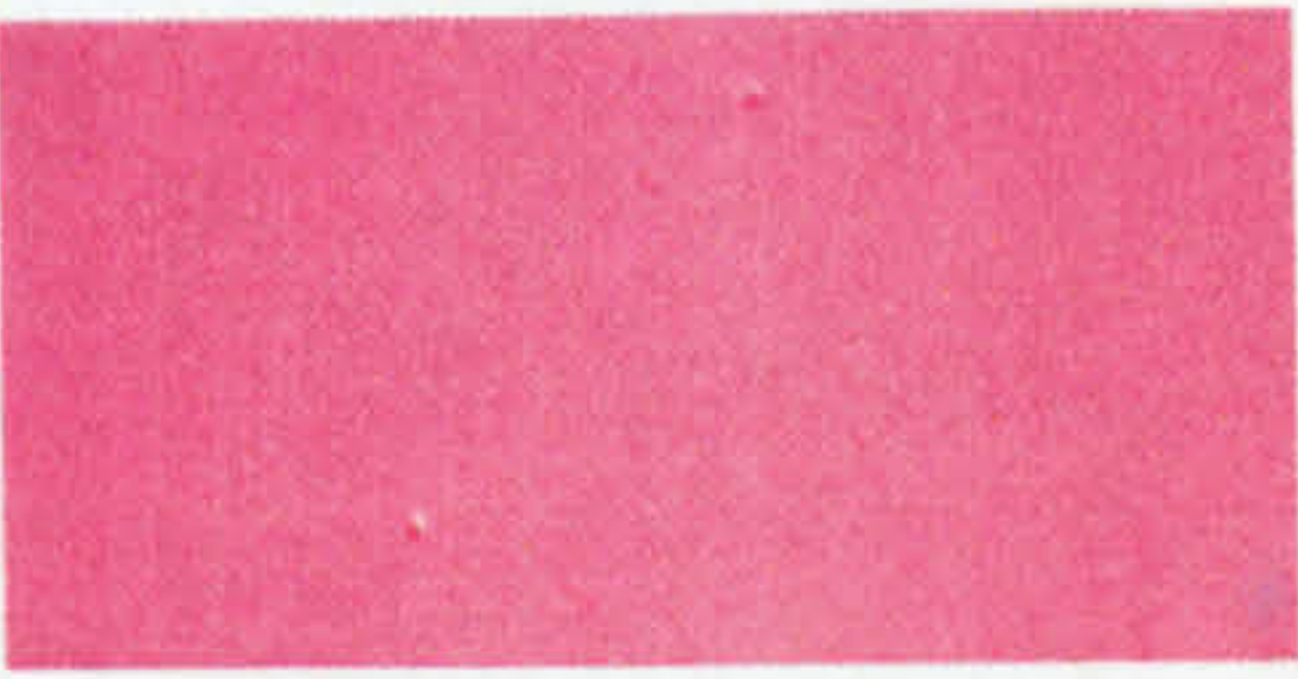

Table 3.5.a Physical properties of Microlith Ink Formulation 1

Physical property tested	Data obtained for Microlith Ink Formulation 1
Viscosity at 60 rpm and 25°C (mPas)	3.21
Surface tension (mNm ⁻¹)	36
Particle size at a 95% limit (nm)	212

It can be seen from the data presented in Table 3.5.a, that Microlith Ink Formulation 1 adhered to the guidelines laid out for the acceptability of an ink for ink jet printing. Importantly, a low particle size and low viscosity were noticed.

Microlith Ink Formulation 1 was printed onto cotton fabric and assessed for wash and rub resistance properties. Images of the printed sample before and after washing along with values for the optical densities of the samples can be seen in Table 3.5.b. The results of the visual assessments made of the colour difference between the washed and unwashed sample according to greyscale are detailed also in Table 3.5.b.

Table 3.5.b Assessment of colour change of cotton printed with Microlith Ink Formulation 1 after application of the washfastness test

Ink formulation	Optical density on cotton		Assessment of colour difference between printed samples before and after washing
	Before washing	After washing	
Printed samples			N/A
Values measured	0.72	0.71	5

It can be seen from Table 3.5.b that the change in optical density of the printed samples after the washfastness test was minimal. The visual assessment of the colour difference between the washed and unwashed samples also suggested that the washfastness of Microlith Ink Formulation 1 on cotton was very good. No staining of the multifibre strip was observed. However, this was as expected due to the colorant being a pigment. Importantly, no colour had been removed from the printed samples and into the wash-bath liquor. SEM analysis of cotton printed using Microlith Ink Formulation 1 was carried out on a sample of unwashed and a sample of washed fabric. The micrographs obtained from this topological analysis can be seen in Figure 3.5.c and Figure 3.5.d.



Figure 3.5.c Micrograph of a sample of cotton printed with Microlith Ink Formulation 1 before washing ($\times 1500$)



Figure 3.5.d Micrograph of a sample of cotton printed with Microlith Ink Formulation 1 after application of the washfastness test ($\times 1500$)

It can be seen from Figure 3.5.c and Figure 3.5.d that there was very little difference between the washed and unwashed cotton samples. Neither micrograph showed evidence of the presence of pigment particles on the surface of the fibres. This was likely to be due to the particle size of the pigment being so small and thus penetrating

into the fibres. The washing process did not appear to cause significant damage to the cotton fibres and as such the colour was not removed.

The results obtained for the rubfastness tests carried out on the printed cotton can be seen in Table 3.5.c. Table 3.5.c shows the optical density of colour removed from the printed substrate onto the cotton lawn pad and the visual assessment of colour difference between rubbed and unrubbed samples.

Table 3.5.c Assessment of the rubfastness of cotton printed with Microlith Ink Formulation 1

Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.11	0.15	4	3/4

It can be seen from Table 3.5.c that the rubfastness results measured were good. Some colour had been transferred from the printed cotton to the cotton lawn rub pads although such an amount was low. On completion of the rubfastness testing, the printed cotton fabric appeared as it was prior to the process of rubbing. Thus, whilst colour had been removed from the cotton, enough remained for the lost colour to be unnoticeable. As such, the rubfastness of the print was deemed acceptable for certain applications.

3.5.3 Properties of Microlith Ink Formulation 2 – Containing Sodium Hydroxide in place of Ammonia

Microlith Ink Formulation 2 incorporated sodium hydroxide as the alkaline element of the ink to provide the dispersion of the pigment. Once formulated, the resulting ink was tested for its suitability for ink jet printing in terms of the required physical properties. The results of the tests carried out to determine the viscosity, surface tension and particle size of Microlith Ink Formulation 2 can be seen in Table 3.5.d.

Table 3.5.d Physical properties of Microlith Ink Formulation 2

Physical property tested	Data obtained for Microlith Ink Formulation 1
Viscosity at 60 rpm and 25°C (mPas)	3.26
Surface tension (mNm ⁻¹)	35.5
Particle size at a 95% limit (nm)	206

It can be seen from the data presented in Table 3.5.d that Microlith Ink Formulation 2 adhered to the parameters set out for ink jet printing. Importantly, a low particle size and low viscosity were observed.

Microlith Ink Formulation 2 was used to print samples of cotton fabric. Once printed and cured, the cotton samples were tested for their washfastness and rubfastness. The results of the washfastness testing of the printed cotton can be seen in Table 3.5.e.

Table 3.5.e Assessment of colour change of cotton printed with Microlith Ink Formulation 2 after application of the washfastness test

Optical density on cotton		Assessment of colour difference between printed samples before and after washing
Before washing	After washing	
0.73	0.71	5

It can be seen from Table 3.5.e that the change in the optical density of colour on the printed samples was minimal on application of the washfastness test. Such a minimal change was confirmed by the results obtained for the visual assessment of the colour change of the sample after washing. On completion of the washfastness test, it should be noted that no colour had been transferred from the printed sample onto the multifibre strip included. Furthermore, no colour had been removed from the printed cotton into the wash-bath liquor. The results suggested that the observed and measured washfastness of the cotton printed using Microlith Ink Formulation 2 was

excellent.

The results obtained for the rubfastness tests carried out on the printed cotton can be seen in Table 3.5.f.

*Table 3.5.f Assessment of the rubfastness of cotton printed with Microlith Ink
Formulation 2*

Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.12	0.16	4	3/4

It can be seen from Table 3.5.f that the results obtained from the rubfastness testing of the printed cotton were encouraging. The optical density of the colour removed from the printed sample onto the cotton lawn fabric was low, indicating that only a small amount of colour had been removed. The wet rub test removed slightly more colour and this was likely to be due to the greater friction and thus abrasion applied to the sample. The presence of water on the cotton lawn pads may also have acted to loosen the fibre structure slightly. This was however a minor point as the force exerted onto the printed sample was likely to disrupt the fibre structure. SEM analysis was carried out on a section of the cotton lawn pad used for dry and wet rubfastness tests to see if any evidence of pigment removal from the printed sample was apparent. The micrographs obtained can be seen in Figure 3.5.e and Figure 3.5.f

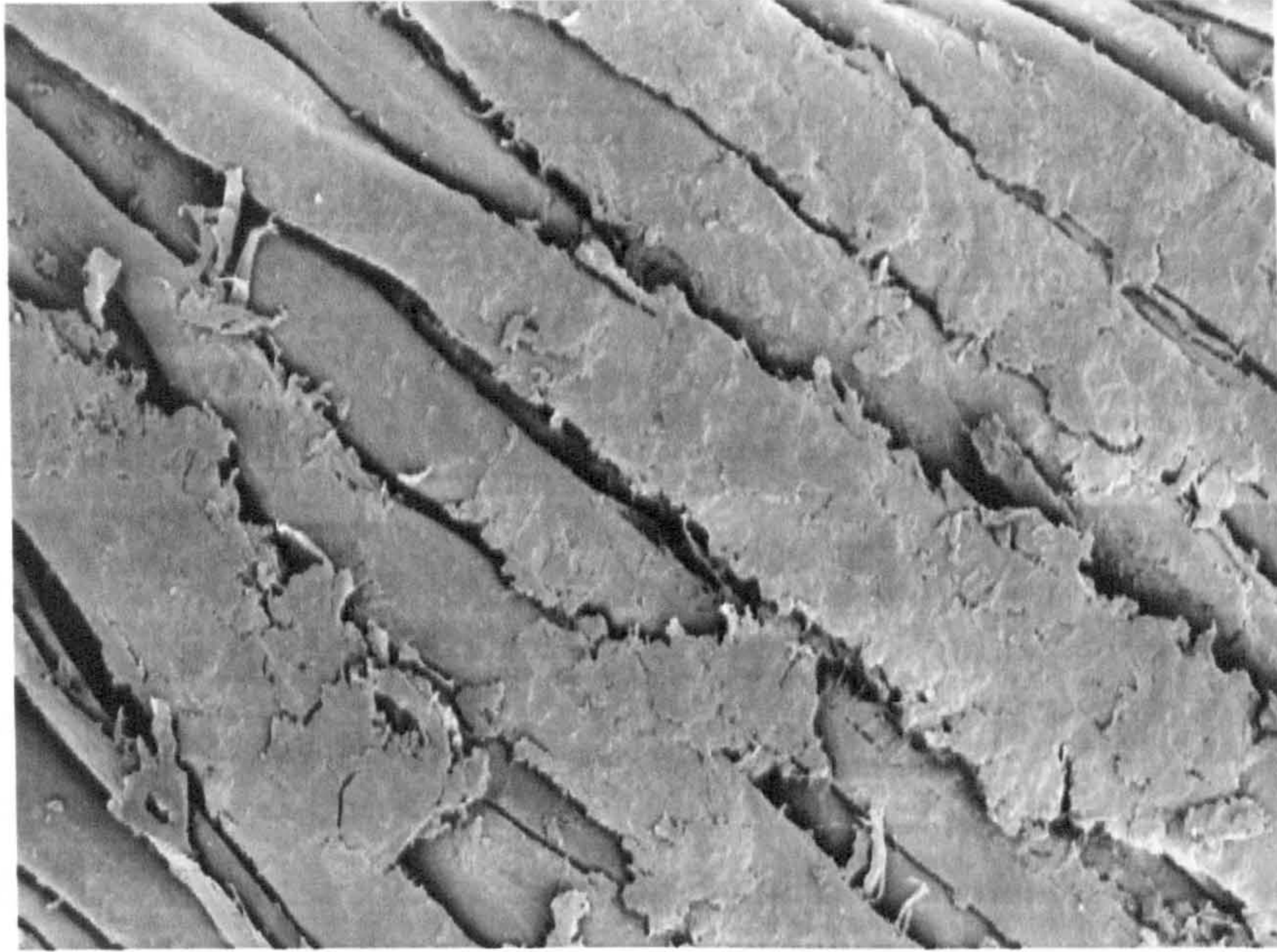


Figure 3.5.e Micrograph of cotton lawn pad after a dry rub test on a cotton sample printed with Microlith Ink Formulation 2 ($\times 1500$)

It can be seen from Figure 3.5.e that there was no evidence of pigment particles on the fibres of the cotton lawn pad used in the dry rub test. It was noticeable that the surface fibres of the pad had become flattened and disrupted by the rub test.



Figure 3.5.f Micrograph of cotton lawn pad after a wet rub test on a cotton sample printed with Microlith Ink Formulation 2 ($\times 1500$)

It can be seen from Figure 3.5.f that no evidence of pigment particles on the fibres of the cotton lawn pad used in the wet rub test was apparent. It was however, noticeable that the extent of the flattening and disruption of the fibres of the pad was greater than that of the dry rub pad. Such disruption was likely to have occurred on the printed fabric also, thus explaining the greater removal of colour on application of the wet rub test. However, it should be noted that the rubfastness measured was acceptable.

3.5.4 Limitations of Microlith Ink Formulations

As with the inks formulated using Toner pigments, a problem with the long-term stability of the inks containing Microlith pigments was observed. Such stability issues lay in the formation of a spongy coloured solid within the ink after a period of 2 months. It is likely that the inclusion of an alkali component within the inks had acted to aid the cross-linking of Synthappret BAP at ambient temperatures. However, the inks formulated using Microlith pigments offered prints with excellent washfastness and good rubfastness. The handle of the fabric was also unaltered by printing. As such, there is scope for inks formulated using Microlith pigments to be used for ink jet printing onto textile materials. One off colours made specifically for a short run of prints would be an ideal area of application for such inks. Also, the Microlith based inks could be used in any textile ink jet printing process in which large volumes of fabric are printed over a short period of time allowing frequent replenishment of the ink supply. In fact, any ink jet printing process in which the ink is not required to have a shelf life of greater than 2 months could incorporate Microlith inks. It is also possible that for certain applications, the ink could be formulated immediately prior to printing, thus allowing for the use of inks incorporating Microlith pigments and Synthappret BAP.

3.6 Formulation and Characterisation of inks using Cab-O-Jet Pigment Dispersions

The following section details the results of the investigation into the use of ink jet printing inks containing Synthappret BAP as the binder and Cab-O-Jet pigment dispersions as the colorant.

3.6.1 Properties of Cabot Ink Formulation 1 – Initial Ink

After formulation of Cabot Ink Formulation 1, the resulting ink was tested for its physical properties. In order to assess the suitability of Cabot Ink Formulation 1 for

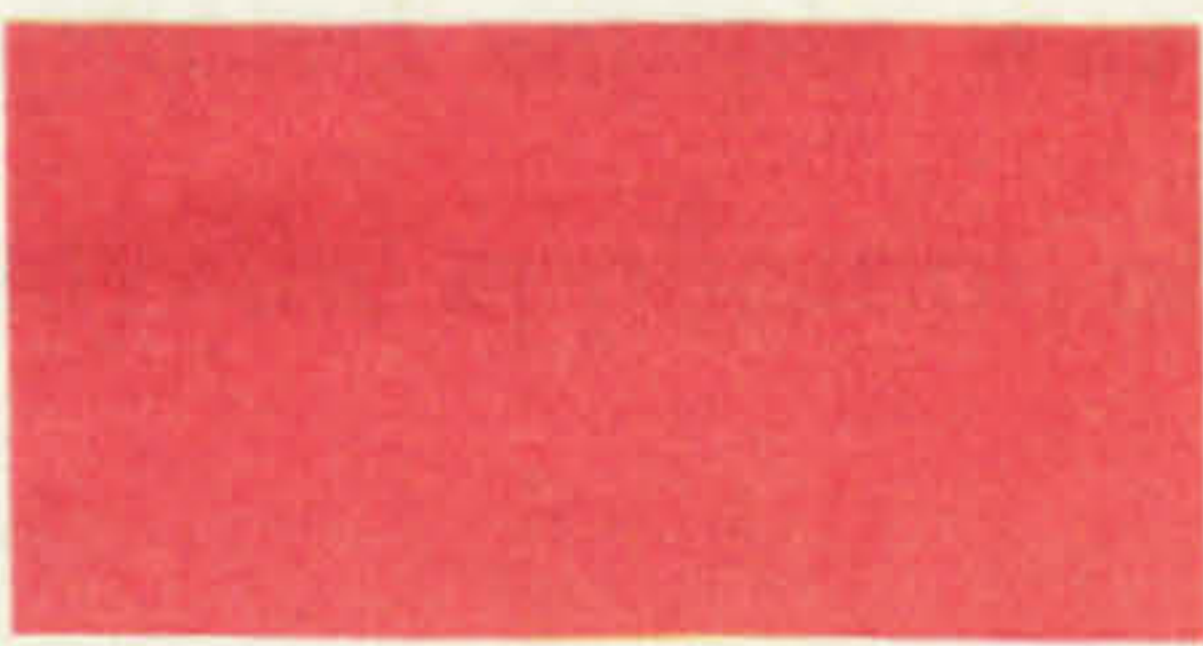
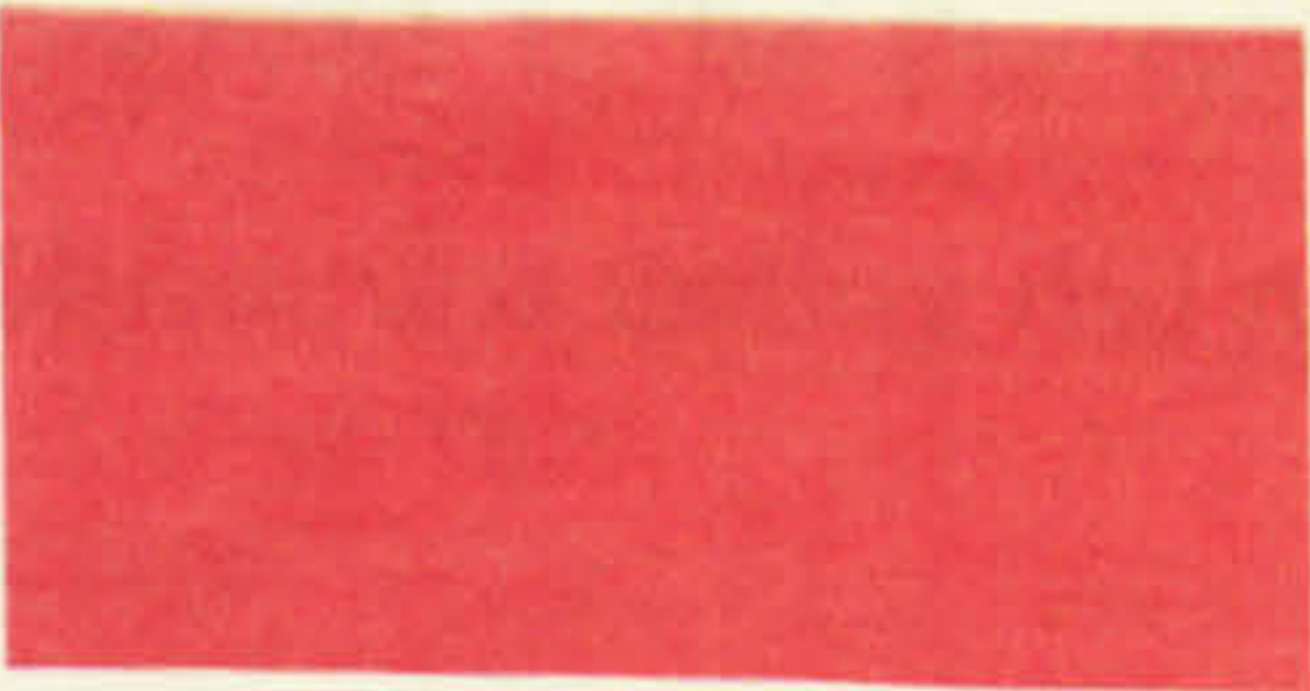
ink jet printing, tests were undertaken to determine its viscosity, surface tension and particle size. The results of such tests are detailed in Table 3.6.a.

Table 3.6.a Physical properties of Cabot Ink Formulation 1

Physical property tested	Data obtained for Cabot Ink Formulation 1
Viscosity at 60 rpm and 25°C (mPas)	2.91
Surface tension (mNm ⁻¹)	36
Particle size at a 95% limit (nm)	109

It can be seen from the data presented in Table 3.6.a that Cabot Ink Formulation 1 adhered to the guidelines laid out for the acceptability of an ink for ink jet printing. In particular, it had a very small particle size and a low viscosity making it ideal for ink jet printing. As such, Cabot Ink Formulation 1 was printed onto cotton fabric using an Apollo P1200 desktop ink jet printer. Once cured, the printed cotton sample was tested for wash and rub resistance. Images of the printed sample before and after washing along with values for the optical densities of the samples can be seen in Table 3.6.b. The results of the visual assessments made of the colour difference between the washed and unwashed sample according to greyscale are detailed also in Table 3.6.b.

Table 3.6.b Assessment of the washfastness of a sample of cotton fabric printed with Cabot Ink Formulation 1

Ink formulation	Optical density on cotton fabric		Assessment of colour difference between printed samples before and after washing
	Before washing	After washing	
Printed samples			N/A
Values measured	0.57	0.56	5

It can be seen from Table 3.6.b that the change in optical density of the printed samples after the washfastness test was minimal. The visual assessment of the colour difference between the washed and unwashed samples also suggested that the washfastness of Cabot Ink Formulation 1 on cotton was very good. No colour was removed from the washed cotton sample into the wash-bath liquor and no staining of the included multifibre strip was apparent. The results attained for the washfastness of the cotton sample printed with Cabot Ink Formulation 1 were excellent and consistent with those expected of high performance ink.

Results obtained for the rubfastness tests carried out on the printed cotton can be seen in Table 3.6.c. The data presented in Table 3.6.c shows the optical density of any colour removed from the printed substrate onto the cotton lawn pad upon wet and dry rub tests and the visual assessment of colour difference between rubbed and unrubbed samples.

Table 3.6.c Assessment of the rubfastness of a sample of cotton fabric printed with Cabot Ink Formulation 1

Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.11	0.15	4	3/4

It can be seen from the results presented in Table 3.6.c that whilst the rubfastness of the printed and cured cotton was improved from prints using Toner and Microlith pigments, there was still a degree of staining of the cotton lawn fabric. However, it should be noted that such an amount of staining would be acceptable for the majority of textile applications. As such, the rubfastness results could be deemed acceptable. This was confirmed by the visual assessment of the colour difference between a clean and rubbed cotton lawn pad. It should also be noted that on completion of the dry and wet rub tests, the printed sample was observed to be the same colour as before rubbing. That is to say, the application of rubfastness testing did not visually discolour the printed samples.

3.6.2 Properties of Cabot Ink Formulation 2 – Containing a Slip Additive

The incorporation of Lubrisil CR 200 within the ink formulation was thought not to have a significant effect on the physical properties of the ink and as such, such parameters were not measured. The minimal effect of incorporation of Lubrisil CR 200 had previously been seen when included in Toner Ink Formulation 4. Cabot Ink Formulation was tested for its fastness properties on cotton fabric once printed and cured. The results of the fastness testing undertaken can be seen in Table 3.6.d and Table 3.6.e.

Table 3.6.d Assessment of the washfastness of a sample of cotton fabric printed with Cabot Ink Formulation 2

Optical density on cotton		Assessment of colour difference between printed samples before and after washing
Before washing	After washing	
0.58	0.56	5

Table 3.6.e Assessment of the rubfastness of a sample of cotton printed with Cabot Ink Formulation 2

Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.09	0.13	4/5	4

It can be seen from Table 3.6.d that the incorporation of a lubricant within Cabot Ink Formulation 2 had very little effect on the washfastness of the printed sample. This was expected, as it is unlikely that the silicone based emulsion used would interfere with the curing mechanism of the Synthappret BAP or the mechanical trapping of the pigment particles printed onto the substrate.

The results for the rubfastness testing of the cotton sample printed with Cabot Ink Formulation 2, seen in Table 3.6.e, show that the incorporation of Lubrisil CR 200 within the ink gave only a slight improvement in the observed rub resistance of the print. The rubfastness results were however very good and showed minimal removal of colour from the printed substrate onto the cotton lawn rub pads. Any colour change of the substrate after application of the rub tests was not visible and as such the print sample was acceptable.

It was noticed that after a few weeks, a white layer appeared on the surface of the ink. It was thought that such a phenomenon was due to the separation of the silicone based emulsion from the bulk solvent of the ink due to it falling out of the dispersion.

3.6.3 Properties of Cabot Ink Formulation 3 – Effects of a Pre-Treatment of the Substrate

Before printing Cabot Ink Formulation 3 onto the cotton substrate, the cotton fabric was pre-treated with a 1 M solution of sodium bicarbonate. Due to it being similar in make-up, it was assumed that the physical properties of Cabot Ink Formulation 3 were similar to those measured for Cabot Ink Formulation 1. As such, Cabot Ink Formulation 3 was printed directly onto the pre-treated cotton substrate. Once cured, the printed cotton was assessed for rub and wash resistance. The results obtained for the washfastness and rubfastness of the printed cotton fabric can be seen in Table 3.6.f and Table 3.6.g.

Table 3.6.f Assessment of the washfastness of a sample of cotton fabric printed with Cabot Ink Formulation 3

Optical density on cotton fabric		Assessment of colour difference between printed samples before and after washing
Before washing	After washing	
0.59	0.58	5

Table 3.6.g Assessment of the rubfastness of a sample of cotton fabric printed with Cabot Ink Formulation 2

Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.11	0.14	4/5	4

It can be seen from Table 3.6.f that the effect of the pre-treatment of the cotton fabric prior to printing had little effect on the washfastness of the printed sample. It should be noted however, that the washfastness results for previous formulations were very good initially, giving results acceptable to industrial standards.

It can be seen from Table 3.6.g that the rubfastness of the printed cotton fabric was similar to that achieved for Cabot Ink Formulation 1. The use of the sodium carbonate pre-treatment was seen to have little or no effect. This may have been due to the fact that the sodium bicarbonate was not in a high enough concentration. Another factor may lie in the fact that the amount of Synthappret BAP actually applied to the substrate was very small and a greater amount may be required for the action of the catalyst to become apparent. It should also be noted that the initial aim of the investigation was to produce an ink to be printed directly onto a textile substrate in a one-pack process. The incorporation of a pre-treatment step increased the complexity of the process and added extra time to the printing process from raw material to printed substrate. As such, it was decided not to continue with further pre-treatment of the substrate due to the limited effect noticed on the performance of the printed fabric. The results attained for previous ink formulations had given excellent washfastness and good rubfastness and as such an extra step in the printing process was deemed unnecessary.

3.6.4 Effect of Additives on the Rub Resistance Properties of Cabot Ink Formulations

Each of the following formulations, Cabot Ink Formulation 4 to Cabot Ink Formulation 6, was printed onto cotton, cured and tested for wash and rub resistance to ascertain the contribution of various slip additives to the performance of the ink in rubfastness tests. The washfastness of the printed cotton was also assessed in each case to see if

inclusion of such slip additives was seen to have a detrimental effect thereon. Each ink formulated was also tested for viscosity and surface tension prior to printing to ensure suitability for ink jet printing. The particle size of the pigment within each ink was not measured due to the known low particle size of the Cab-O-Jet pigment dispersions used.

3.6.4.1 Cabot Ink Formulation 4 – Containing Lubit 64

Cabot Ink Formulation 4 containing Lubit 64 supplied by Bayer was prepared. The results of the viscosity and surface tension testing can be seen in Table 3.6.h. The results obtained for the washfastness and rubfastness of Cabot Ink Formulation 4 on cotton fabric can be seen in Table 3.6.i and Table 3.6.j.

Table 3.6.h Physical properties of Cabot Ink Formulation 4

Physical property tested	Data obtained for Cabot Ink Formulation 4
Viscosity at 60 rpm and 25°C (mPas)	2.95
Surface tension (mNm ⁻¹)	35.5

It can be seen from Table 3.6.h that the inclusion of Lubit 64 in Cabot Ink Formulation 4 had a minor effect on the viscosity and surface tension of the final ink. Due to its relatively high viscosity, the inclusion of a higher concentration of Lubit 64 within the ink formulation would lead to an increase in the overall viscosity of the ink. In terms of Cabot Ink Formulation 4, both the measured viscosity and surface tension were compliant with the requirements of an ink for use in an ink jet printing process.

Table 3.6.i Assessment of the washfastness of a sample of cotton fabric printed with Cabot Ink Formulation 4

Optical density on cotton		Assessment of colour difference between printed samples before and after washing
Before washing	After washing	
0.58	0.57	5

Table 3.6.j Assessment of the rubfastness of a sample of cotton fabric printed with Cabot Ink Formulation 4

Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.10	0.14	4	4

It can be seen from Table 3.6.i that the incorporation of a Lubit 64 within Cabot Ink Formulation 4 had very little effect on the washfastness of the printed sample. The results obtained for the washfastness of the sample printed with Cabot Ink Formulation 4 were consistent with the results achieved for Cabot Ink Formulation 1.

It can be seen from Table 3.6.j that the results obtained for the rubfastness of the cotton sample printed with Cabot Ink Formulation 4 showed that the incorporation of Lubit 64 had little to no effect on the measured and observed rubfastness of the printed cotton fabric. However, the results obtained showed no detrimental effects of the inclusion of Lubit 64. The values obtained were consistent with those previously measured for Cabot Ink Formulation 1 and as such were acceptable for the majority of textile applications. As with tests on previous printed cotton samples, the rubbed area did not exhibit any colour degradation after the rubfastness tests.

3.6.4.2 Properties of Cabot Ink Formulation 5 – Containing Dow Corning 51 Additive

Cabot Ink Formulation 5 containing Dow Corning 51 Additive supplied by Dow Corning was prepared. The results of the viscosity and surface tension testing can be seen in Table 3.6.k. The results obtained for the washfastness and rubfastness of Cabot Ink Formulation 5 on cotton fabric can be seen in Table 3.6.l and Table 3.6.m.

Table 3.6.k Physical properties of Cabot Ink Formulation 5

Physical property tested	Data obtained for Cabot Ink Formulation 5
Viscosity at 60 rpm and 25°C (mPas)	3.06
Surface tension (mNm ⁻¹)	35.5

It can be seen from Table 3.6.k that the inclusion of Dow Corning 51 Additive within Cabot Ink Formulation 5 had no great effect on the viscosity or surface tension of the ink. This was likely to be due to the low levels of Dow Corning 51 Additive included within the ink formulation. It was expected that at higher concentrations some change in the viscosity would be observed. The measured viscosity and surface tension of Cabot Ink Formulation 5 were within the parameters required for an ink to be viable for ink jet printing.

Table 3.6.l Assessment of the washfastness of a sample of cotton fabric printed with Cabot Ink Formulation 5

Optical density on cotton fabric		Assessment of colour difference between printed samples before and after washing
Before washing	After washing	
0.58	0.57	5

Table 3.6.m Assessment of the rubfastness of a sample of cotton fabric printed with Cabot Ink Formulation 5

Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.09	0.13	4/5	4

It can be seen from Table 3.6.l that the inclusion of a Dow Corning 51 Additive within the ink had little or no effect on the washfastness of the cotton sample printed using Cabot Ink Formulation 5. The results obtained for the washfastness of the sample printed with Cabot Ink Formulation 5 were consistent with those achieved for Cabot Ink Formulation 1.

It can be seen from Table 3.6.m that the results obtained for the rubfastness of the cotton sample printed with Cabot Ink Formulation 4 were seen to be consistent with those achieved for Cabot Ink Formulation 1. As such, the incorporation of Dow Corning 51 Additive was seen to have a negligible effect on the measured and observed rubfastness of the printed cotton. However the results obtained were acceptable for a number of applications of printed textiles. As with tests on previous printed cotton samples, the rubbed area did not exhibit any colour degradation after rubfastness tests.

3.6.4.3 Properties of Cabot Ink Formulation 6 – Containing Michem Lube 182

Cabot Ink Formulation 6 containing Michem Lube 182 supplied by Michelman Inc was prepared. The results of the viscosity and surface tension testing can be seen in Table 3.6.n. The results obtained for the washfastness and rubfastness of Cabot Ink Formulation 6 on cotton fabric can be seen in Table 3.6.o and Table 3.6.p.

Table 3.6.n Physical properties of Cabot Ink Formulation 6

Physical property tested	Data obtained for Cabot Ink Formulation 6
Viscosity at 60 rpm and 25°C (mPas)	2.91
Surface tension (mNm ⁻¹)	35.5

It can be seen from Table 3.6.n that the inclusion of Michem Lube 182 had a minor effect on the viscosity and surface tension of the final ink. Both parameters measured were compliant with the requirements of the ink for use in an ink jet printing process.

Table 3.6.o Assessment of the washfastness of a sample of cotton fabric printed with Cabot Ink Formulation 6

Optical density on cotton		Assessment of colour difference between printed samples before and after washing
Before washing	After washing	
0.59	0.58	5

Table 3.6.p Assessment of the rubfastness of a sample of cotton fabric printed with Cabot Ink Formulation 6

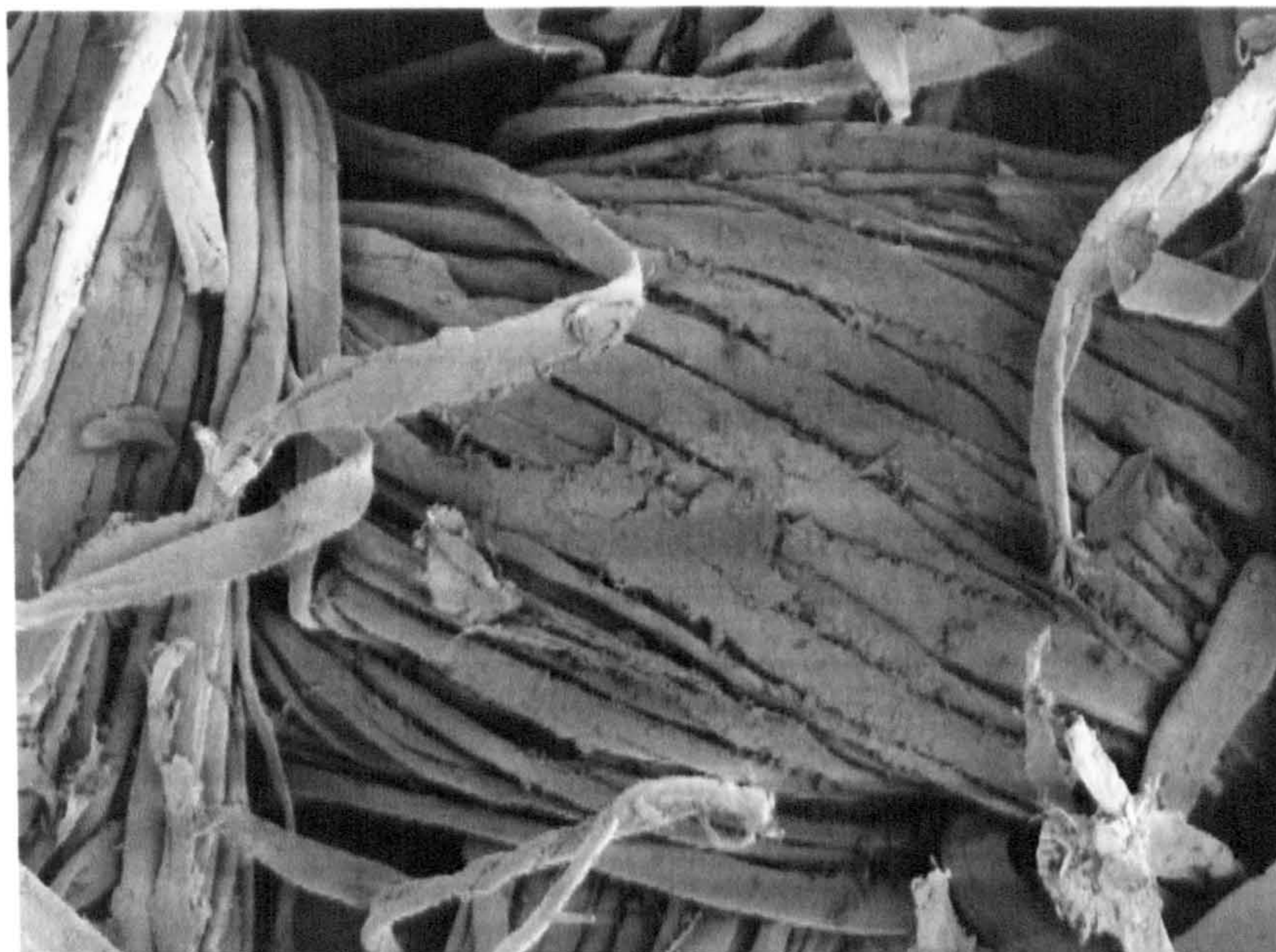
Optical density of cotton lawn rubbing fabric after rub test		Assessment of colour difference between printed samples before and after washing	
Dry rub	Wet rub	Dry rub	Wet rub
0.10	0.14	4	4

It can be seen from Table 3.6.o that the incorporation of Michem Lube 182 within Cabot Ink Formulation 6 had very little effect on the washfastness of the printed sample. The results obtained for the washfastness of the sample printed with Cabot Ink Formulation 6 were consistent with the results achieved for Cabot Ink Formulation 1. As such, the washfastness of the printed cotton fabric was found to be excellent.

It can be seen from Table 3.6.p that the results obtained for the rubfastness of the cotton sample printed with Cabot Ink Formulation 6 were consistent with those achieved for Cabot Ink Formulation 1. As such, little or no improvement was observed suggesting that the inclusion of Michem Lube 182 within the ink formulation reduced the amount of colour removed from the printed substrate onto the cotton lawn rub pads. It should be noted that the rubbed area was not seen to exhibit any colour degradation after the application of the rubfastness tests.

It can be seen from the results obtained for Cabot Ink Formulations 4, 5 and 6 that the difference in the observed washfastness and rubfastness were negligible in comparison to those obtained for Cabot Ink Formulation 1. Such a small effect may be due to the application of the slip additives in relatively low concentrations. However, an increase in the amount of slip additive added to each formulation may have an adverse effect

on the physical properties of the ink, especially the viscosity and the compatibility of the system. There is an argument that it was inevitable that a small amount of colour would be removed from the cotton substrate on application of a rub test. The chances of removing no colour with low levels of binder within the ink were small. As such, the incorporation of a slip additive within the system would act to reduce such colour removal. The low binder levels were required in order to achieve the correct physical properties of the ink for ink jet printing whilst maintaining acceptable handle of the fabric. Therefore, at the binder levels incorporated into each of the inks printed, it is likely that the fixation of the pigment to the substrate offered by the binder was enough to produce the measured rubfastness results without the incorporation of a slip additive. A further argument to suggest that the incorporation of a slip additive at low levels within the system would have little or no effect on the observed rubfastness of the printed substrate lies in the extent of penetration of the ink. For a slip additive to work at its most effective in terms of limiting colour removal from the substrate, the slip additive would ideally be located on the top surface of the fibres. If the ink was seen to penetrate the fibres, much of the slip additive may also penetrate and become located below the top layer of threads. As such, its effectiveness may be compromised. It is also likely that the application of a rub test would provide enough abrasion to damage the surface fibres of the substrate and therefore come into contact with other coloured fibres causing removal of pigment particles onto the cotton lawn pads. SEM analysis was carried out on a rubbed sample and the micrograph obtained can be seen in Figure 3.6.a.



*Figure 3.6.a Micrograph of a sample of cotton fabric after application of a dry rub test
($\times 500$)*

It can be seen from Figure 3.6.a that the rubfastness tests on a printed sample of cotton acted to flatten many of the fibres exposed. In some cases, it can be seen that the fibres had snapped. With this extent of abrasion, it is very unlikely to expect no removal of colour from the rubbed area of substrate. As such, the results obtained for the rubfastness of printed cotton fabric were very good.

The slight removal of colour during the rubfastness testing was the only real obstacle encountered when formulating and printing ink jet inks based of Cab-O-Jet pigment dispersions. As such, it can be said that the ink formulation was very successful and it is likely that such formulations could be used within industry for a wide range of applications. As such, it was decided to formulate a full four colour set of inks based on Cab-O-Jet pigment dispersions for further analysis.

3.7 The effect of Increased Amounts of Synthappret BAP within an Ink Jet Ink

The following section details the results gained from the investigation into the effects of increasing the amount of Synthappret BAP within an ink jet ink formulation.

When the amount of Synthappret BAP within an ink formulation was increased, the viscosity was increased. The results of the viscosity measurements can be seen in Table

3.7.a.

Table 3.7.a Effect of increased Synthappret on the viscosity of an ink jet ink

Shear Rate (1/s)	Viscosity of ink Formulation (mPa.s)					
	5%	10%	15%	20%	25%	40%
1.22	3.60	4.20	6.00	7.20	10.80	14.40
6.11	2.64	3.24	4.32	5.16	7.08	12.12
12.20	2.58	3.12	3.96	4.98	6.78	11.58
30.60	2.42	2.88	3.65	4.66	6.36	11.58
73.40	2.34	2.82	3.54	4.61	6.30	11.00

It can be seen from Table 3.7.a that as the amount of Synthappret BAP within the formulation was increased, so did the viscosity. However, the viscosity at a shear rate of 73.40 (equivalent of 60 rpm) when there was 25% Synthappret BAP contained within the formulation was still within the acceptable limits for an ink jet ink. The effect of the increased Synthappret BAP on the viscosity at 60 rpm can be seen in Figure 3.7.a and a representation of the viscosity profile for each ink in Figure 3.7.b.

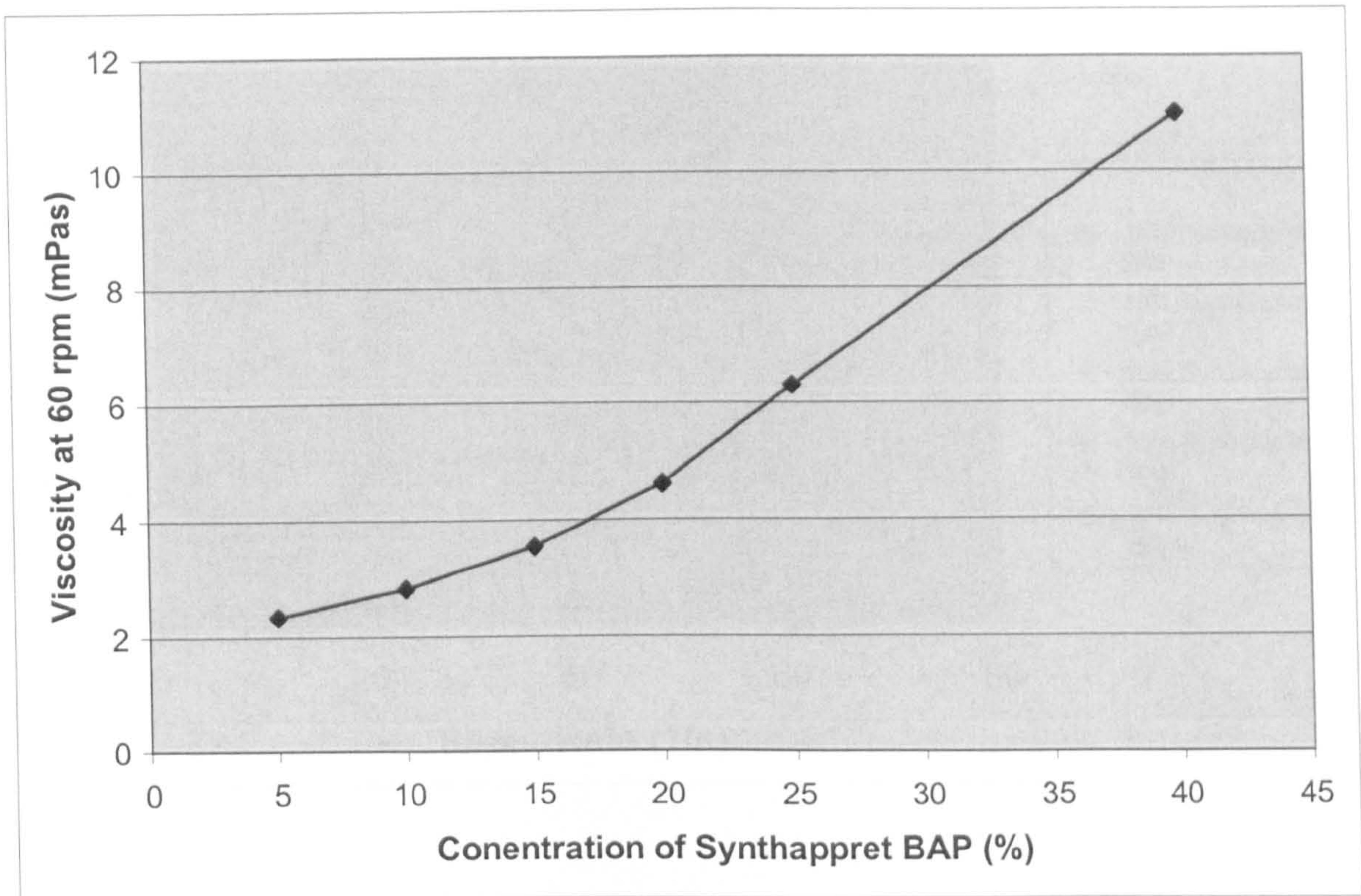


Figure 3.7.a Graph detailing the viscosity change of an ink with an increasing concentration of Synthappret BAP

It can be seen from Figure 3.7.a that the viscosity increased steadily to 15% before increasing to a greater extent as further Synthappret BAP was added to the ink formulation. Thus, the greater the proportion of Synthappret BAP within the ink formulation, the greater the change in its viscosity. This phenomenon was confirmed on comparing the viscosity profiles as seen in Figure 3.7.b. Whilst the formulation containing 25% Synthappret BAP was seen to have a viscosity within the acceptable limits for ink jet printing, further addition of pigment or humectants may adversely affect this when compared to an ink containing a lower level of Synthappret BAP.

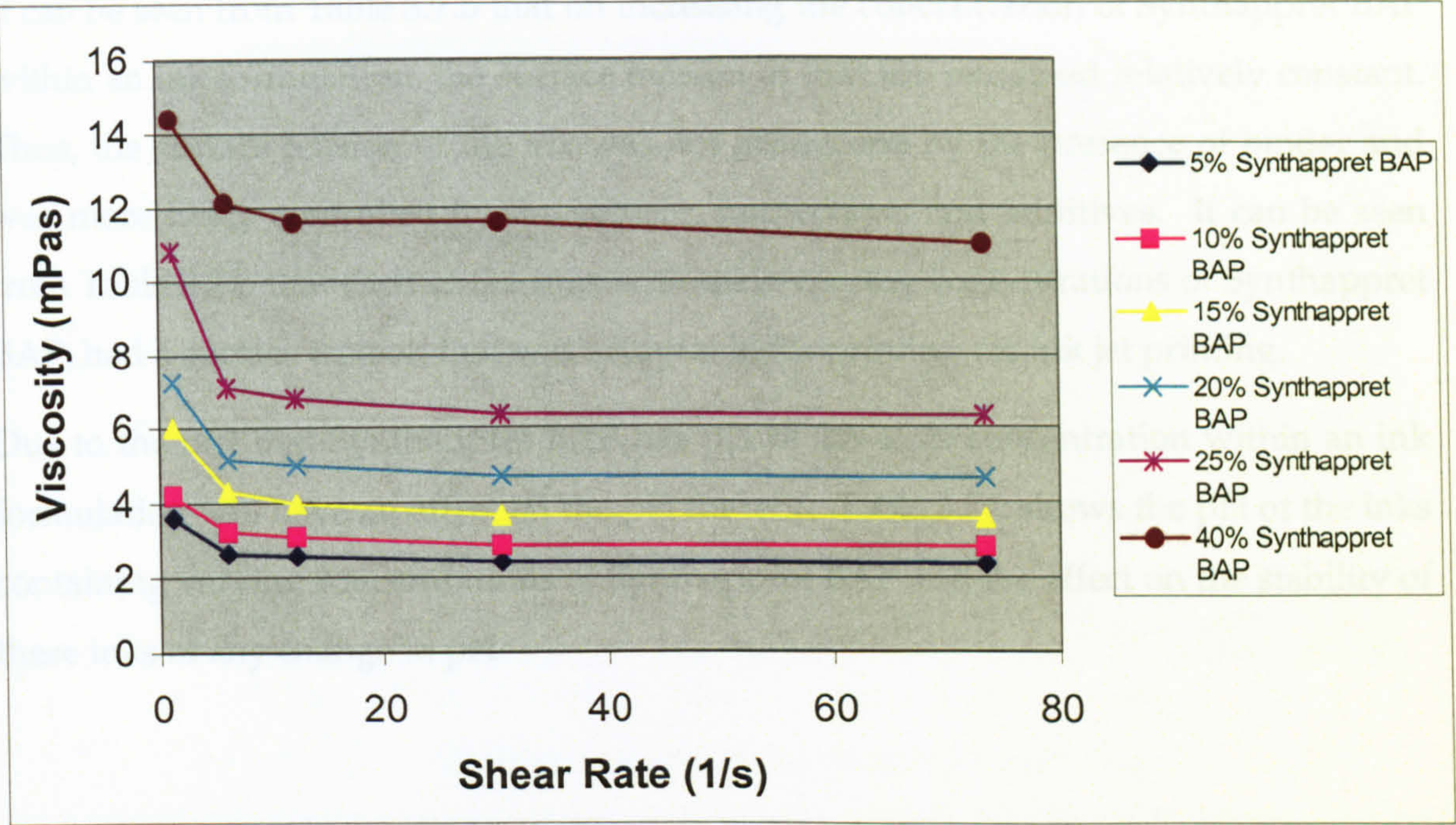


Figure 3.7.b Graph detailing a comparison of viscosity profiles for inks containing an increasing concentration of Synthappret BAP

The effect of increased Synthappret BAP within the ink formulations on their surface tension can be seen in Table 3.7.b.

Table 3.7.b Effect of increasing concentrations of Synthappret BAP on the surface tension of an ink formulation

Concentration of Synthappret BAP within the formulation	Surface Tension (mNm ⁻¹)
5%	35.5
10%	35.5
15%	35.0
20%	35.0
25%	35.0
40%	35.0

It can be seen from Table 3.7.b that on increasing the concentration of Synthappret BAP within an ink formulation, the surface tension of that ink remained relatively constant. Thus, the surface tension of the ink was not influenced by the presence of binder and was more likely controlled by the solvent, humectants and additives. It can be seen from Table 3.7.b that each of the inks with their varying concentrations of Synthappret BAP, had a surface tension that was acceptable for printing via ink jet printing.

Due to the fact that Synthappret BAP has pH of 2.5-4, its concentration within an ink formulation will have an effect on the pH thereof. Table 3.7.c shows the pH of the inks containing varying concentrations of Synthappret BAP and the effect on the stability of these inks of any change in pH.

Table 3.7.c Effect of increasing concentrations of Synthappret BAP on the pH of an ink formulation

Concentration of Synthappret BAP within the formulation	pH	Stability of ink formulation
5%	3.8	Good
10%	3.4	Good
15%	3.0	Good
20%	2.7	Good
25%	2.6	Good
40%	2.6	Good

As can be seen from Table 3.7.c the pH of the formulations became more acidic with an increase in the concentration of Synthappret BAP contained therein. However, as the amount of Synthappret BAP increased, the change in pH became less each time until a plateau was reached where the pH remained constant. This effect can be seen in Figure 3.7.c.

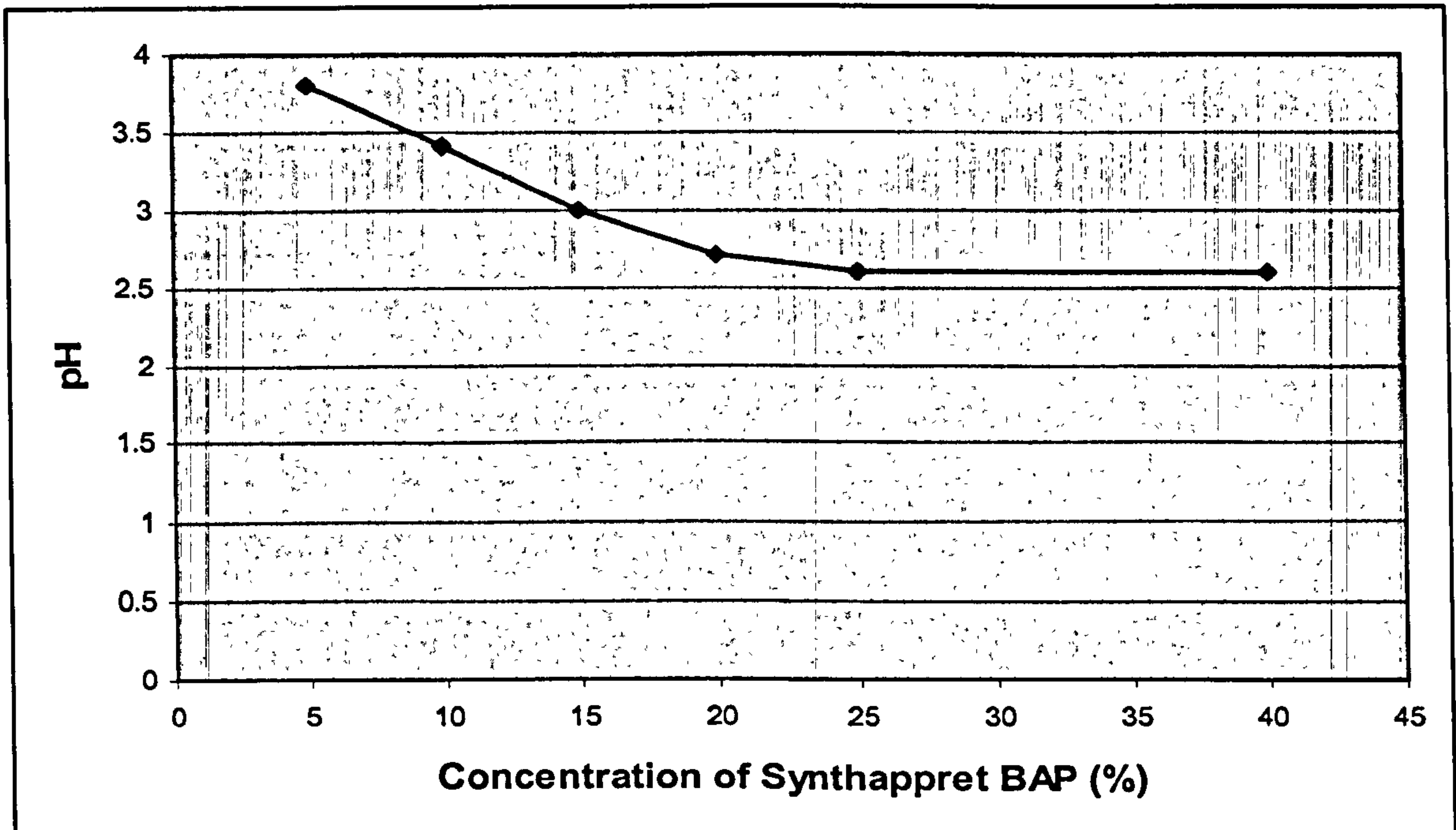


Figure 3.7.c Graph showing the effect of an increased concentration of Synthappret BAP on the pH of an ink formulation

In terms of the stability of the ink formulations, Table 3.7.c shows that the concentration of Synthappret BAP contained within an ink had no adverse effect on the visible stability of the system. However, it should be noted that whilst holding true for an ink containing Cab-O-Jet Magenta 260 M, this may not be the case for all pigments.

The effect of an increase in the concentration of Synthappret BAP within an ink on the particle size of the pigment contained therein is shown in Table 3.7.d.

Table 3.7.d Effect of increasing concentration of Synthappret BAP on the pigment Particle size of Cab-O-Jet Magenta 260 M within an ink formulation

Concentration of Synthappret BAP within the formulation	Particle size of the pigment to 95% limit (nm)
5%	92.5
10%	94
15%	93.5
20%	94.5

Concentration of Synthappret BAP within the formulation	Particle size of the pigment to 95% limit (nm)
25%	95
40%	95.5

It can be seen from Table 3.7.d that the particle size of the pigment contained within the ink was not adversely affected by an increase in the amount of Synthappret BAP contained within the system.

The effect of the increasing amounts of Synthappret BAP within an ink formulation on the observed fastness properties of the printed substrate was investigated. The results of washfastness and rubfastness testing in terms of optical densities can be seen in Table 3.7.e and Table 3.7.f.

Table 3.7.e *Effect of increasing concentration of Synthappret BAP on the washfastness of printed cotton and polyester fabrics*

Concentration of Synthappret BAP within the formulation	Optical density			
	On cotton		On polyester	
	Before washing	After washing	Before washing	After washing
5%	0.60	0.57	0.57	0.54
10%	0.60	0.59	0.58	0.56
15%	0.61	0.61	0.57	0.56
20%	0.61	0.61	0.59	0.58
25%	0.59	0.59	0.57	0.56
40%	N/A	N/A	N/A	N/A

Table 3.7.f Effect of increasing concentration of Synthappret BAP on the rubfastness of printed cotton and polyester fabrics

Concentration of Synthappret BAP within the formulation	Optical density of cotton lawn rubbing fabric after rub test			
	On cotton		On polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
5%	0.08	0.11	0.15	0.16
10%	0.06	0.09	0.15	0.16
15%	0.04	0.07	0.12	0.13
20%	0.04	0.07	0.12	0.13
25%	0.03	0.05	0.11	0.13
40%	N/A	N/A	N/A	N/A

It can be seen from Table 3.7.e and Table 3.7.f that the performance of the inks in the fastness tests improved between 5% and 15% concentration of Synthappret BAP within the ink. However, there was very little difference seen in the fastness properties on further increasing the amount of Synthappret BAP. It can therefore be concluded that in terms of ink performance there was little or no difference between an ink containing 15% Synthappret BAP and an ink containing 25% Synthappret BAP. The ink containing 15% Synthappret BAP had a lower viscosity, lower pH, equal surface tension and similar particle size as that containing 25% Synthappret BAP. Therefore, in terms of obtaining an optimum concentration of Synthappret BAP within an ink for the ink jet printing of textiles, an ink containing 15% Synthappret BAP was preferred.

3.8 Suitability of Pigments for Ink Jet Printing

This section details the results obtained for the evaluation of the three pigment types chosen for their suitability with regards to ink jet printing.

Various pigment dispersions and ink formulations were prepared, analysed, printed and cured. The quality of the printed and cured images was also analysed. Relevant results are reported here.

3.8.1 Particle Size and Particle Size Distribution

The particle size characteristics of the three pigment dispersions were assessed as a part of the investigation on the suitability of the pigments for inkjet printing. Relevant results are shown in Tables 3.8.a and 3.8.b, where values for the mean diameter of the pigment particles and the particle size falling within a 95% limit are given.

Table 3.8.a Particle size of pigment dispersions held over a period of time

Storage time	Particle size characteristics of pigment dispersions (nm)					
	Clariant Toner Magenta E02		Ciba Microlith Magenta B-WA		Cab-O-Jet Magenta 260M	
	Mean Diameter	95% Limit	Mean Diameter	95% Limit	Mean Diameter	95% Limit
1 day	597	644	177	184	92.5	95.5
1 week	322	341	183	192	98.6	102
4 weeks	247	260	157	164	84.1	86.6

It can be seen from Table 3.8.a that both pigment dispersions containing Microlith Magenta B-WA and Cab-O-Jet Magenta 260M had significantly smaller particles than that containing the Clariant Toner Magenta E02. It can also be seen, from Table 3.8.a, that such a particle size characteristic remained fairly unchanged throughout the storage period of four weeks. However, all three pigment dispersions appeared to be suitable for application in inkjet printing inks, indicated by their particle size being close to or below 500 nm.

The effect of freeze-thaw cycling on the particle size of each pigment dispersion can be seen in Table 3.8.b.

Table 3.8.b Effect of freeze-thaw cycling on particle size of the pigment dispersion

Number of Cycles	Mean particle size of pigment after freeze-thaw cycle (nm)		
	Clariant Toner Magenta E02	Ciba Microlith Magenta B-WA	Cab-O-Jet Magenta 260M
1	206	200	109
4	400	442	229

It can be seen from Table 3.8.b that the effect of freeze-thaw cycling on the particle size of each pigment dispersion was significant. This was indicated by the considerable increase of the particle size after 4 freeze-thaw cycles. Such increases in particle size were likely to be due to the flocculation of the pigment particles caused by the dramatic change in temperature. The pigment dispersion containing the Microlith Magenta B-WA had the greatest increase in particle size after four freeze-thaw cycles. Such a drastic increase was considered to be due to the evaporation of ammonia at 60°C resulting in the lowering of the pH, thus causing a reduction in the affinity between the pigment and the medium. A graphic representation of the change in pigment particle size after application of freeze-thaw cycling can be seen in Figure 3.8.a.

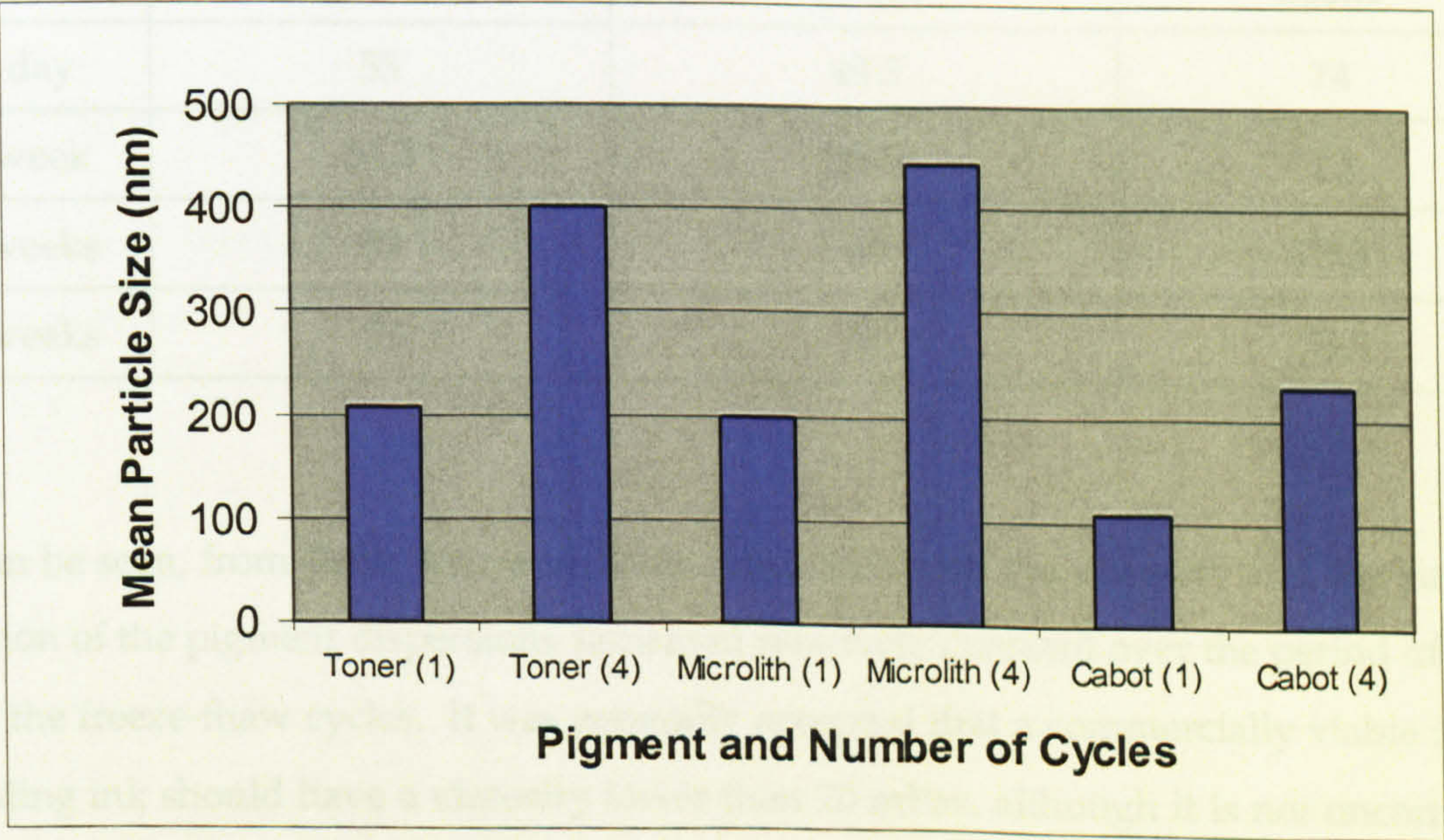


Figure 3.8.a Effect of freeze-thaw cycling on the mean particle size of pigments within a dispersion

3.8.2 Ink Jet Parameters and Stability of Dispersions

The inkjet parameters, including the viscosity, the surface tension and the pH stability of the pigment dispersions, over a period of time, are shown in Table 3.8.c and Table 3.8.d.

Table 3.8.c Viscosity of the pigment dispersions held over a period of time

Storage time	Viscosity of pigment dispersion (mPas) at 60rpm		
	Clariant Toner Magenta E02	Ciba Microlith Magenta B-WA	Cab-O-Jet Magenta 260M
1 day	1.15	1.19	1.09
2 days	1.21	1.20	1.11
7 days	1.22	1.21	1.11
14 days	1.19	1.14	1.06

Table 3.8.d Effect of storage on the surface tension of the pigment dispersions

Storage time	Surface tension of pigment dispersions (mNm)		
	Clariant Toner Magenta E02	Ciba Microlith Magenta B-WA	Cab-O-Jet Magenta 260M
1 day	53	49.5	74
1 week	51.5	48.5	73
2 weeks	53	50	73.5
4 weeks	53	50	73.5

It can be seen, from Table 3.8.c and Table 3.8.d, that both the viscosity and the surface tension of the pigment dispersions remained relatively constant over the period of time and the freeze-thaw cycles. It was generally accepted that a commercially viable inkjet printing ink should have a viscosity lower than 20 mPas, although it is not uncommon for an inkjet printing ink to have a viscosity up to 30 MPas. (Kipphan, 2001). Thus it can be seen from Table 3.8.c, that all pigment dispersions had a low viscosity, making them suitable for inkjet printing.

Ideally, inks for application via inkjet printing, should have a surface tension in the range of 25-60 dynes cm⁻¹. (MacFaul, 2003) It can be seen, from Table 3.8.d, that both the pigment dispersions containing Clariant Toner Magenta E02 and Ciba Microlith Magenta B-WA had a surface tension within the operational range. The pigment dispersion containing the Cab-O-Jet Magenta 260 M had a surface tension higher than 60 dynes cm⁻¹. However, on completion of a full ink formulation, the surface tension would be lowered by the inclusion of humectants and or co-solvents such as isopropyl alcohol.

The viscosity and the surface tension of three ink formulations prepared are given in Table 3.8.e. From Table 3.8.e, it can be seen that all three ink formulations had satisfactory viscosity and surface tension for inkjet printing.

Table 3.8.e Viscosity and surface tension of inkjet ink formulations

Ink Formulation	Viscosity (mPas) at 60rpm	Surface tension (mNm)
Clariant Toner Magenta E02	3.0	36
Ciba Microlith Magenta B-WA	2.8	35
Cab-O-Jet Magenta 260M	2.5	35

3.8.3 Effect of pH on the Stability of the Pigment Dispersions

The results obtained from the pH stability testing carried out on the pigment dispersions can be seen in Table 3.8.f.

Table 3.8.f Effect of changing the pH on the stability of pigment dispersions


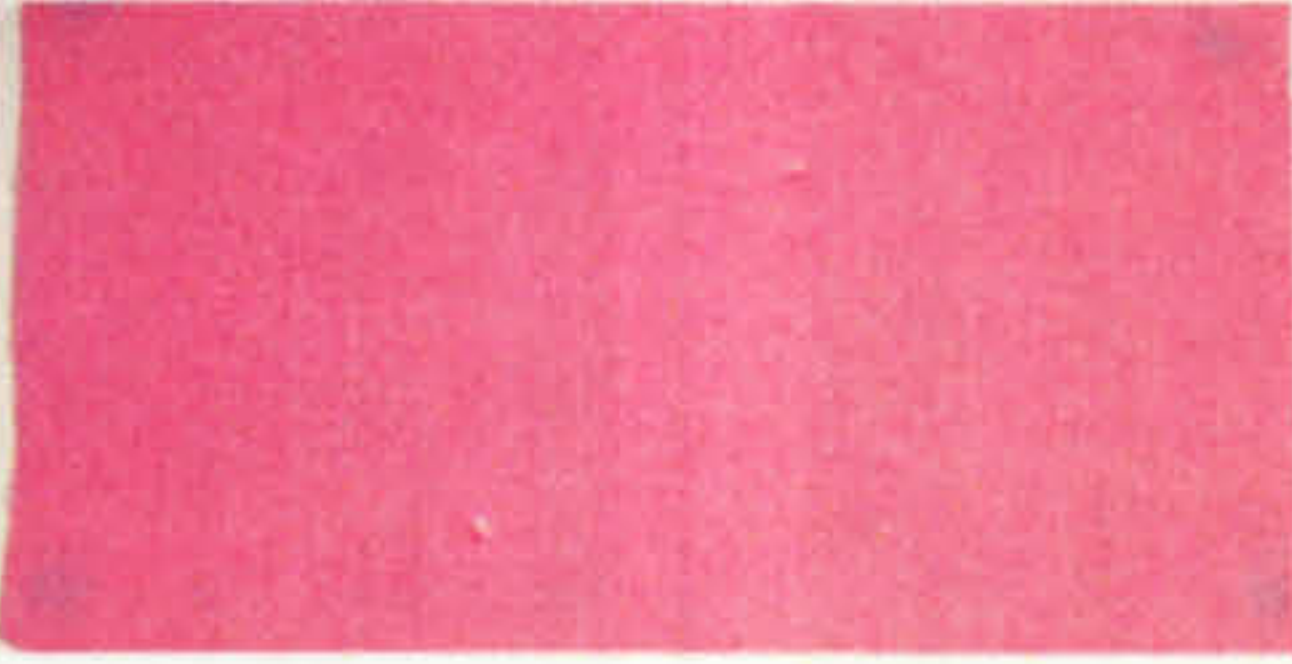
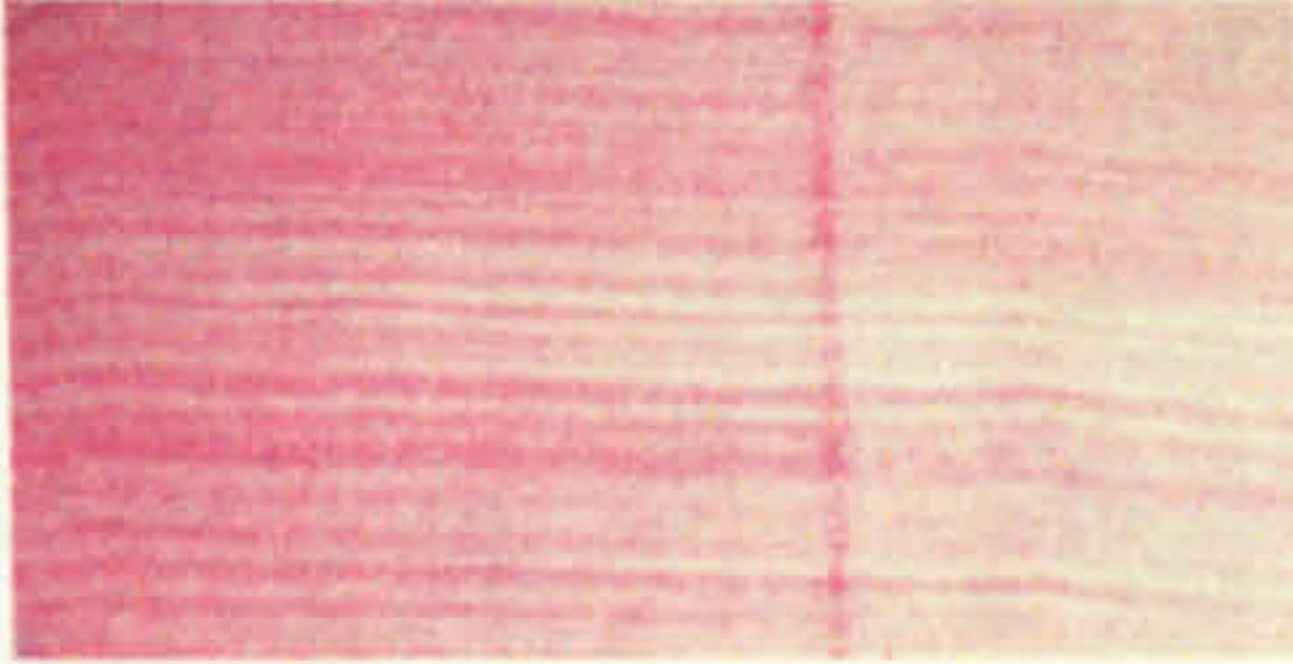



Storage time	Stability of pigment dispersion								
	Clariant Toner Magenta E02			Ciba Microlith Magenta B-WA			Cab-O-Jet Magenta 260M		
	pH 2	pH 3	pH 12	pH 2	pH 3	pH 12	pH 2	pH 3	pH 12
1 day	No	No	Yes	No	Yes	Yes	Yes	Yes	Yes
2 days	No	No	No	No	Yes	Yes	Yes	Yes	Yes
1 week	No	No	No	No	Yes	Yes	Yes	Yes	Yes
4 weeks	No	No	No	No	Yes	Yes	Yes	Yes	Yes

It can be seen from Table 3.8.f that pH had a significant effect on the stability of the pigment dispersions containing the Clariant Toner Magenta E02 or the Ciba Microlith Magenta B-WA. Both pigment dispersions containing Ciba Microlith Magenta B-WA and Cab-O-Jet Magenta 260 M were stable over the storage time at high pH. The pigment dispersion containing Clariant Toner Magenta E02 was unstable at extreme acidity or extreme alkalinity.

3.8.4 Jettability and Quality of the Printed Image Printed using Formulations Containing Different Pigments

Images of the printed fabric samples can be seen in Table 3.8.g. Visible comparisons could be made and it was clear that the formulation containing Toner Magenta E02 gave very poor print quality when compared to its counterparts.

Table 3.8.g Visual assessment of the print quality of the pigmented inks on cotton and polyester substrates

Substrate	Ink Formulation		
	Cab-O-Jet Magenta 260 M	Ciba Microlith Magenta B-WA	Clariant Toner Magenta E02
Cotton			
Polyester			
Overall Rating	Good	Good	Poor

The dot area, the dot roundness and the centre-to-extremity distances data obtained through measurement using the ImageXpert are shown in Tables 3.8.h to 3.8.k. The ImageXpert software measured roundness on a scale of 0 to 1 with 1 being perfectly round. It should be noted that due to its poor image quality, no image analysis was made on the prints produced using the ink containing Clariant Toner Magenta E02.

The profiles of the typical printed dots on both the cotton and the polyester are shown in Table 3.8.h.

Table 3.8.h Representation of the area of printed substrate measured for dot quality

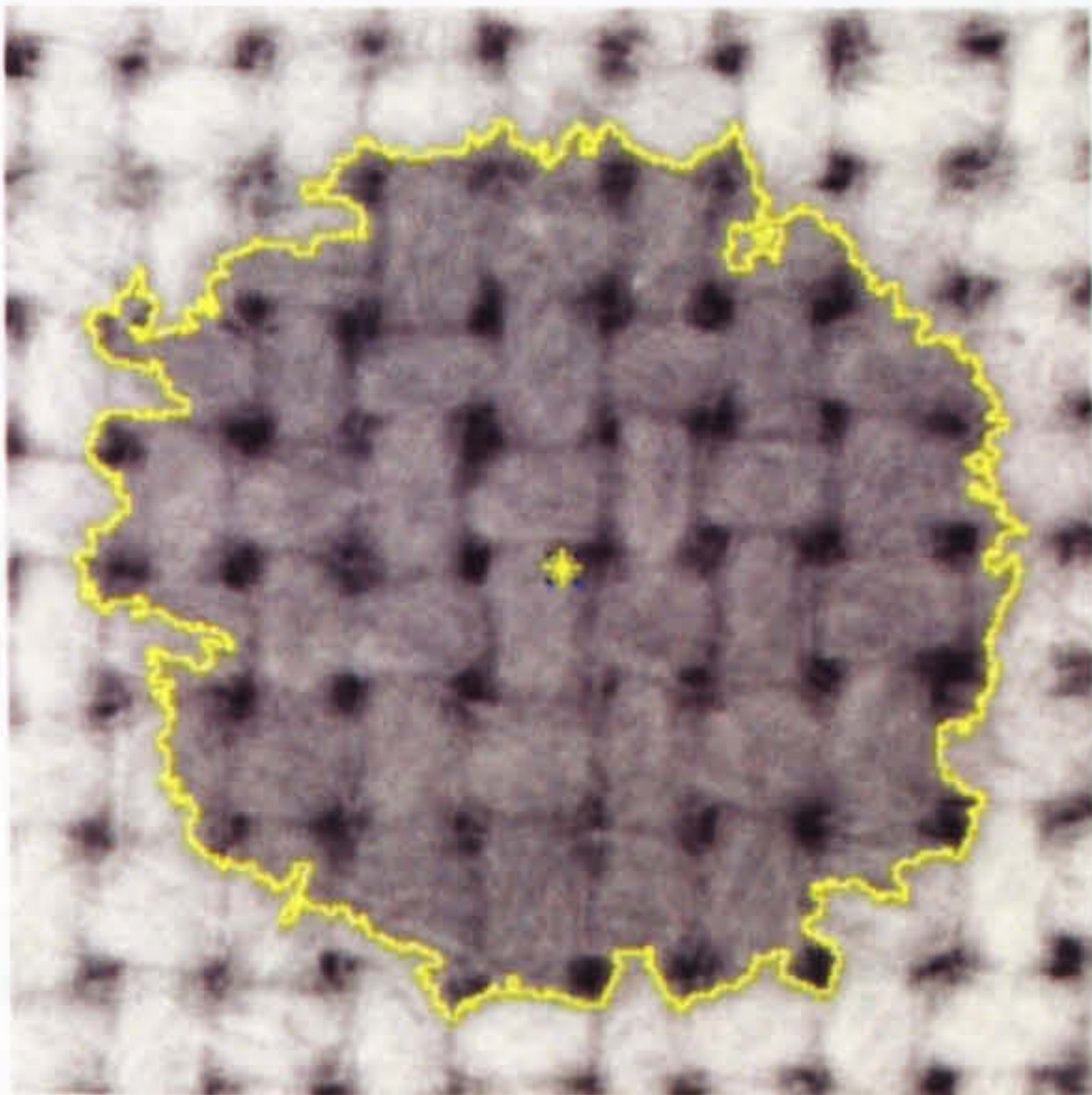
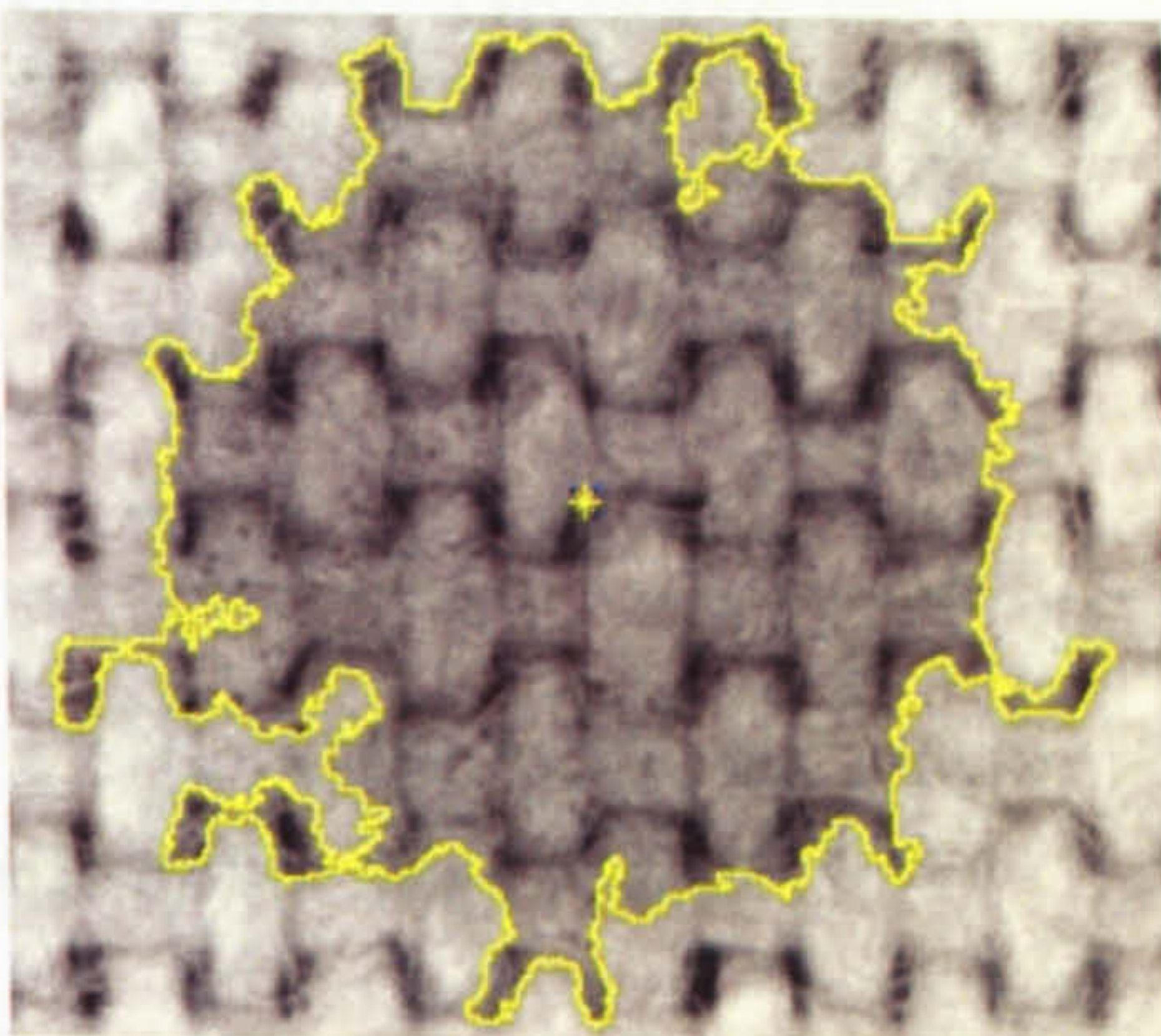
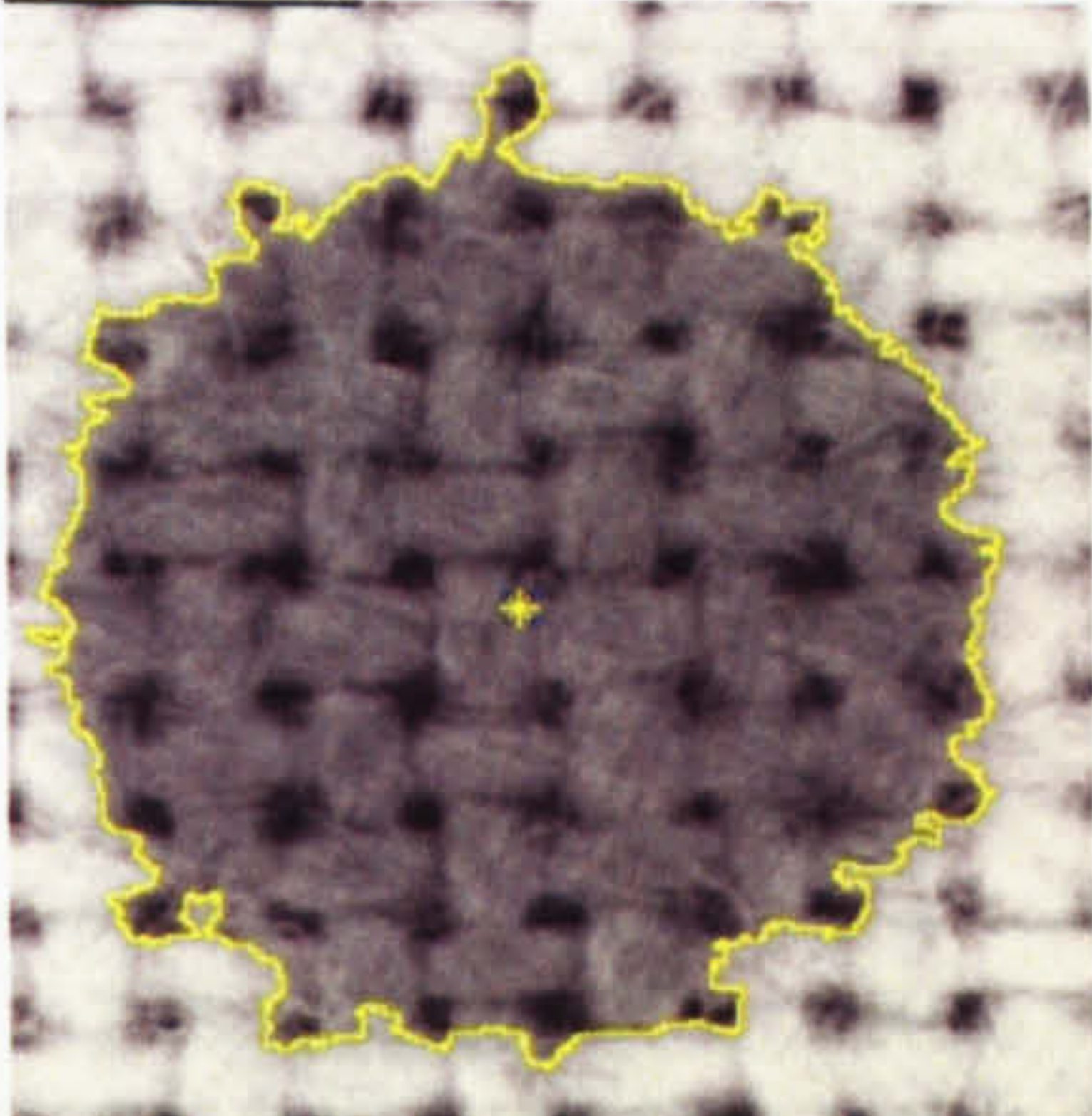
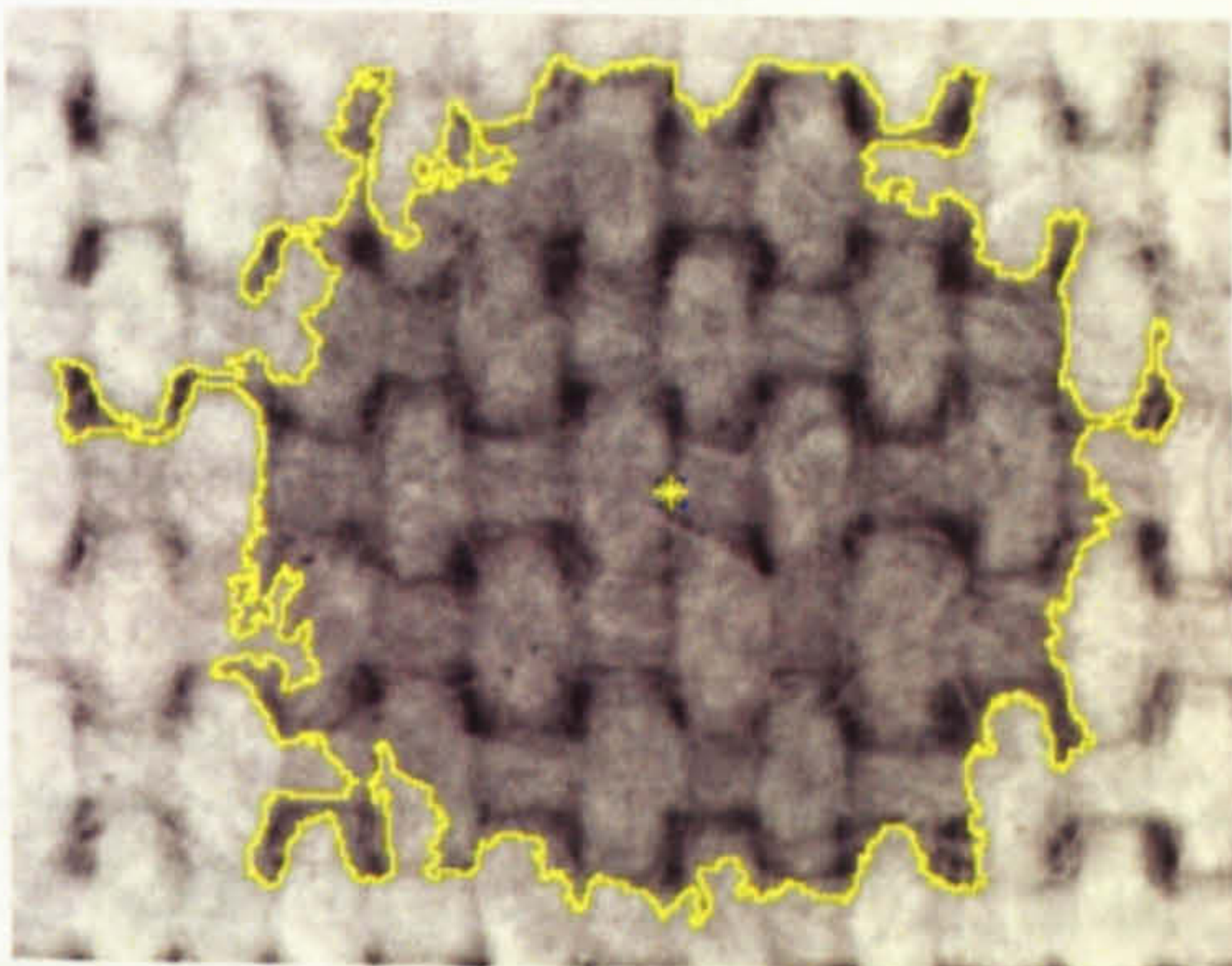
Ink formulations	On cotton	On polyester
Ciba Microlith Magenta B-WA		
Cab-O-Jet Magenta 260 M		

Table 3.8.i Values obtained for dot areas of the same dot print on various substrates

Ink/toner formulation	Area of dot (mm ²)					
	On paper	On cotton	On polyester	On paper	On cotton	On polyester
Laser black on paper	12.27	N/A	N/A	3.50	N/A	N/A
Ciba Microlith Magenta B-WA	N/A	16.80	14.32	N/A	4.10	3.78
Cab-O-Jet Magenta 260M	N/A	17.70	15.21	N/A	4.21	3.90

Table 3.8.j Assessment of the roundness of the circular image area

Ink/toner formulations	Roundness		
	On paper	On cotton	On polyester
Laser black	0.91	N/A	N/A
Ciba Microlith Magenta B-WA	N/A	0.26	0.12
Cab-O-Jet Magenta 260M	N/A	0.35	0.12

Table 3.8.k Centre to point measurements of the image area

Ink/toner formulations	Point to point Measurements (mm)				
		Centre to Left	Centre to Right	Centre to Bottom	Centre to Top
Laser black	On paper	2.86	2.86	2.80	2.82
Ciba Microlith Magenta B-WA	On cotton	3.34	3.19	3.18	3.10
	On polyester	4.28	4.24	4.04	3.93
Ciba Microlith Magenta B-WA	On cotton	3.30	3.30	3.22	3.30
	On polyester	4.85	4.10	3.46	3.54

It can be seen from the data given in Tables 3.8.h to 3.8.k that the structure and the type of the textile fabrics had an effect on the interaction between the ink and the substrate. Thus, the printed dot on cotton had a greater roundness and a smaller dot gain. This was likely to be due to the significant absorbency offered by the cotton fabrics. There is an argument to say that due to a large majority of the ink remaining near the surface of the polyester, a greater degree of wicking along the surface occurred.

3.8.5 Fastness Properties of Prints Prepared using Three Different Pigments

In order to assess the effect of wash-fastness of the images printed and cured on the textile fabrics, the optical densities of the images before and after washing were measured. Relevant optical density results are given in Table 3.8.l.

Table 3.8.1 Optical density of prints before and after washing

Ink formulations	Optical density			
	On cotton		On polyester	
	Before washing	After washing	Before washing	After washing
Clariant Toner Magenta E02	0.30	0.30	0.37	0.35
Ciba Microlith Magenta B-WA	0.43	0.43	0.52	0.49
Cab-O-Jet Magenta 260M	0.61	0.61	0.56	0.54

Visual comparisons of the printed substrates before and after washing in terms of the colour difference observed between washed and unwashed samples according to greyscales can be seen in Table 3.8.m to Table 3.8.o.

Table 3.8.m Visual assessments of the washfastness of cotton and polyester fabrics printed with the ink containing Toner Magenta E02

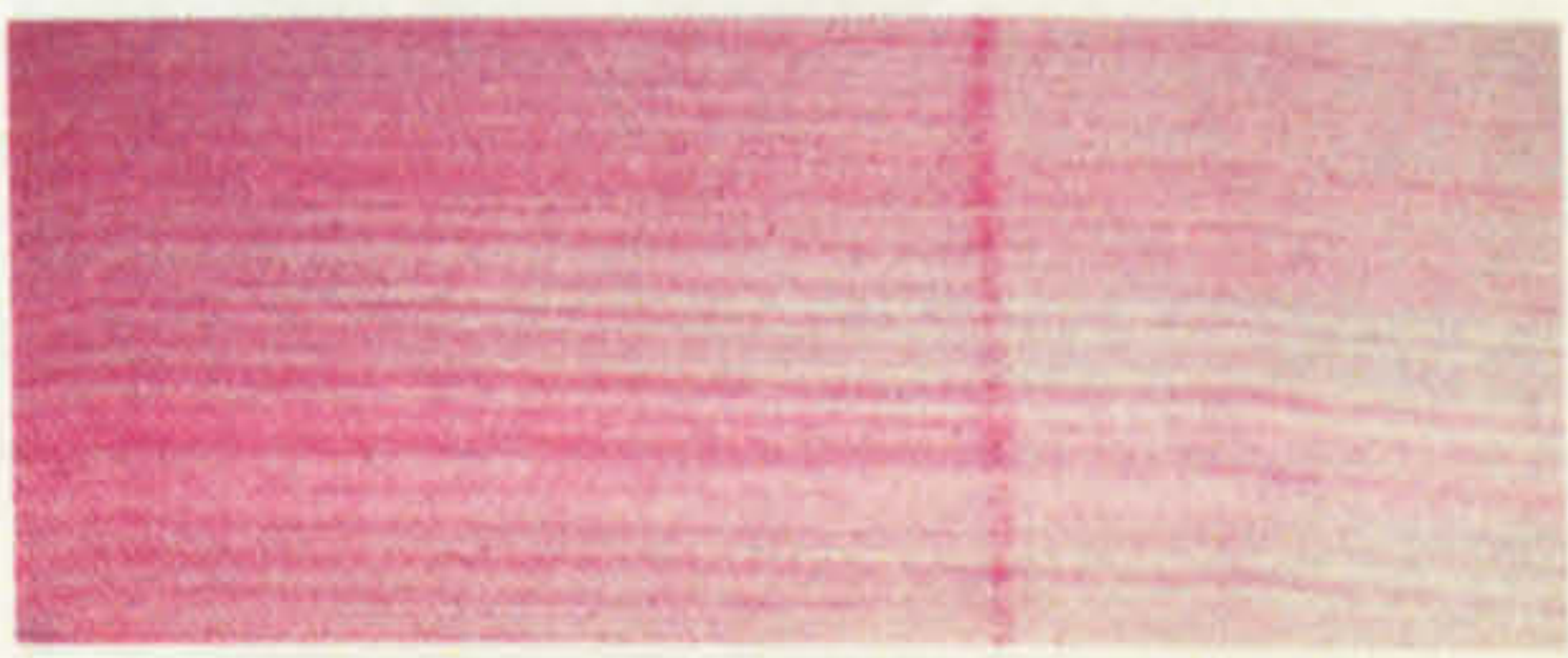

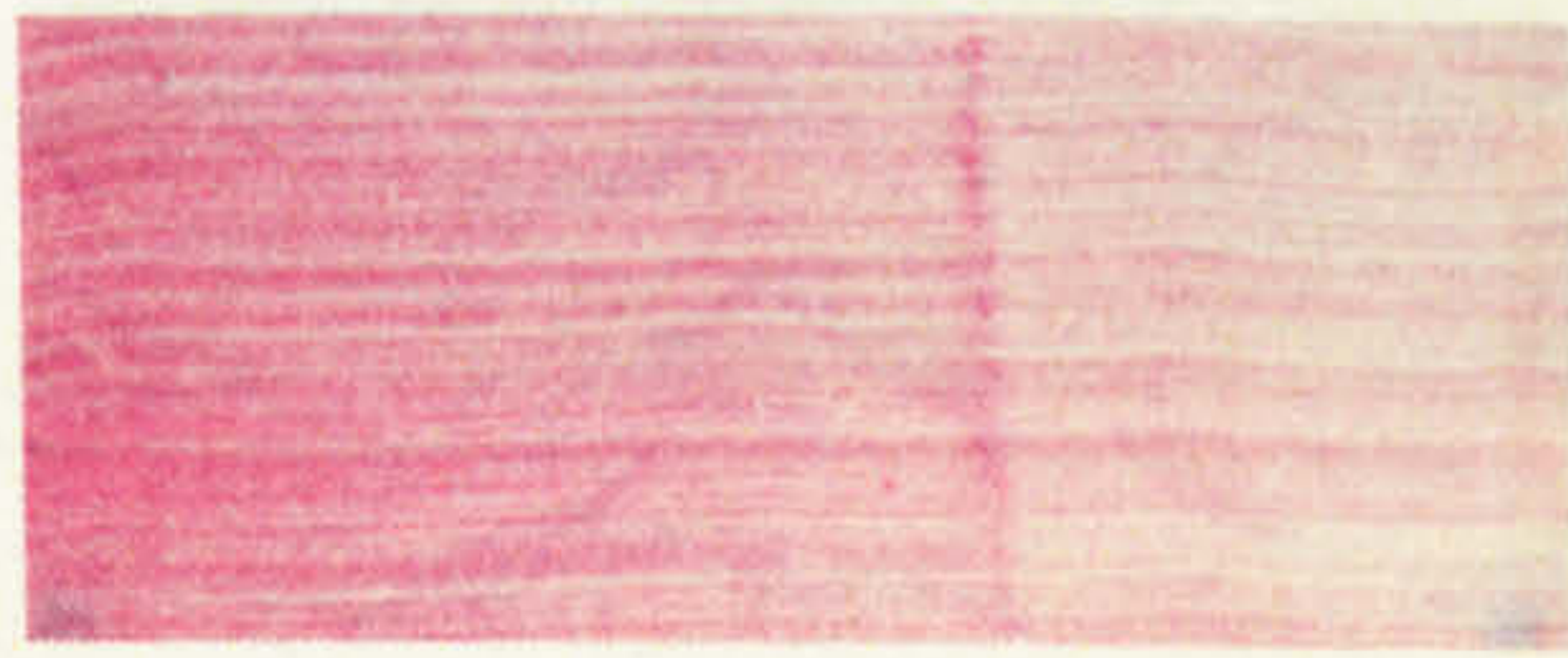

	Substrate printed	
	Cotton	Polyester
Before washing		
After washing		
Assessment of colour difference between printed samples before and after washing	4/5	4/5

Table 3.8.n Visual assessments of the washfastness of cotton and polyester fabrics printed with the ink containing Microlith Magenta BWA









	Substrate printed	
	Cotton	Polyester
Before washing		
After washing		
Assessment of colour difference between printed samples before and after washing	5	5

Table 3.8.o Visual assessments of the washfastness of cotton and polyester fabrics printed with the ink containing Cab-O-Jet Magenta 260 M

	Substrate printed	
	Cotton	Polyester
Before washing		
After washing		
Assessment of colour difference between printed samples before and after washing	5	5

It can be seen from Table 3.8.1 that all printed and cured images had a good washfastness, indicated by the negligible changes of the optical densities before and after

wash. The results for the optical density measurements were supported by the visual assessments carried out (Table 3.8.m to Table 3.8.o). Such a good wash-fastness was not unexpected, as the Synthappret BAP binder included in the ink formulations was known to have a good affinity with textile fibres and to give a high degree of cross-linking.

However, it was also noticeable that images on cotton fabrics had a better wash-fastness than those on polyester fabrics. This was likely to be due to the greater absorbance of the ink offered by cotton.

The results of the rub-fastness tests are shown in Figure 3.8.b. In each case, the top pair of cotton lawn pads is after rubbing cotton and bottom pair after rubbing polyester with dry rub on the left and wet rub on the right.

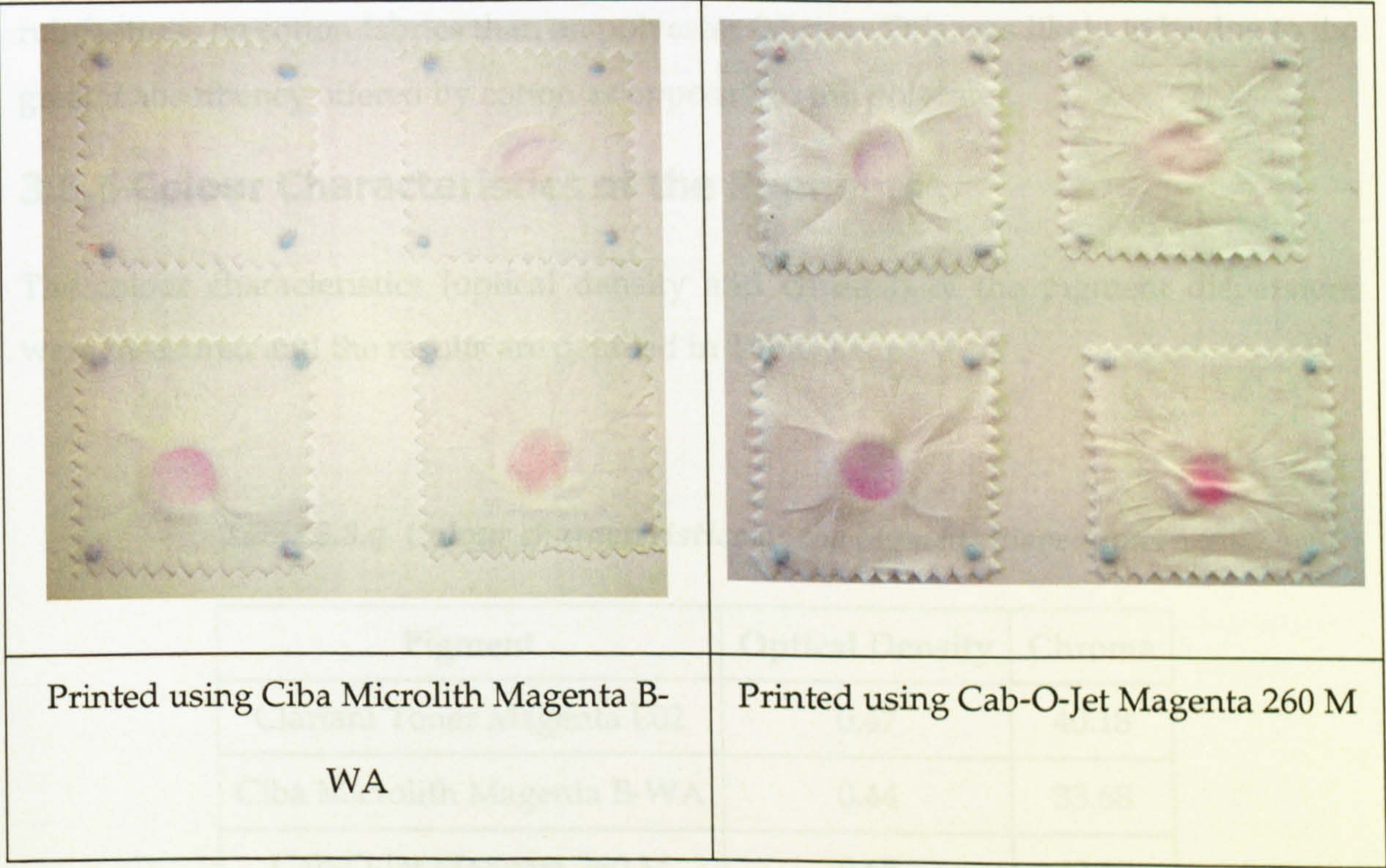


Figure 3.8.b Cotton lawn pads used in rubfastness tests for cotton and polyester fabrics printed with inks containing Microlith Magenta BWA and Cab-O-Jet Magenta 260 M

Rubfastness was also more scientifically assessed, by measuring the optical density of the cotton lawn rubbing fabric after rubbing the substrate. Relevant results are shown in Table 3.8.p.

Table 3.8.p Optical density of cotton lawn pads after rub test

Ink formulations	Optical density of cotton lawn rubbing fabric after rub test			
	On cotton		On polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
Ciba Microlith Magenta B-WA	0.01	0.02	0.04	0.05
Cab-O-Jet Magenta 260M	0.07	0.02	0.15	0.16

It can be seen from Table 3.8.p, that the ink formulation containing Ciba Microlith Magenta B-WA gave prints of better rub-fastness than did the ink formulation containing Cab-O-Jet 260 M. It can also be noticed that both inks gave prints of better rub-fastness on cotton fabrics than on polyester fabrics. This was likely to be due to the greater absorbency offered by cotton as opposed to the polyester.

3.8.6 Colour Characteristics of the Pigments

The colour characteristics (optical density and chroma) of the pigment dispersions were measured and the results are detailed in Table 3.8.q.

Table 3.8.q Colour characteristics of the pigment dispersions

Pigment	Optical Density	Chroma
Clariant Toner Magenta E02	0.47	40.18
Ciba Microlith Magenta B-WA	0.44	33.68
Cab-O-Jet Magenta 260 M	0.65	43.19

It can be seen from Table 3.8.q that Cab-O-Jet Magenta 260M had a higher optical density and a higher chroma than the other two pigments.

3.9 Effect of pH on the Stability of Synthappret BAP

This section details the results obtained from the investigation into the effects of various alkaline substances on the stability of Synthappret BAP.

Once the relevant ink formulations were mixed and adjusted to the required pH using the various alkali components selected, the inks were left for a period of time for observation. Any changes in the ink were noted and recorded. Such observations are detailed Table 3.9.a for the formulations magnetically stirred and in Table 3.9.b for the formulations mixed using a lab emulsifier.

Table 3.9.a Stability assessments of inks prepared by mechanical stirring

Alkali component used	pH	Observations on ink stability		
		1 day	1 week	2 weeks
Ammonia	8	Stable dispersion	Stable dispersion	Stable dispersion
	11	Stable dispersion	Spongy solid formed	Complete separation of solid from solvent
	14	Some pigment flocculation	Spongy solid formed	Spongy solid formed
Diethanolamine	8	Stable dispersion	Stable dispersion	Some spongy solid formed
	11	Stable dispersion	Spongy solid formed	Spongy solid formed
	14	Some pigment flocculation	Spongy solid formed	Complete separation of solid from solvent
Triethanolamine	8	Stable dispersion	Stable dispersion	Some spongy solid formed
	11	Stable dispersion	Spongy solid formed	Spongy solid formed
	14	Some pigment flocculation	Spongy solid formed	Complete separation of solid from solvent
Sodium hydroxide	8	Stable dispersion	Stable dispersion	Stable dispersion

	pH	Observations on ink stability	Alkali component used	pH
	11	Stable dispersion	Spongy solid formed	Complete separation of solid from solvent
	14	Some pigment flocculation	Spongy solid formed	Complete separation of solid from solvent
Ethylene diamine	8	Stable dispersion	Some spongy solid formed	Spongy solid formed
	11	Some pigment flocculation	Spongy solid formed	Complete separation of solid from solvent
	14	High degree of flocculation	Complete separation of solid from solvent	Complete separation of solid from solvent

Table 3.9.b Stability assessment of inks prepared using a lab emulsifier

Alkali component used	pH	Observations on ink stability		
		1 day	1 week	2 weeks
Ammonia	8	Stable dispersion	Stable dispersion	Stable dispersion
	11	Stable dispersion	Spongy solid formed	Complete separation of solid from solvent
	14	Some pigment flocculation	Spongy solid formed	Spongy solid formed
Diethanolamine	8	Stable dispersion	Stable dispersion	Some spongy solid formed
	11	Stable dispersion	Spongy solid formed	Spongy solid formed

	14	Some pigment flocculation	Spongy solid formed	Complete separation of solid from solvent
Triethanolamine	8	Stable dispersion	Stable dispersion	Some spongy solid formed
	11	Stable dispersion	Spongy solid formed	Spongy solid formed
	14	Some flocculation	Spongy solid formed	Complete separation of solid from solvent
Sodium hydroxide	8	Stable dispersion	Stable dispersion	Stable dispersion
	11	Stable dispersion	Spongy solid formed	Complete separation of solid from solvent
	14	Some flocculation	Spongy solid formed	Complete separation of solid from solvent
Ethylene diamine	8	Some flocculation	Some spongy solid formed	Spongy solid formed
	11	High degree of flocculation instantly	Spongy solid formed	Complete separation of solid from solvent
	14	High degree of flocculation instantly	Complete separation of solid from solvent	Complete separation of solid from solvent

It can be seen from the data presented in Table 3.9.a and Table 3.9.b that predominantly the ink was stable at a pH 8. When the pH was raised, the stability of the system becomes a problem. It was thought that the alkali component of the ink in each case caused some degree of cross-linking of the Synthappret BAP. In each case a spongy solid was formed which encompassed the Synthappret BAP and the pigment separating from the bulk solvent. A schematic representation of this phenomenon can be seen in Figure 3.9.a.

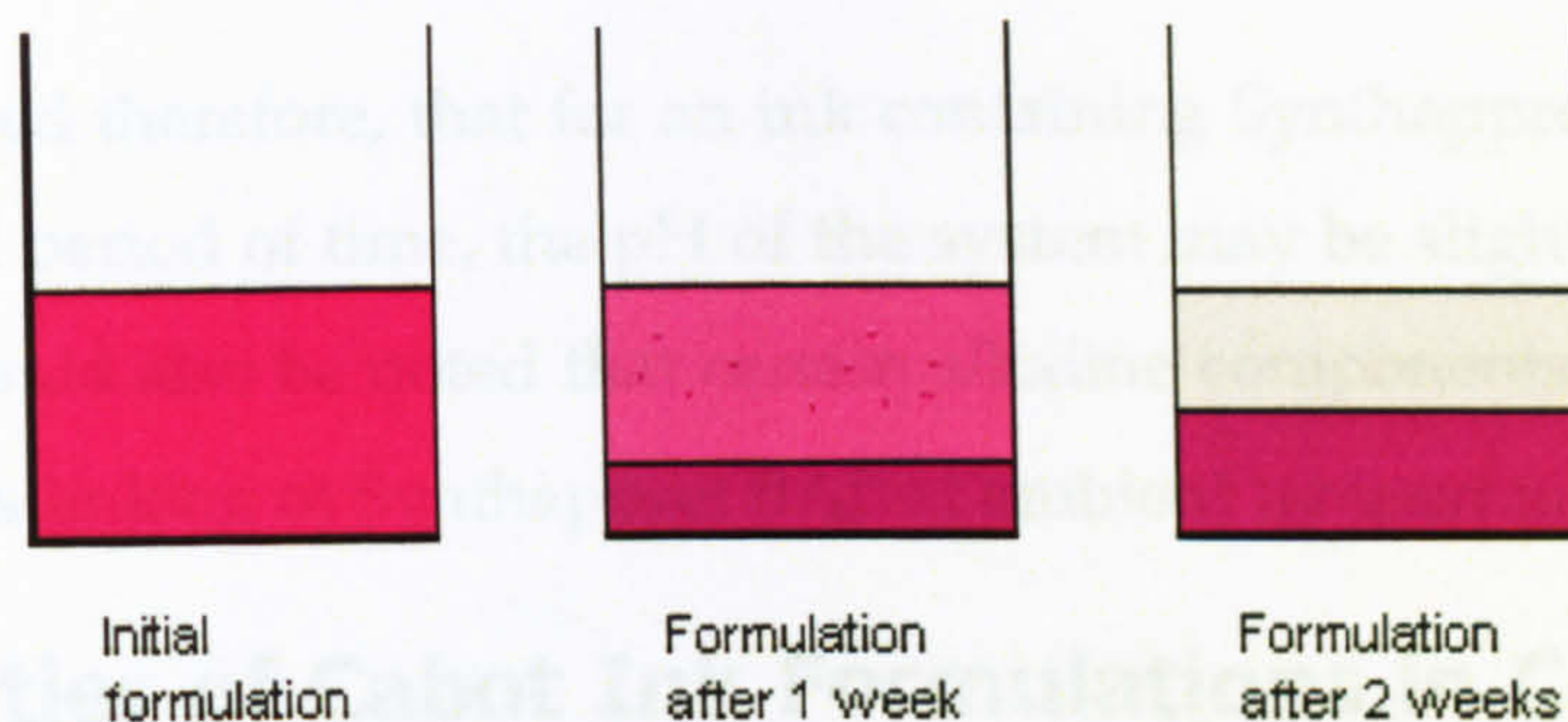


Figure 3.9.a Schematic diagram of the stability problems encountered at high pH

In order to see the scale of the cross-linking of the Synthappret BAP in the separated spongy solid, a cross-section of such a solid was cut and viewed using SEM. The micrograph obtained can be seen in Figure 3.9.b.

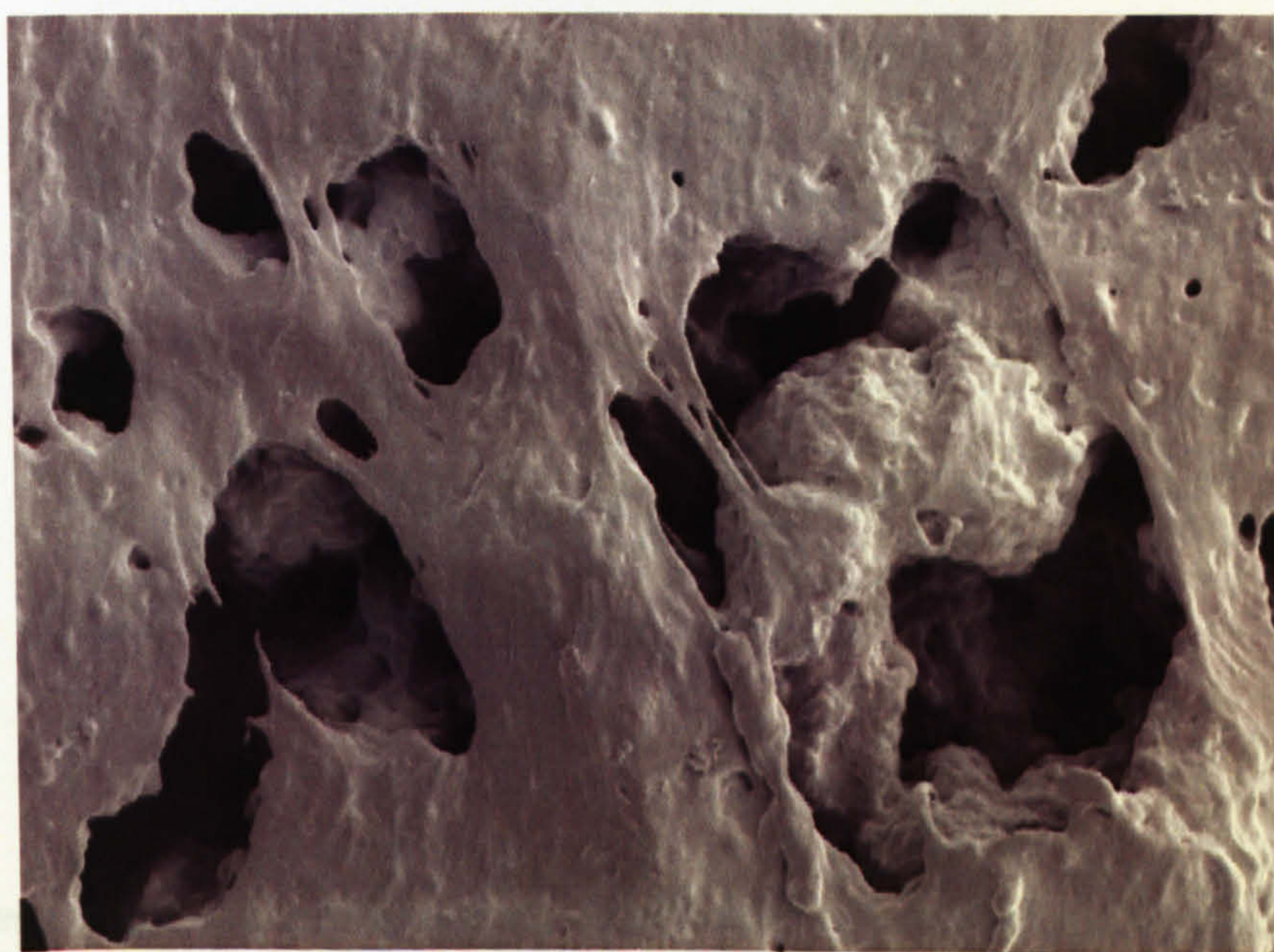


Figure 3.9.b Micrograph of a section of cross-linked Synthappret BAP within an ink formulation ($\times 2000$)

It can be seen from Figure 3.9.b that the Synthappret BAP formed a lattice and was almost “rubbery” in consistency. There was little visual evidence for the presence of

pigment particles although due to the dense nature of the cross-linked Synthappret BAP it was likely that any particles were embedded within the polymer matrix.

It can be concluded therefore, that for an ink containing Synthappret BAP to be stable over an extended period of time, the pH of the system may be slightly alkaline but not exceed 8.5. It should also be noted that certain alkaline components had a less marked effect on the cross-linking of Synthappret BAP at ambient temperatures.

3.10 Properties of Cabot Ink Formulations in Comparison to an Alternative Commercially Available Set of Inks

The following section outlines the results obtained from the analysis carried out on a set of commercially available inks for ink jet printing of textiles. The inks used were from the Irgaphor range supplied by Ciba Speciality Chemicals.

The results from the particle size analysis carried out on the Irgaphor inks can be seen in Table 3.10.a.

Table 3.10.a Particle size of Irgaphor ink jet inks

Ink	Particle size (95% limit)(nm)
Irgaphor Red	241
Irgaphor Yellow	267
Irgaphor Blue	98.5
Irgaphor Black	98.0

It can be seen from Table 3.10.a that whilst the blue and black Irgaphor inks had a particle size equivalent to those attainable using Cab-O-Jet pigment dispersions, the yellow and red inks had a significantly larger particle size. However, each ink was seen to comply with the guidelines set out for an ink to be acceptable for ink jet printing.

The Irgaphor inks were also tested for their viscosity and the values obtained are given in Table 3.10.b. The viscosities are quoted at 60 rpm at 25°C, as this is an accepted

value used by industry. A comparison of the viscosity profiles of the inks is shown in Figure 3.10.a.

Table 3.10.b Viscosities of Irgaphor ink jet inks

Ink	Viscosity at 60 rpm (mPas)
Irgaphor Red	5.92
Irgaphor Yellow	4.91
Irgaphor Blue	5.51
Irgaphor Black	5.20

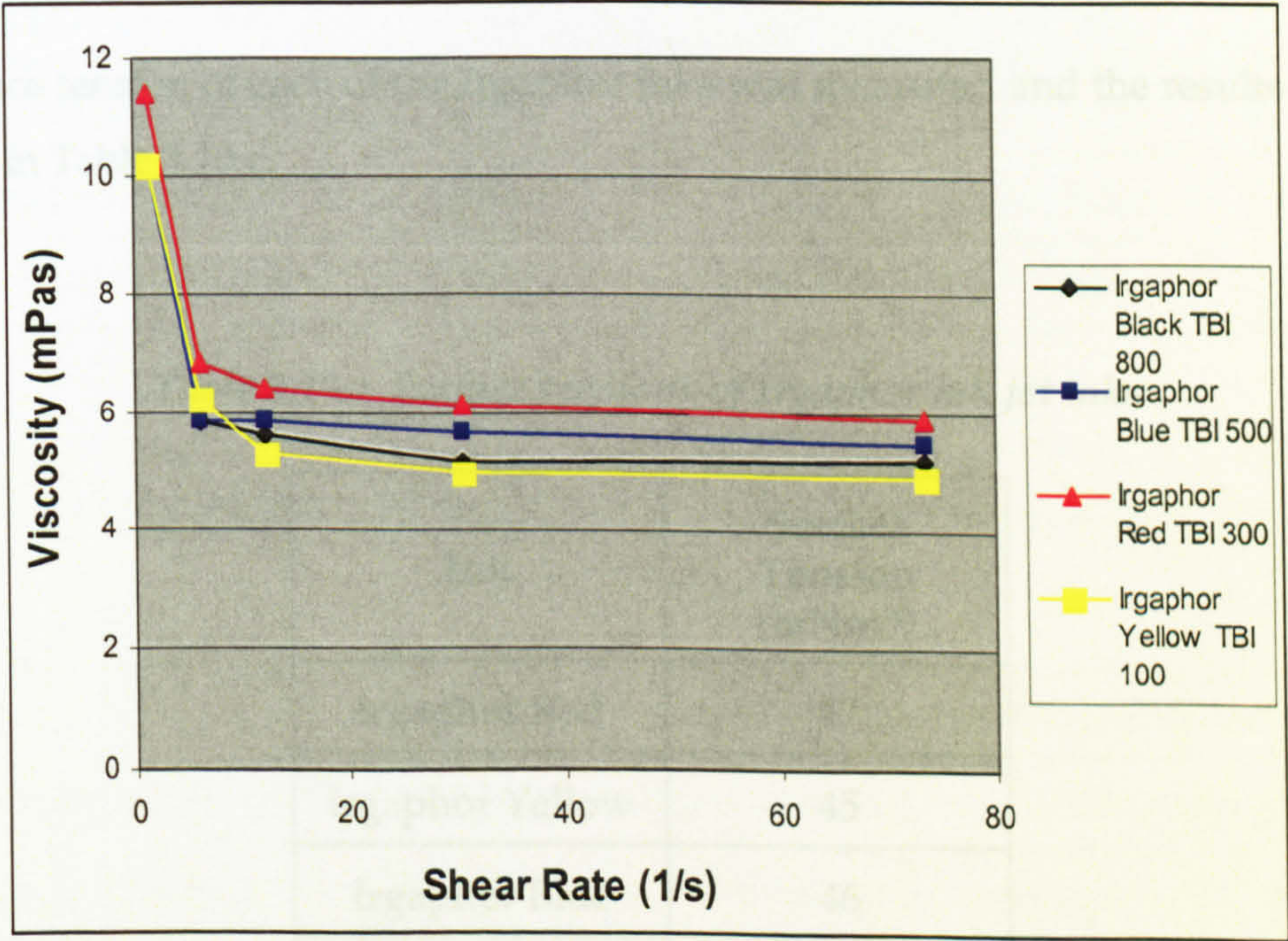


Figure 3.10.a Viscosity profiles of Irgaphor ink jet inks

It can be seen from these viscosity results that each of the Irgaphor inks was acceptable for ink jet printing, although higher in viscosity than the values obtained for Cabot Ink Formulation 1. A comparison of Cabot Ink Formulation 1 and the corresponding Irgaphor Red TBI 300 can be seen in Figure 3.10.b.

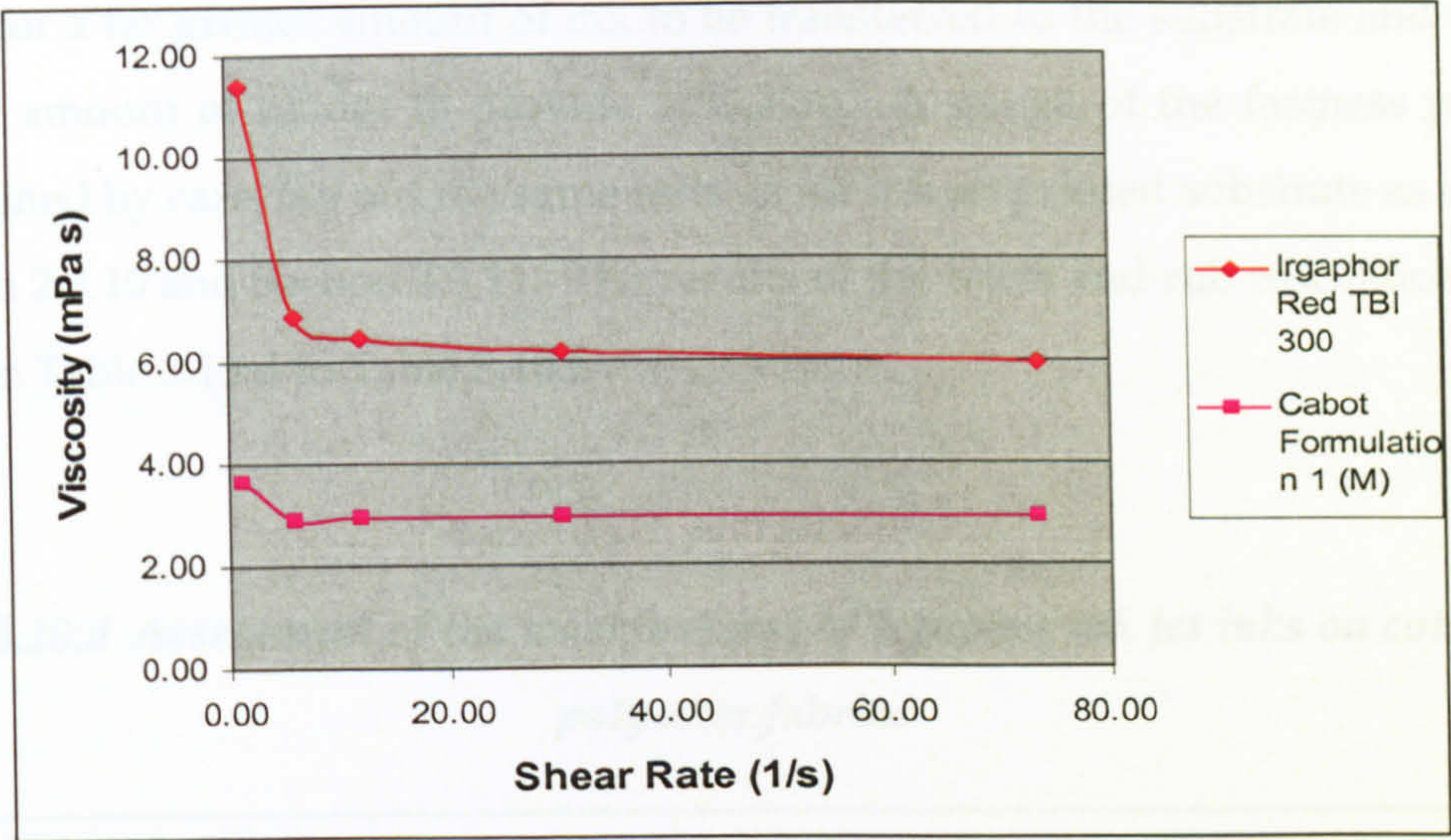


Figure 3.10.b Comparison of the viscosity profiles of Irgaphor Red TBI 300 and Cabot Ink Formulation 1 (Magenta)

The surface tension of each of the Irgaphor inks was measured and the results obtained reported in Table 3.10.c.

Table 3.10.c Surface tensions of Irgaphor ink jet inks

Ink	Surface Tension (mNm ⁻¹)
Irgaphor Red	47
Irgaphor Yellow	45
Irgaphor Blue	46
Irgaphor Black	45

It should be noted that whilst they had acceptable properties in terms of the physical parameters required for ink jet printing, the Irgaphor inks were unable to be printed using the available thermal ink jet technology. Therefore, comparisons relating to the wash and rub fastness of these inks with any novel formulations were subjective. Instead of printing, the inks were dripped onto the substrate before being thermally cured at 170°C for 3 minutes in a Werner Mathis KTF 4099 curing oven. This method

allowed for a far greater amount of ink to be transferred to the substrate and therefore a greater amount of binder to provide adhesion. A gauge of the fastness properties was obtained by carrying out the same tests as for ink jet printed substrate as described in Section 2.3.10 and Section 2.3.11. The results of the wash and rub resistance tests can be seen in Table 3.10.d to Table 3.10.f.

Table 3.10.d Assessment of the washfastness of Irgaphor ink jet inks on cotton and polyester fabrics

Ink	Optical density			
	On cotton		On polyester	
	Before washing	After washing	Before washing	After washing
Irgaphor Black TBI 800	1.63	1.54	1.62	1.50
Irgaphor Blue TBI 500	1.45	1.36	1.60	1.24
Irgaphor Red TBI 300	1.41	1.32	1.34	1.20
Irgaphor Yellow TBI 100	0.75	0.71	0.75	0.70

Table 3.10.e Assessment of the rubfastness of Irgaphor ink jet inks on cotton and polyester fabrics

Ink formulation	Optical density of cotton lawn rubbing fabric after rub test			
	On cotton		On polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
Irgaphor Black TBI 800	0.15	0.18	0.18	0.20
Irgaphor Blue TBI 500	0.12	0.14	0.14	0.16
Irgaphor Red TBI 300	0.12	0.15	0.15	0.16
Irgaphor Yellow TBI 100	0.06	0.08	0.09	0.11

Table 3.10.f Visual assessment of the fastness properties of Irgaphor inks on cotton and polyester fabrics

Ink formulation	Assessment of colour difference between printed samples before and after washing	Assessment of colour difference between rubbed and unrubbed cotton lawn pads	
		Dry	Wet
Irgaphor Black TBI 800	4/5	3/4	3/4
Irgaphor Blue TBI 500	4/5	3/4	3/4
Irgaphor Red TBI 300	4/5	3/4	3/4
Irgaphor Yellow TBI 100	5	4	4

It can be seen from Table 3.10.d to Table 3.10.f that the wash and rub resistance of the Irgaphor inks was not as good as those for the Cabot Ink Formulations. This may be in part due to the amount of ink applied to the substrate when compared to an ink jet printed sample. However, if a greater amount of ink was applied to the substrate, it would follow that a greater amount of binder was applied and thus greater fixation might be expected.

It can be concluded from the analysis carried out on the Irgaphor range of pigmented ink jet inks that the results obtained for the inks formulated throughout this investigation were comparable to commercially available inks. As such, a four colour set of inks required formulating for further analysis.

3.11 Characteristics of a Four Colour Set of Inks for the Ink Jet Printing of Textiles

The following section outlines the results obtained for analysis carried out on a four colour set of inks based on Synthappret BAP as a binder system and Cab-O-Jet pigment dispersions as the colorant. In each case, the inks are labelled FCS (Four Colour Set).

The results obtained from the testing of the physical properties of the inks formulated can be seen in Table 3.11.a.

Table 3.11.a Physical properties of the four colour set

Ink formulation	Viscosity at 60 rpm (mPa.s)	Surface tension (mNm ⁻¹)	Particle size at a 95% limit (nm)
FCS Yellow	2.94	35.5	184
FCS Magenta	2.84	35.5	124
FCS Cyan	2.82	36	106
FCS Black	2.98	35.5	114

It can be seen from Table 3.11.a that each of the inks adhered to the parameters for acceptance of an ink for ink jet printing. It should be noted that due to the low particle size of the pigment within the inks, stability was likely to be very good as proved in previous sections. Once passed for physical properties the inks were used to print cotton and polyester fabrics.

The printed samples of cotton and polyester were subjected to tests to ascertain their wash and rub resistance. Washed samples were compared to the originals in terms of their optical densities as well as assessments of colour difference according to the SDC greyscales for colour change. The data obtained from the measurements of the measured change in colour density of the washed and unwashed samples can be seen in Table 3.11.b and Table 3.11.c.

Table 3.11.b Washfastness of printed cotton fabric

Pigmented ink formulation	Optical density on cotton		
	Before washing	After washing	Difference
FCS Yellow	0.63	0.62	0.01
FCS Magenta	0.43	0.41	0.02
FCS Cyan	0.49	0.48	0.01
FCS Black	1.07	1.05	0.02

Table 3.11.c Washfastness of printed polyester fabric

Pigmented ink formulation	Optical density on polyester		
	Before washing	After washing	Difference
FCS Yellow	0.62	0.59	0.03
FCS Magenta	0.45	0.43	0.02
FCS Cyan	0.54	0.42	0.02
FCS Black	0.95	0.93	0.02

It can be seen from Table 3.11.b and Table 3.11.c that the change in optical density of the printed samples the washfastness test was minimal. Such minimal changes in the colour difference showed that the washfastness of the printed samples was excellent. It should also be noted that on completion of the washing cycle, no colour was transferred from the printed substrate to the multifibre strip. As well as this, no colour was removed from the printed substrate into the wash-bath liquor.

The greyscale evaluations made to determine the visual change in colour of the printed samples after washing can be seen in Table 3.11.d to Table 3.11.g for each colour alongside pictures of the printed and washed samples.

Table 3.11.d Visual assessment of washfastness of FCS Yellow





	Substrate printed	
	Cotton	Polyester
Before washing		
After washing		
Assessment of colour difference between printed samples before and after washing	5	5

Table 3.11.e Visual assessment of washfastness of FCS Magenta

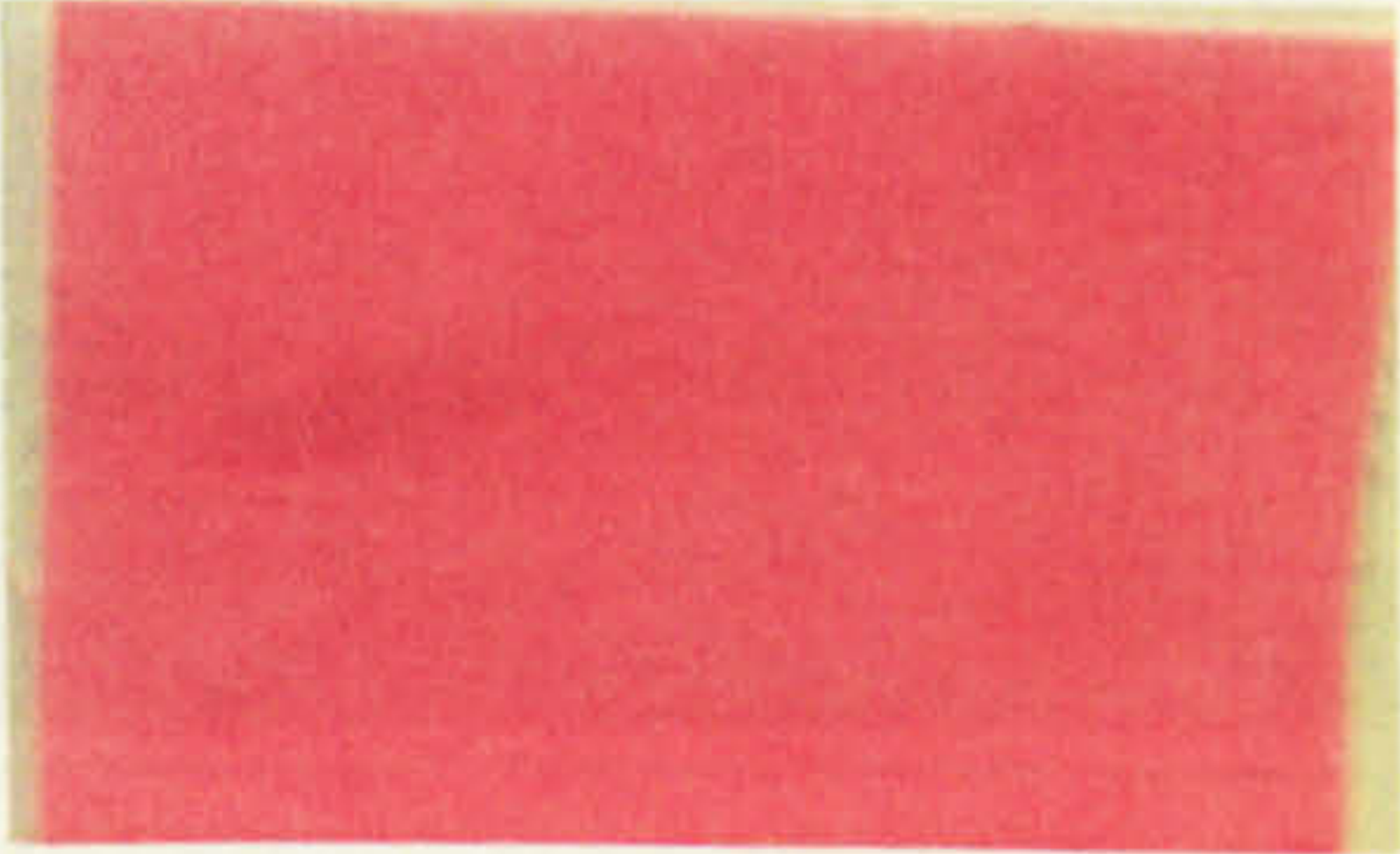


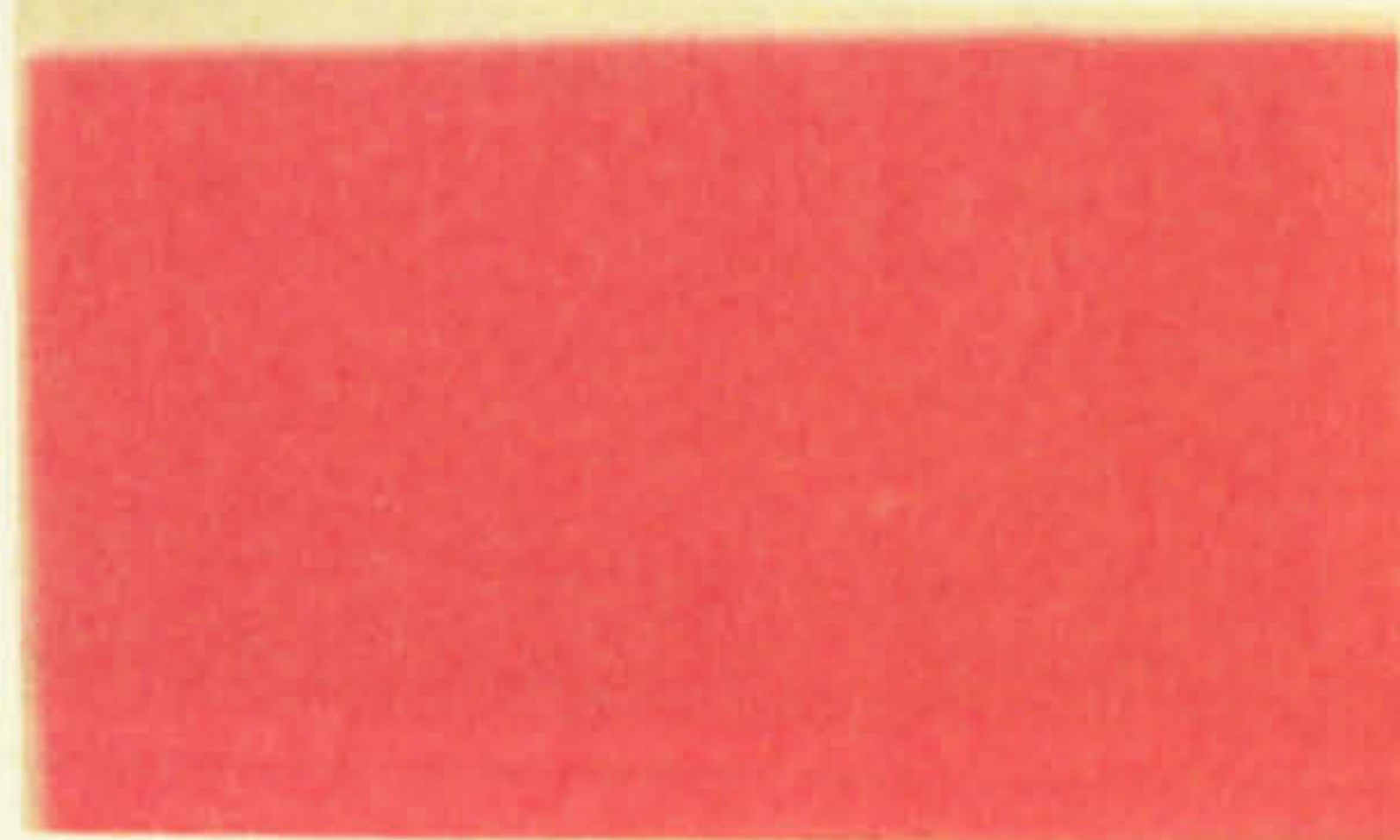
	Substrate printed	
	Cotton	Polyester
Before washing		
After washing		
Assessment of colour difference between printed samples before and after washing	5	5

Table 3.11.f Visual assessment of washfastness of FCS Cyan









	Substrate printed	
	Cotton	Polyester
Before washing		
After washing		
Assessment of colour difference between printed samples before and after washing	5	5

Table 3.11.g Visual assessment of washfastness of FCS Black

	Substrate printed	
	Cotton	Polyester
Before washing		
After washing		
Assessment of colour difference between printed samples before and after washing	4/5	4/5

It can be seen from Table 3.11.d to Table 3.11.g that the visual assessment of the colour difference between washed and unwashed substrate gave excellent results. The results obtained supported the data collected for the colour densities of the prints before and after the washing process. It could be concluded from the testing carried out that each of the colours printed onto cotton and polyester fabrics had outstanding washfastness. Such prints would therefore be acceptable to industrial standards. Commercially available inks may be able to impart similar resistance properties to a printed fabric, however, the fabric handle is often compromised. As such the results obtained for the four colour set of inks are comparable and in terms of handle, superior to commercially available ink jet inks.

Scanning electron microscopy was carried out on the coloured samples to see whether any changes could be seen between the printed fibres before and after washing. The micrograph obtained for the printed cotton samples can be seen in Figure 3.11.a to Figure 3.11.f.



Figure 3.11.a Micrograph of FCS Cyan on cotton fabric (×1500)

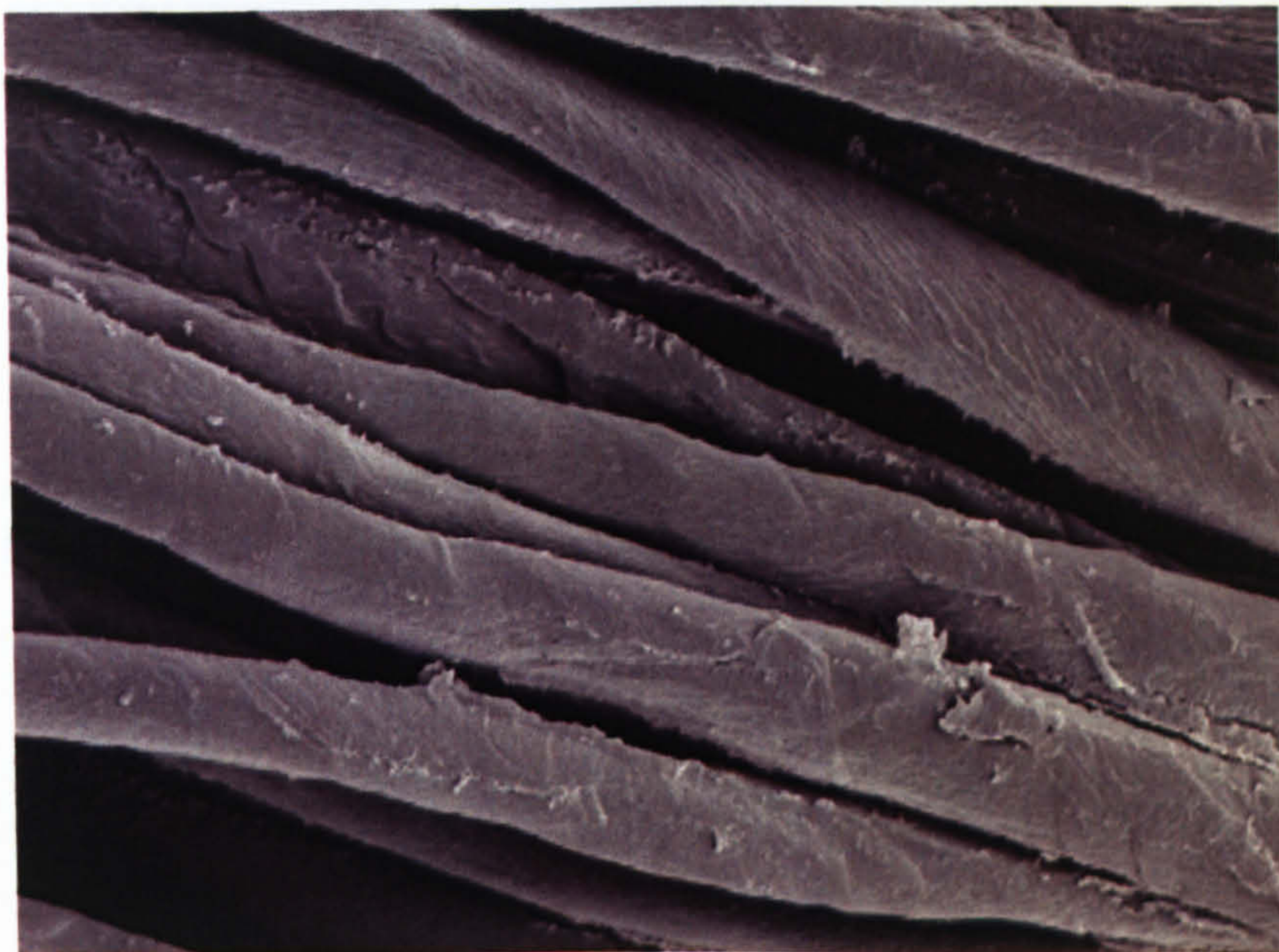


Figure 3.11.b Micrograph of FCS Cyan on cotton fabric after washing (×1500)



Figure 3.11.c Micrograph of FCS Magenta on cotton fabric (×1500)



Figure 3.11.d Micrograph of FCS Cyan on cotton fabric after washing (×1500)

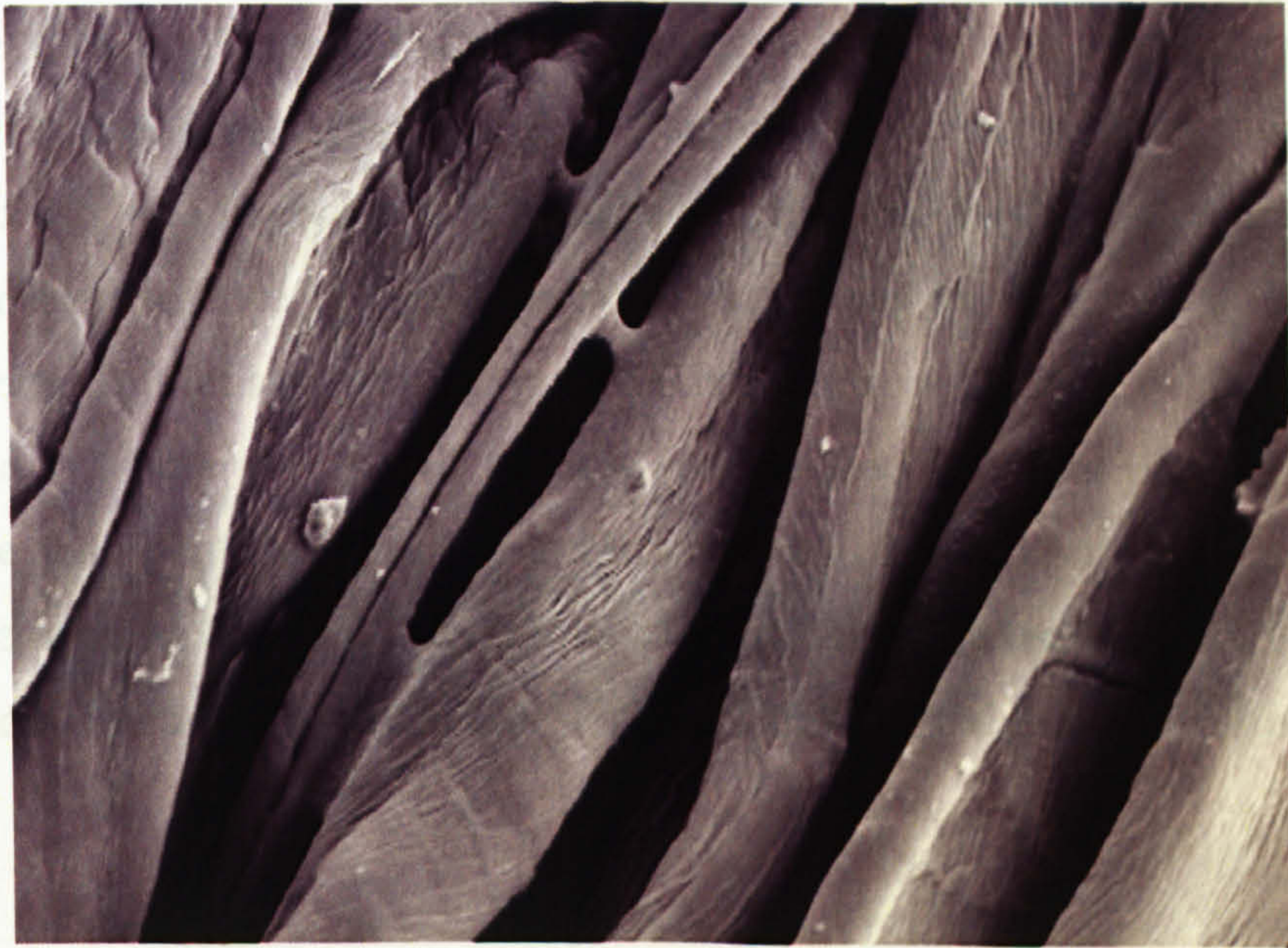


Figure 3.11.e Micrograph of FCS Yellow on cotton fabric (×1500)

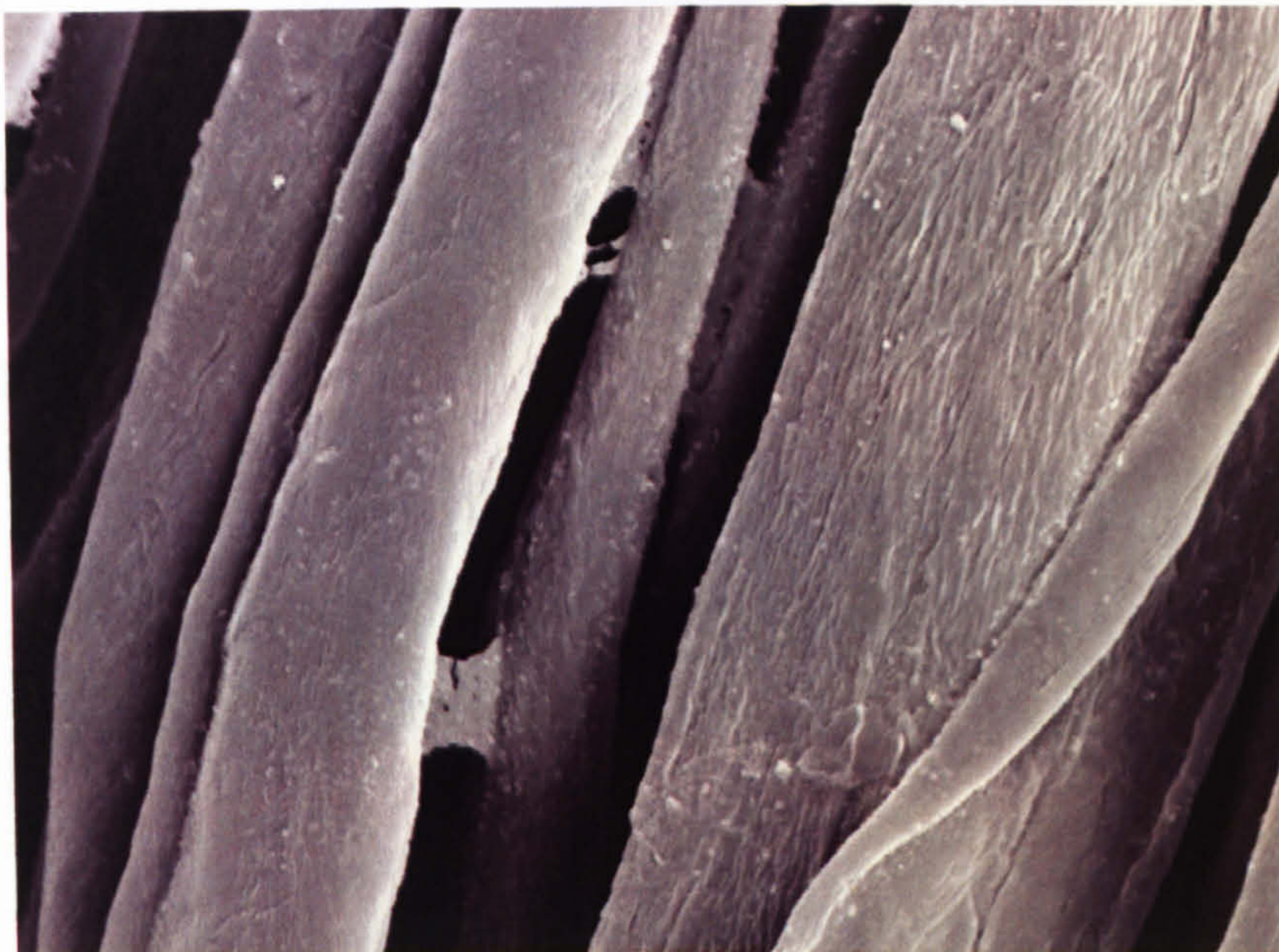
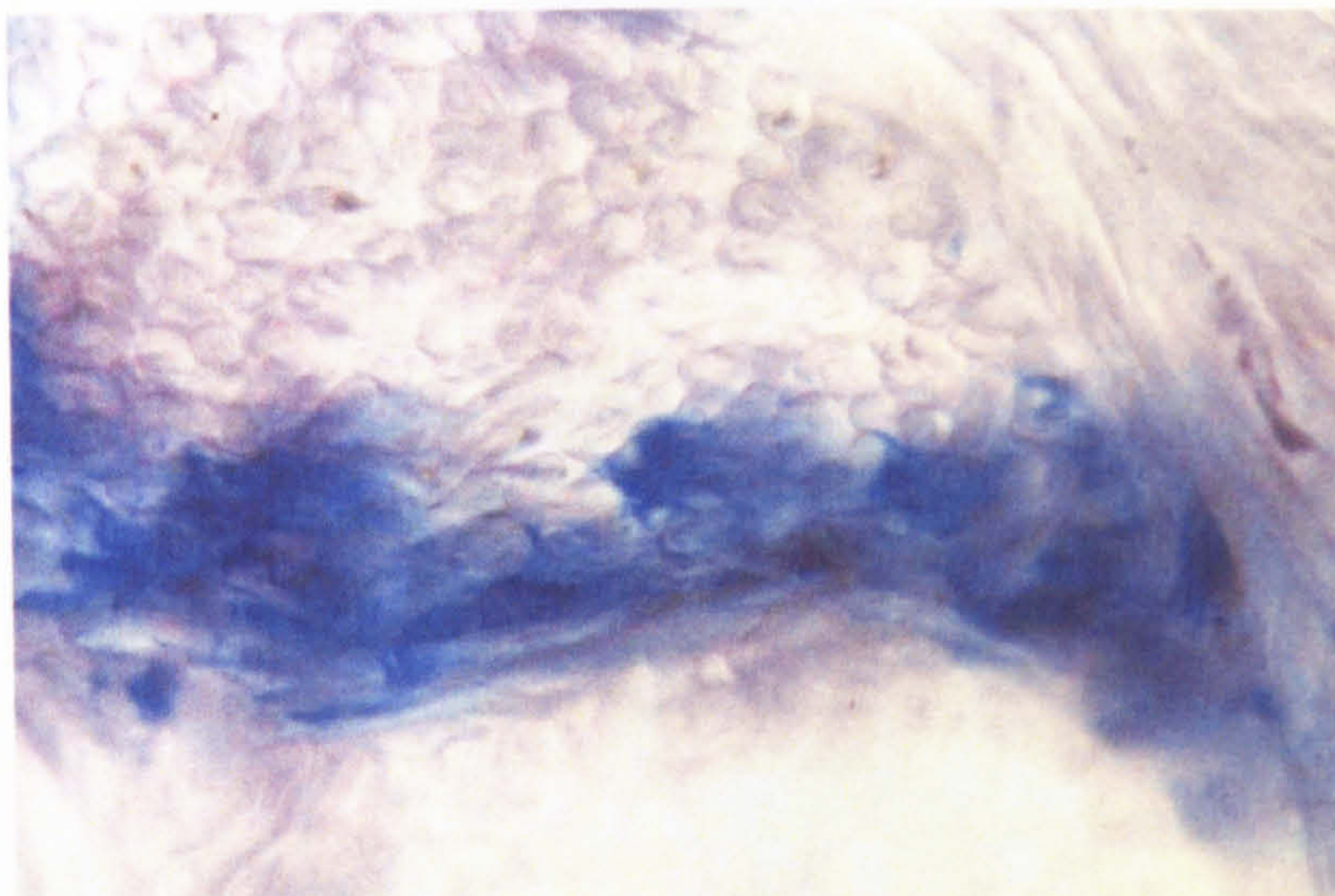


Figure 3.11.f Micrograph of FCS Yellow on cotton fabric after washing (×1500)

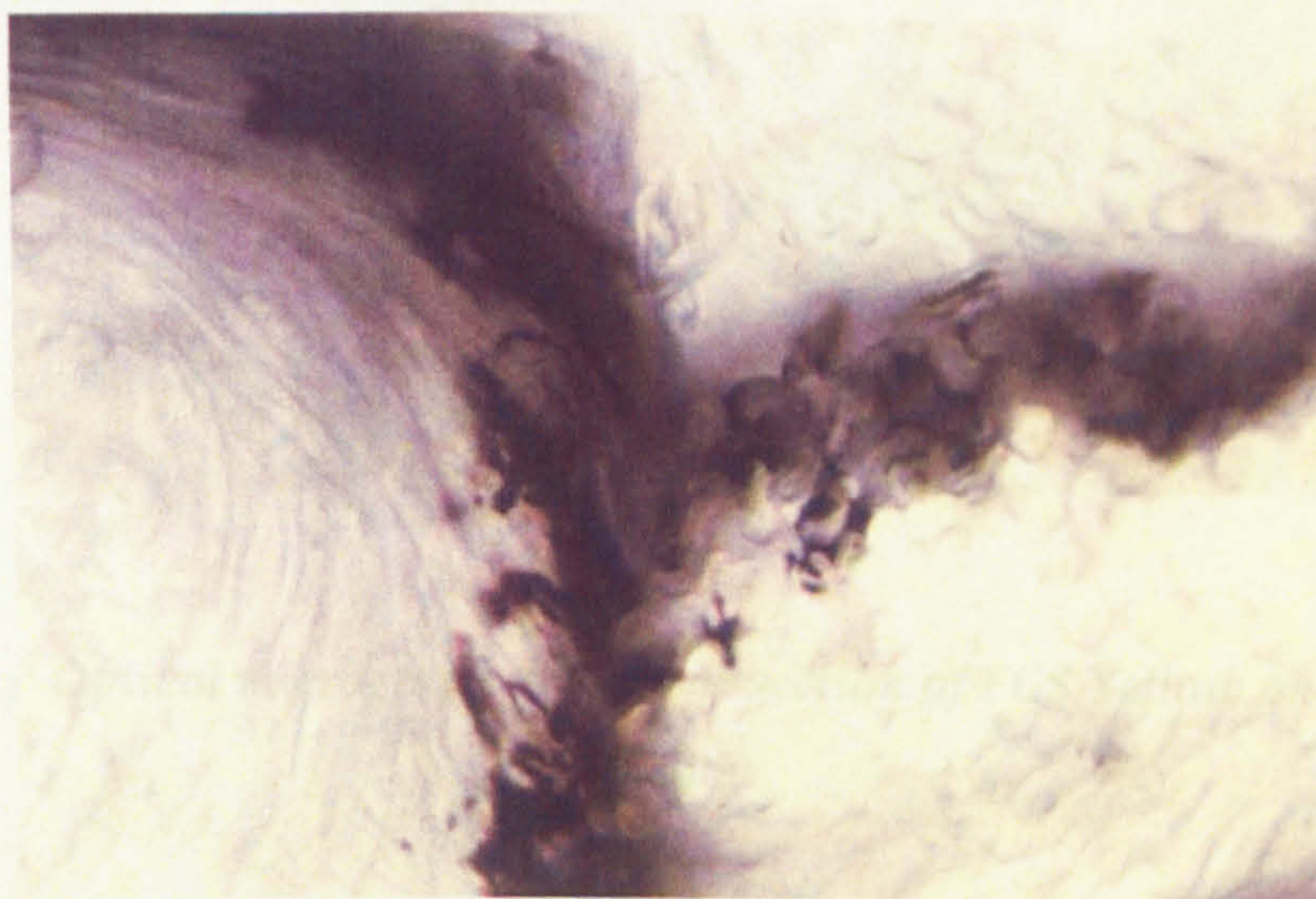
From Figure 3.11.a to Figure 3.11.f it can be seen that there was very little difference in the observed cotton fibres after washing. The washed cotton sample showed signs of abrasion and this was likely to have occurred during the washing process. There was evidence for the presence of binder between the fibres in some areas although there was little evidence that suggested pigment particles to be present on the surface. It is likely that, due to the very small particle size of the Cab-O-Jet pigment dispersions used and the absorbent nature of the cotton substrate, that the pigment particles as part of the ink penetrated the fibres. Evidence of such fibre penetration of FCS Cyan can be seen in optical micrographs of a cross-section of the printed substrate shown in Figure 3.11.g.

Figure 3.11.h Optical micrograph of a cross-section of FCS Black on cotton fabric (×500)

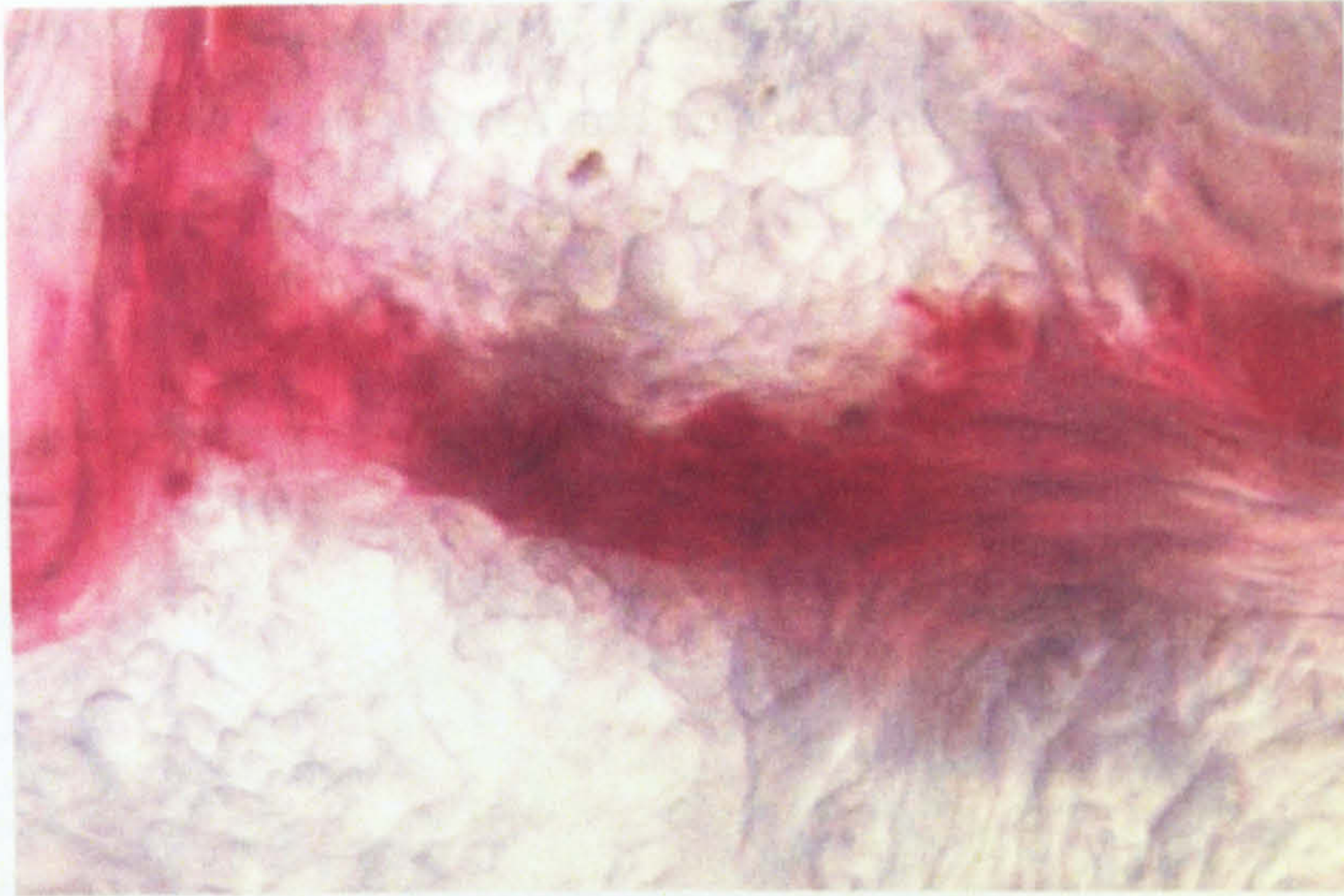


*Figure 3.11.g Optical micrograph of a cross-section of FCS Cyan on cotton fabric
(×400)*

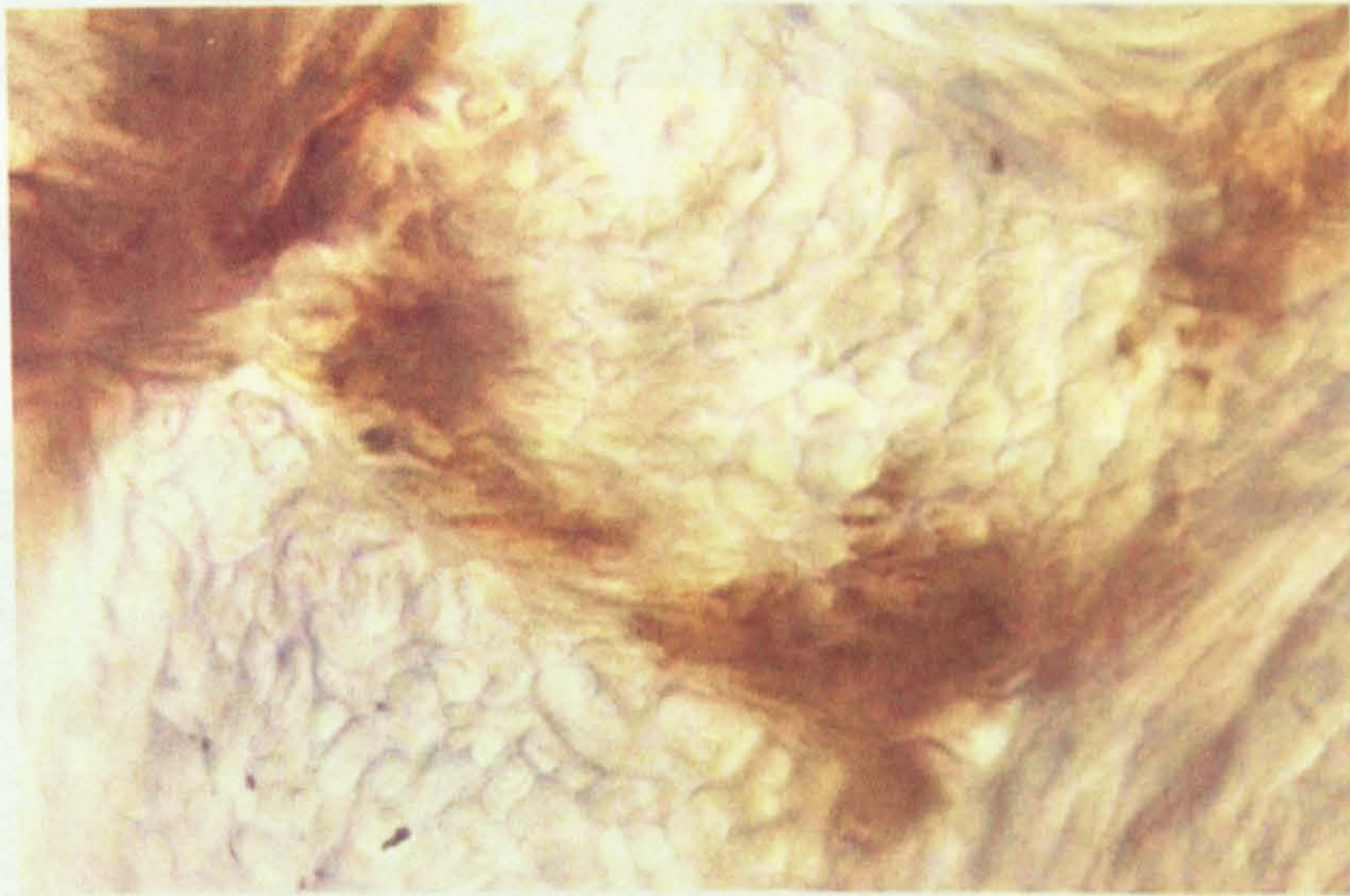
The other inks printed onto cotton fabric were also seen to penetrate the fibres to the same extent. The optical micrograph obtained from this analysis can be seen in Figure 3.11.h to Figure 3.11.j.



*Figure 3.11.h Optical micrograph of a cross-section of FCS Black on cotton fabric
(×400)*



*Figure 3.11.i Optical micrograph of a cross-section of FCS Magenta on cotton fabric
(×400)*



*Figure 3.11.j Optical micrograph of a cross-section of FCS Yellow on cotton fabric
(×400)*

The effect of washing the printed polyester substrate produced slightly greater changes in colour density from the unwashed sample as can be seen in Table 3.11.c. The visual assessment and grading of the colour difference between printed and washed samples

according to the greyscale also showed that the washfastness of printed polyester was not as good as printed cotton. However, the results shown in Table 3.11.b and Table 3.11.c confirm that the washfastness of both printed cotton and polyester fabrics was excellent. SEM analysis of the printed and washed polyester fibres was carried out and the micrographs obtained are shown in Figure 3.11.k to Figure 3.11.p.

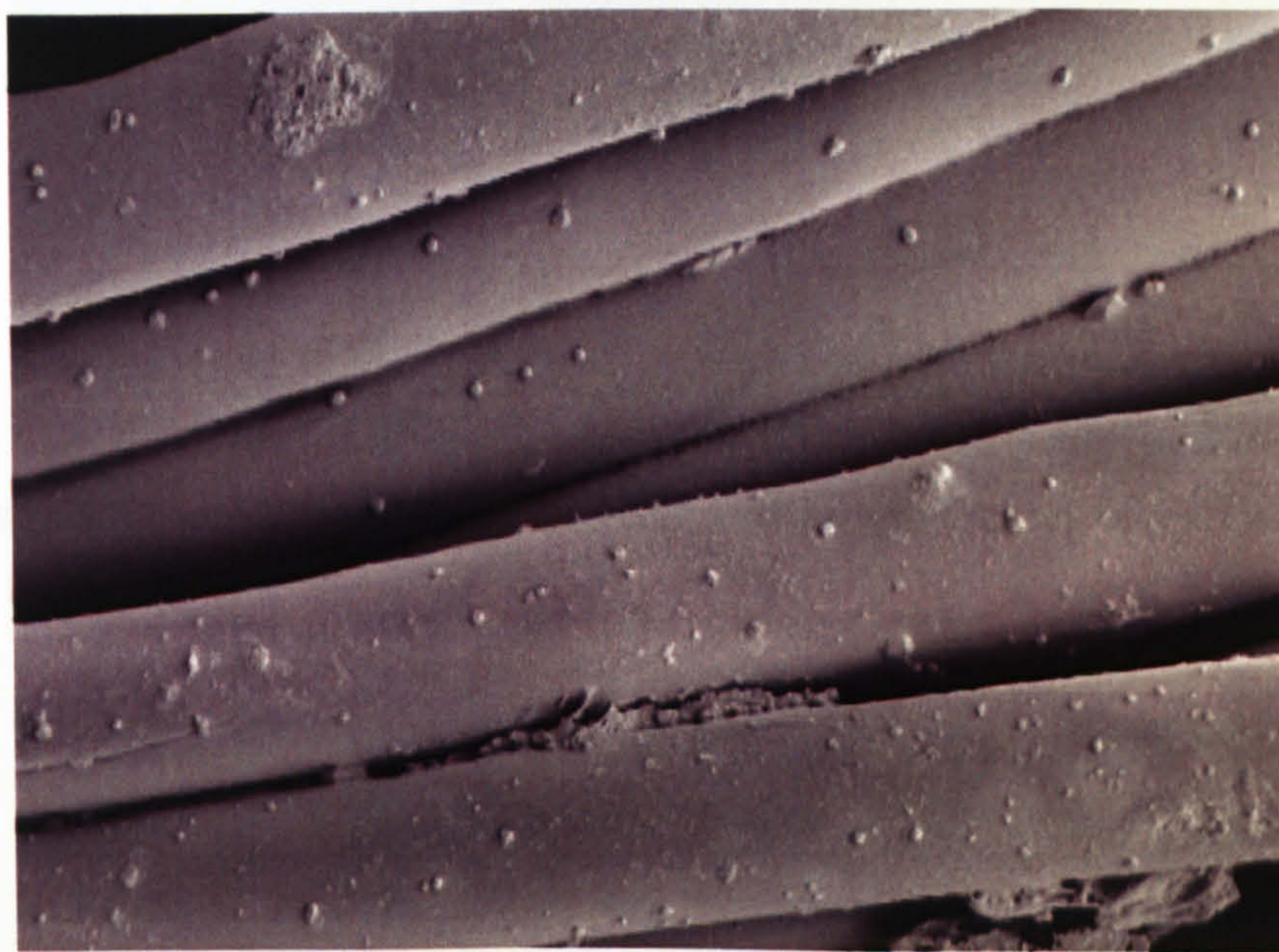


Figure 3.11.k Micrograph of FCS Cyan on polyester fabric (×1500)



Figure 3.11.l Micrograph of FCS Cyan on polyester fabric after washing (×1500)

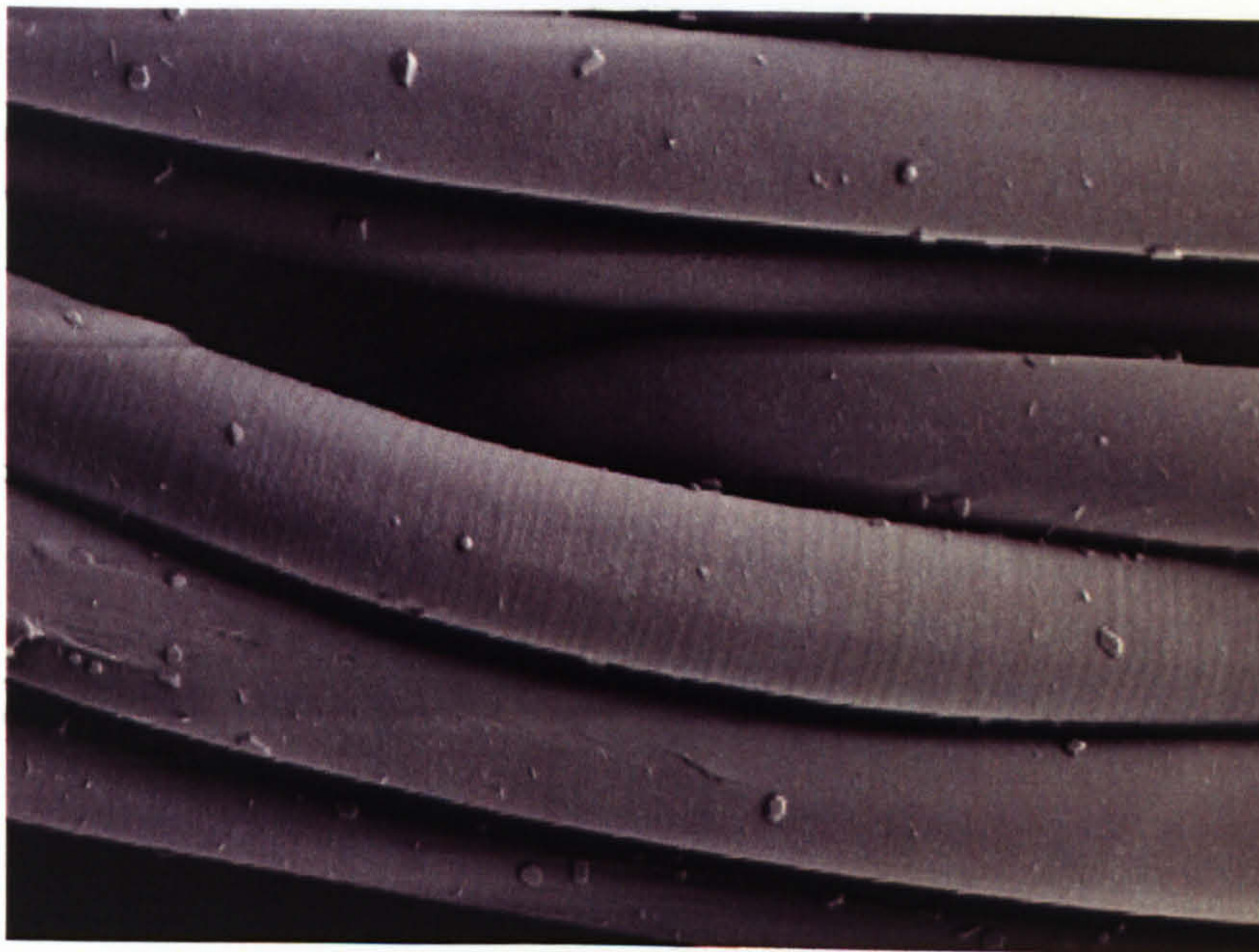


Figure 3.11.m Micrograph of FCS Magenta on polyester fabric ($\times 1500$)

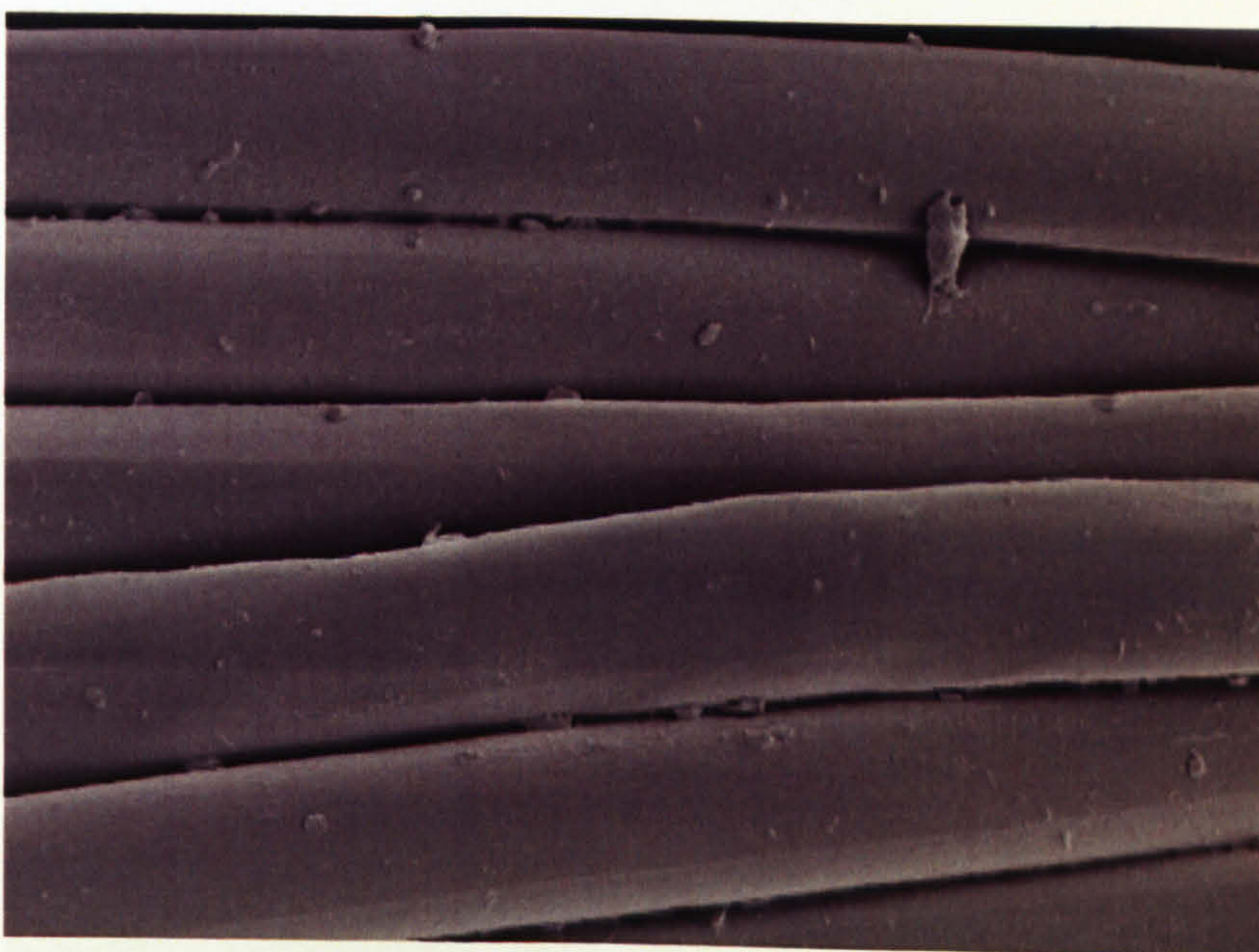


Figure 3.11.n Micrograph of FCS Magenta on polyester fabric after washing ($\times 1500$)

Figure 3.11.k shows a scanning electron micrograph of polyester fabric printed with FCS Cyan prior to being washed. It can be seen from Figure 3.11.k that a number of particles could be seen on the surface of the fibres. The washed sample of printed polyester fabric depicted in Figure 3.11.l shows that while some particulates remained, the majority of these had been removed in the washing process. Such a

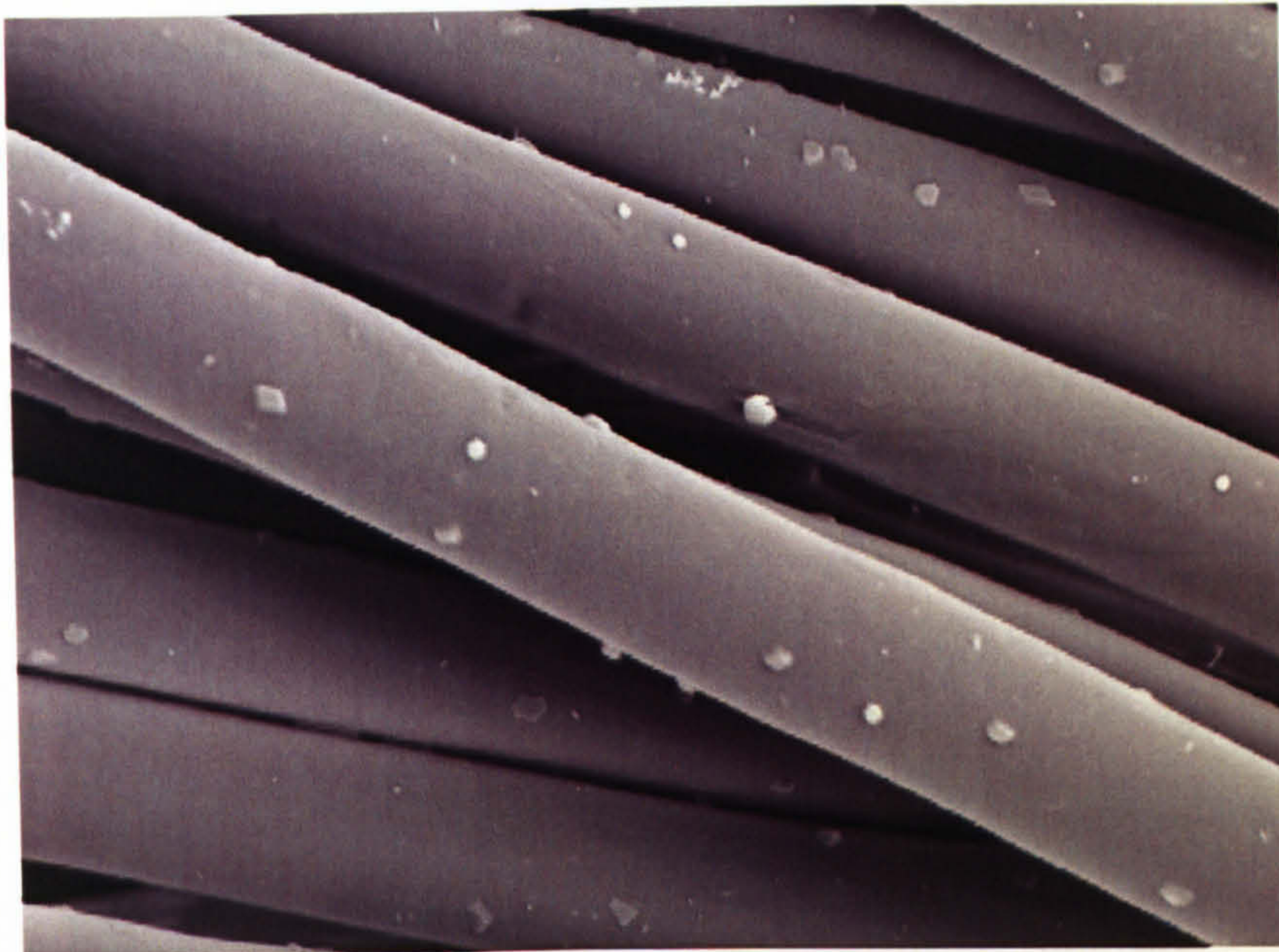


Figure 3.11.o Micrograph of FCS Yellow on polyester fabric ($\times 1500$)

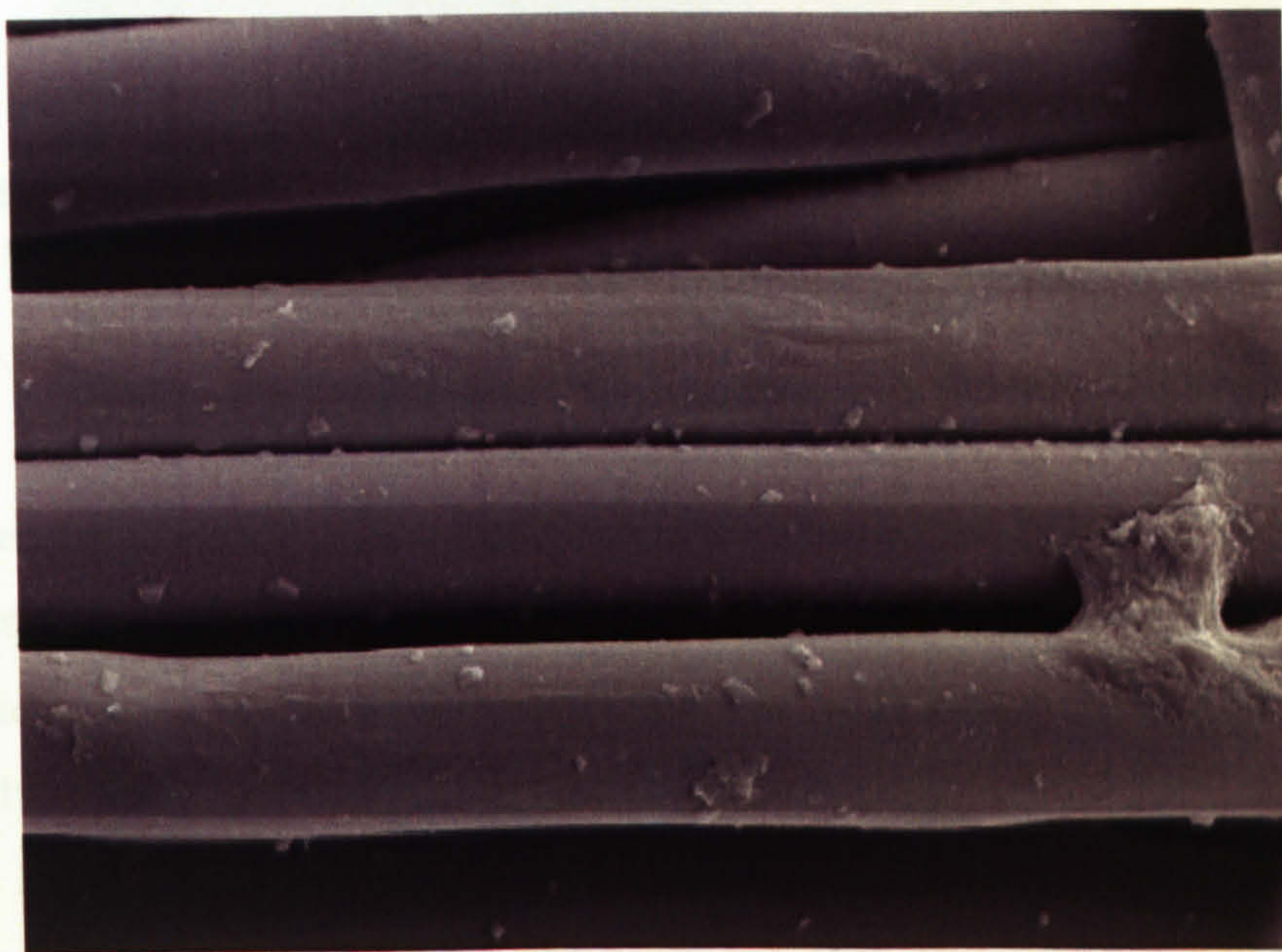


Figure 3.11.p Micrograph of FCS Yellow on polyester fabric after washing ($\times 1500$)

Figure 3.11.k shows a scanning electron micrograph of polyester fabric printed with FCS Cyan prior to being washed. It can be seen from Figure 3.11.k that a number of particles could be seen on the surface of the fibres. The washed sample of printed polyester fabric, depicted in Figure 3.11.l, shows that while some particulates remained, the majority of these had been removed in the washing process. Such a

phenomenon was observed for each of the coloured inks printed onto polyester fabric.

Optical microscopy of a cross-section of the printed polyester fabric confirmed that the ink had penetrated the fibres. This phenomenon can be seen in Figure 3.11.q

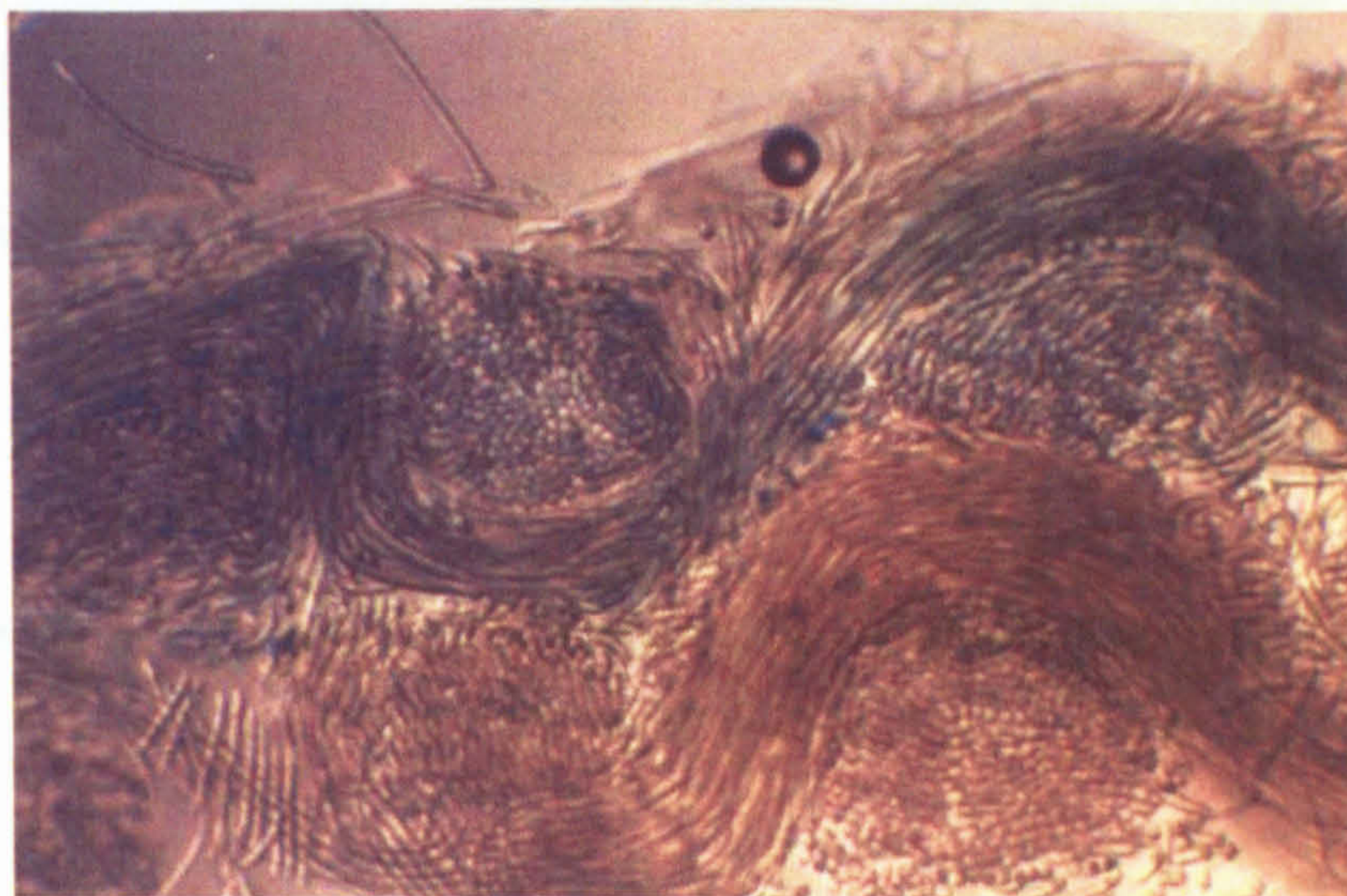


Figure 3.11.q Optical micrograph of a cross-section of polyester fabric printed with FCS Cyan (×250)

It can be seen from Figure 3.11.q that the ink penetrated the full depth of the fabric. It should be noted that the uncoloured layer was a clean piece of polyester used to provide rigidity to the cross-section. This was a strange occurrence as usually it is only a disperse dye which is seen to colour polyester to such an extent. Optical micrographs were taken for prints of the other inks in the set to ascertain whether such coloration and penetration of the fibres was common for each ink. The optical micrographs obtained are shown in Figure 3.11.r to Figure 3.11.t.

Figure 3.11.s Optical micrograph of a cross-section of polyester fabric printed with FCS Magenta (×250)

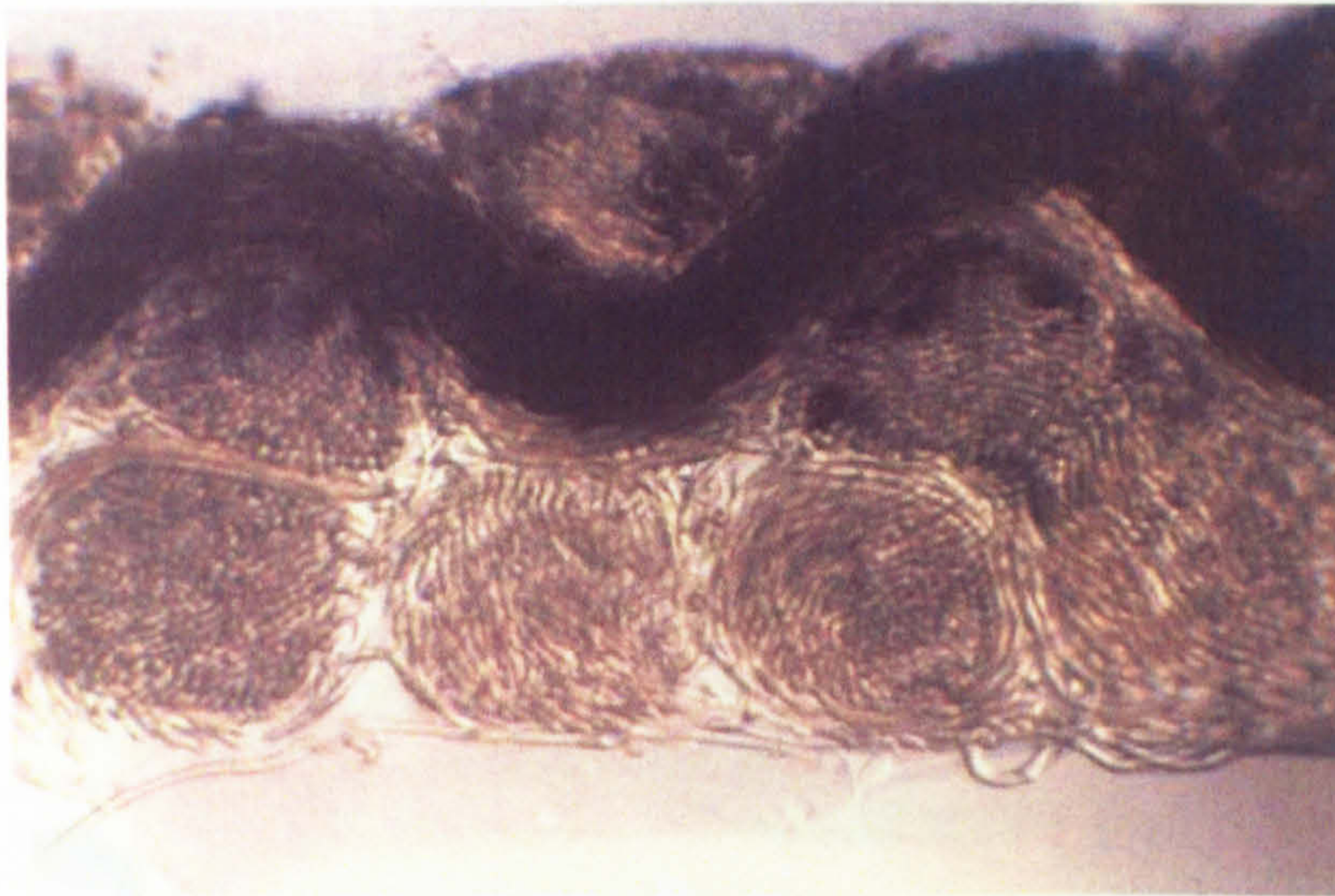


Figure 3.11.r Optical micrograph of a cross-section of polyester fabric printed with FCS Black (×250)

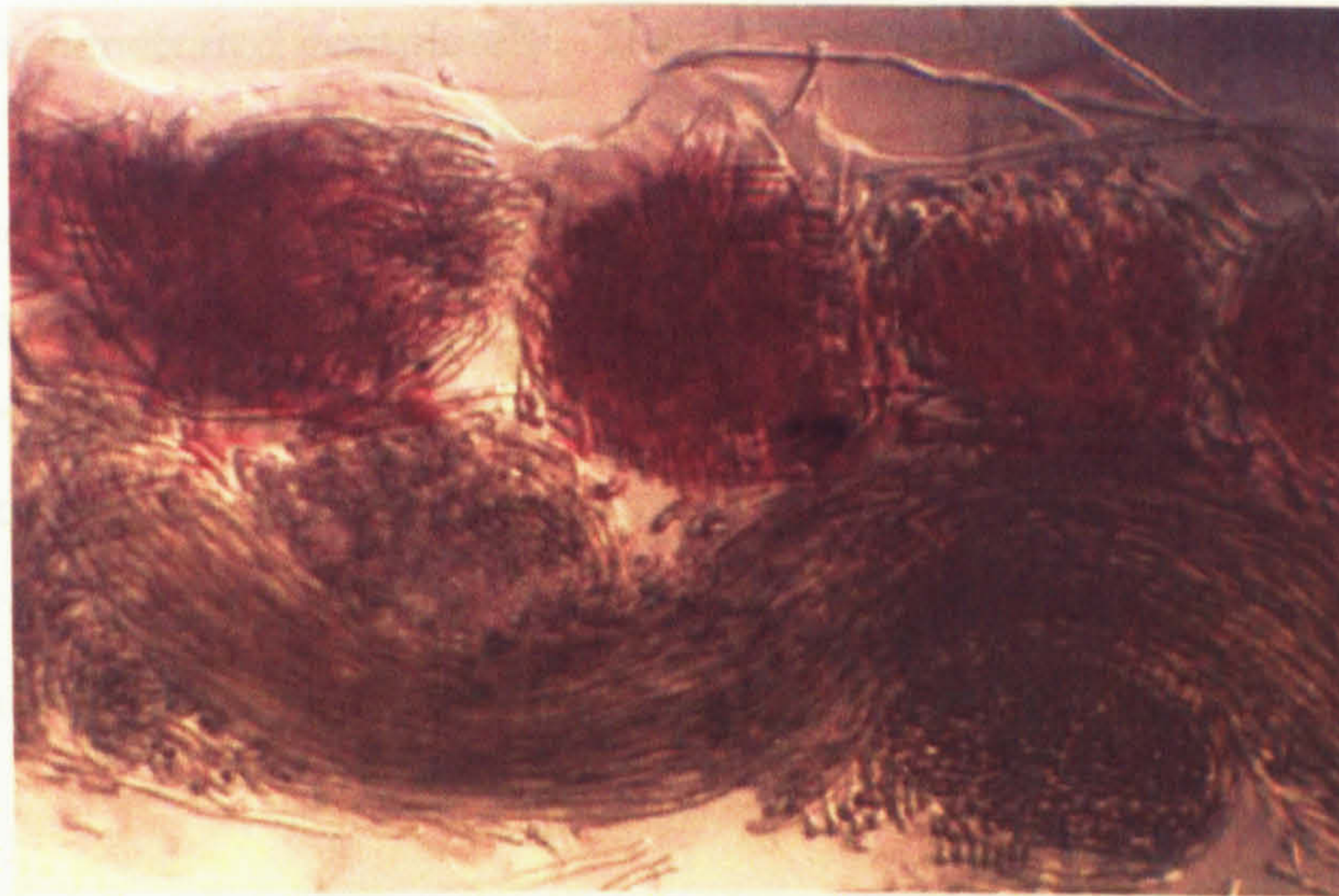


Figure 3.11.s Optical micrograph of a cross-section of polyester fabric printed with FCS Magenta (×250)

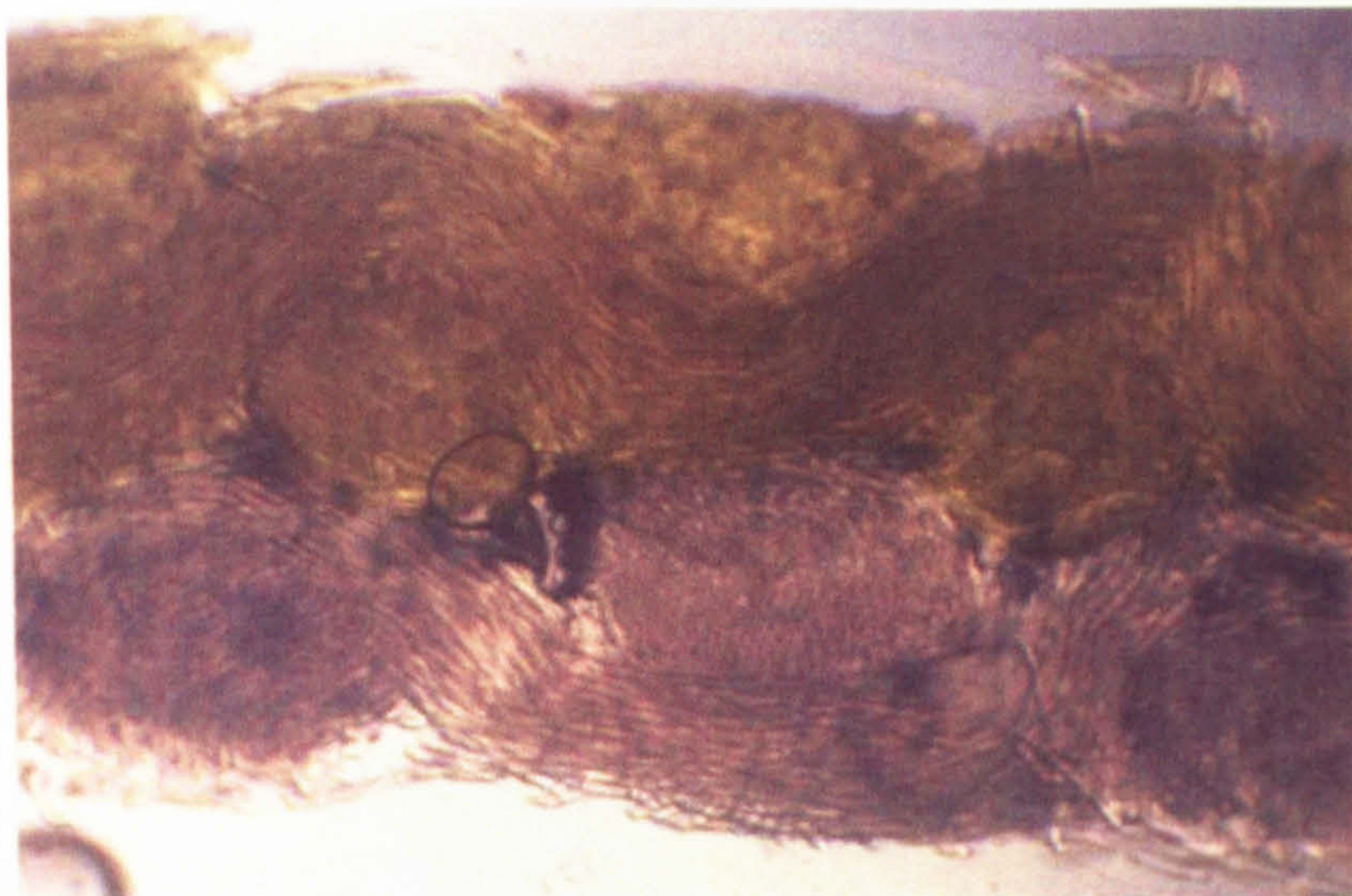


Figure 3.11.t Optical micrograph of a cross-section of polyester fabric printed with FCS Yellow (×250)

It can be seen from Figure 3.11.r to Figure 3.11.t that in each case, the fibres of the polyester were penetrated completely. The greatest coloration was seen in the sample printed with FCS Yellow. This may however have been due to the higher levels of pigment dispersion contained within this ink. As a result of this penetration of the fibre, the pigments were tested for their thermal characteristics to see whether they bore any resemblance to a disperse dye. Initially, the pigment dispersions were dried at 40°C in order to obtain crystalline pigment particles. The dried pigment was then used to carry out DSC and TGA investigations. The DSC plot for Cab-O-Jet Yellow 270 Y can be seen in Figure 3.11.u.

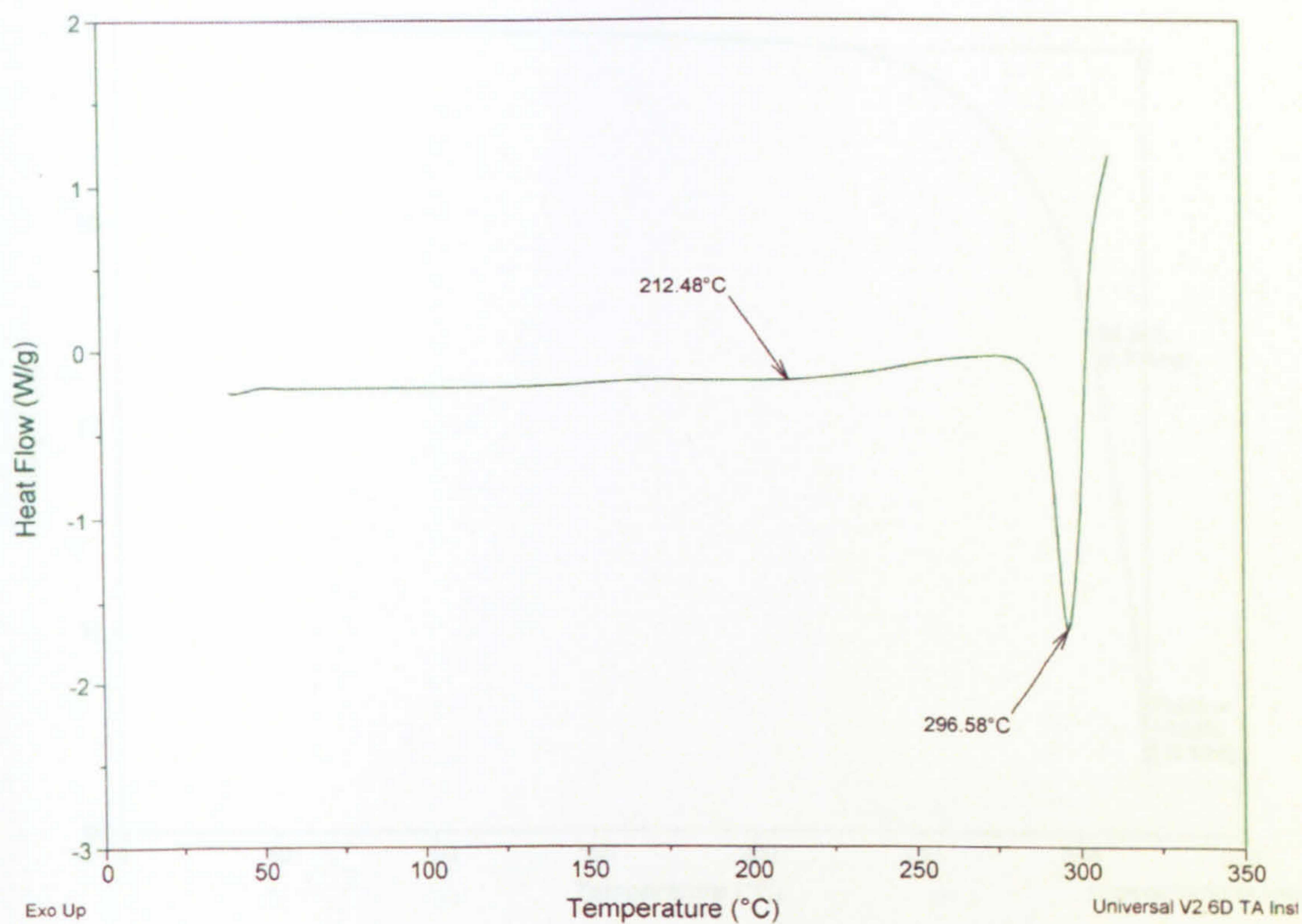


Figure 3.11.u DSC plot of Cab-O-Jet Yellow 270 Y

Figure 3.11.u shows that the pigment used in Cab-O-Jet Yellow 270 Y was stable up to 296.58°C. This stability was confirmed when considering the TGA plot obtained for the same pigment, which can be seen in Figure 3.11.v. A standard disperse dye sublimates at temperatures between 120°C and 180°C whereas the pigment is thermally stable within this region.

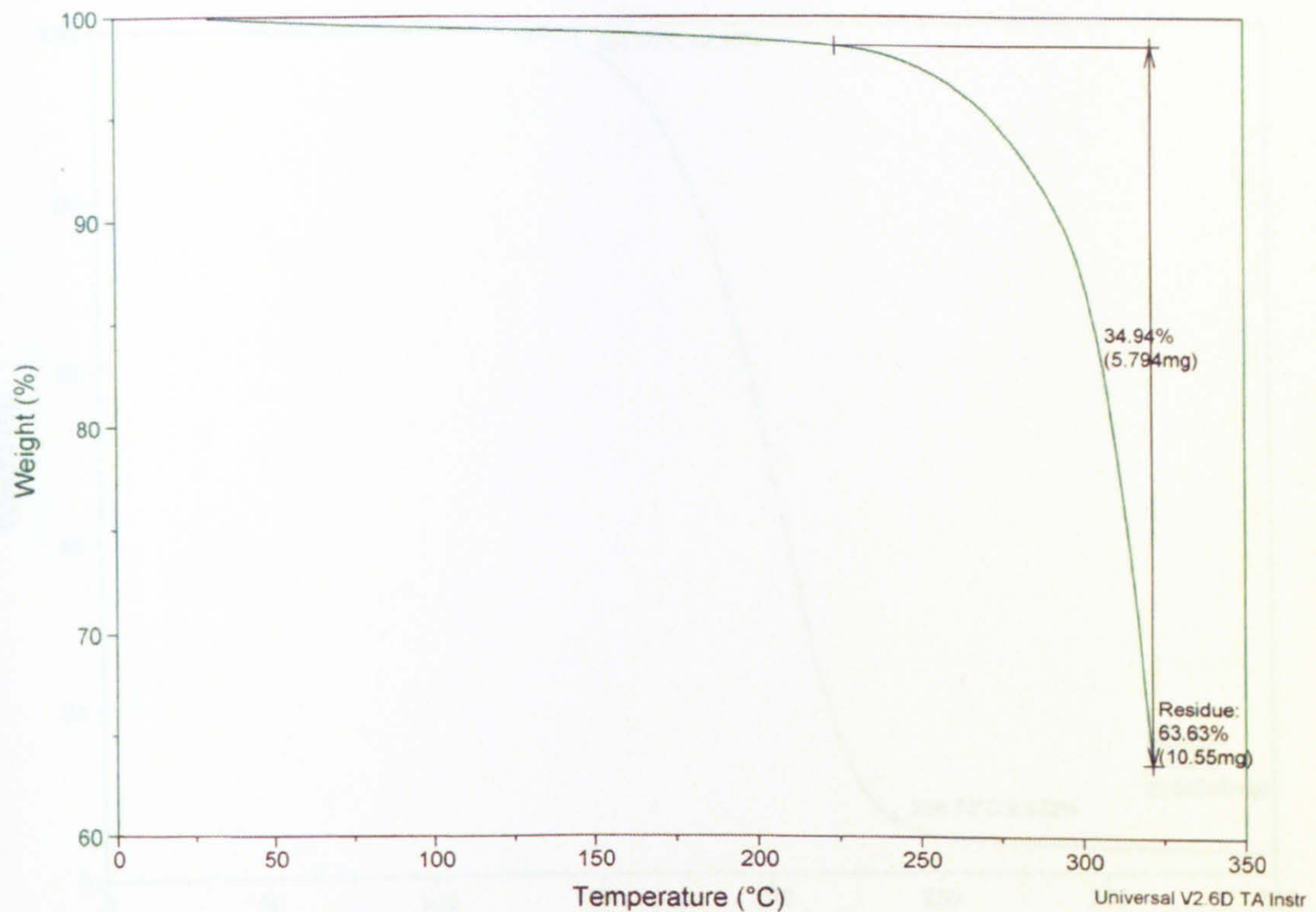


Figure 3.11.v TGA plot of Cab-O-Jet Yellow 270 Y

Thermogravimetric analysis was also carried out on a disperse dye in order to prove that its thermal profile was different to that of the pigments used within the ink formulations. The TGA plot obtained can be seen in Figure 3.11.w.

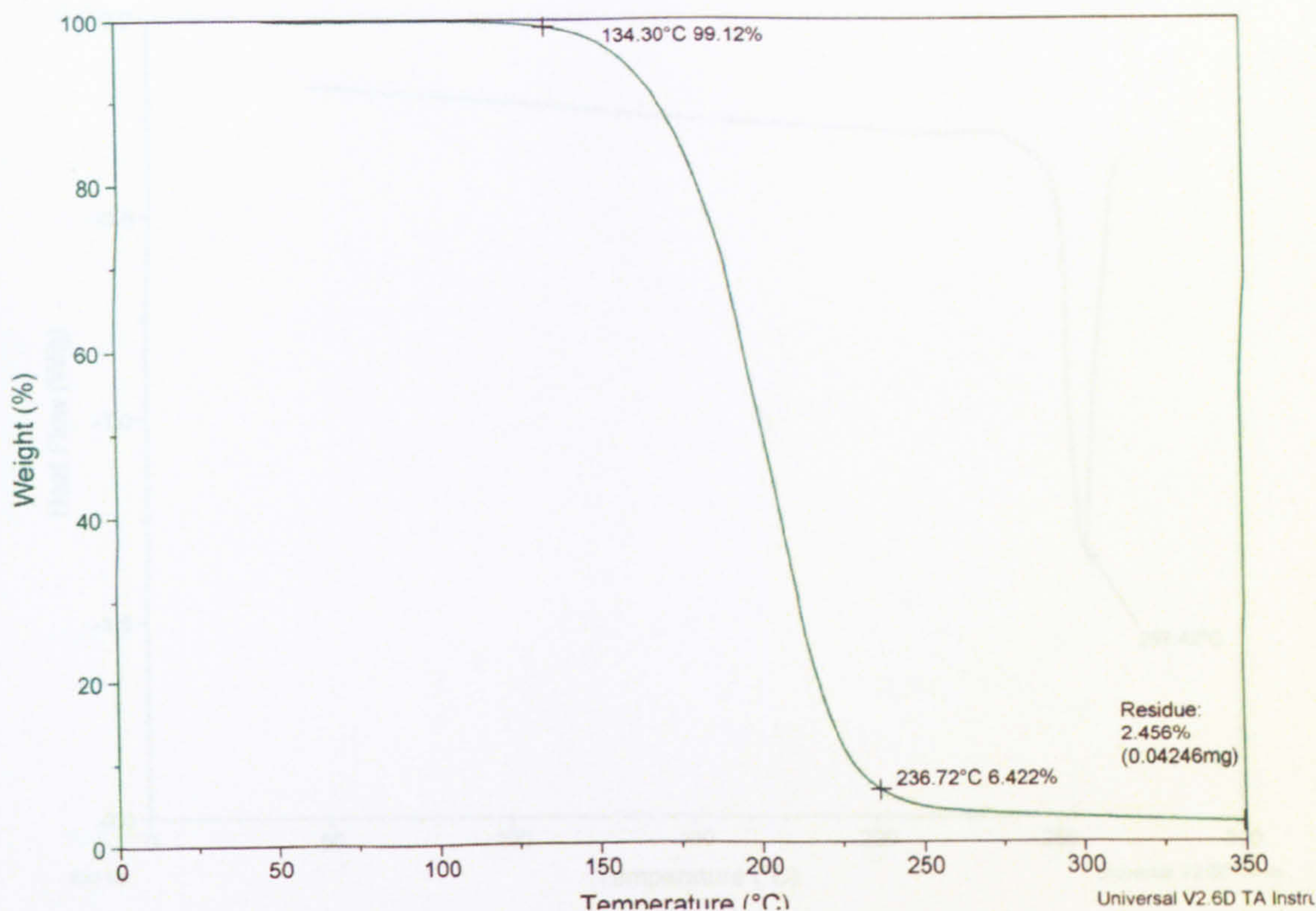


Figure 3.11.w TGA plot of a standard disperse dye

Figure 3.11.w shows that the disperse dye thermally decomposed at 134.40°C and lost the majority of its weight by 236.72°C. This decomposition was consistent with the expected sublimation of the dye. Therefore, it can be concluded that the pigment did not resemble a disperse dye in terms of its thermal properties and thus in its coloration of the polyester. Therefore, there must be another reason for the pigment to penetrate the polyester fibres to such an extent. It is likely that, because the particle size of the Cab-O-Jet pigments was so small that the particles penetrated the fibre under heating. Once contained within the fibre, it was thought that the Synthappret BAP within the ink cross-linked thus forming a matrix trapping the pigment as well as the polyester fibres relaxing to allow penetration before contracting to provide further trapping of the pigment. It was thought that on reaching its T_g , the polyester relaxed its structure slightly, thus allowing small particles to penetrate. In order to ascertain the T_g of polyester fabric, DSC was undertaken on a sample of uncoloured polyester fabric. The analysis was carried out on polyester and re-heated polyester. The DSC plots obtained can be seen in Figure 3.11.x, Figure 3.11.y and Figure 3.11.z.

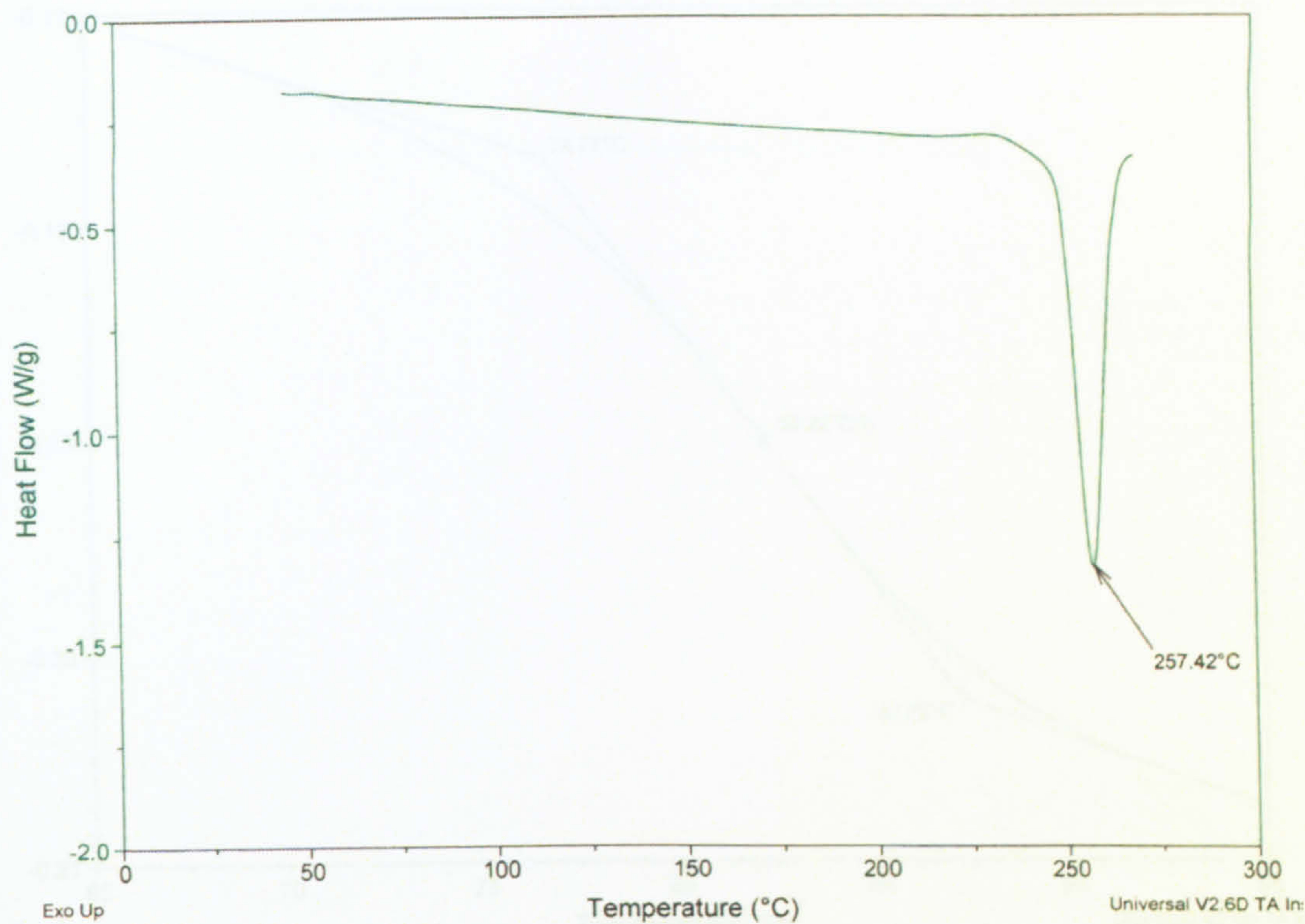


Figure 3.11.x DSC plot for polyester fibres

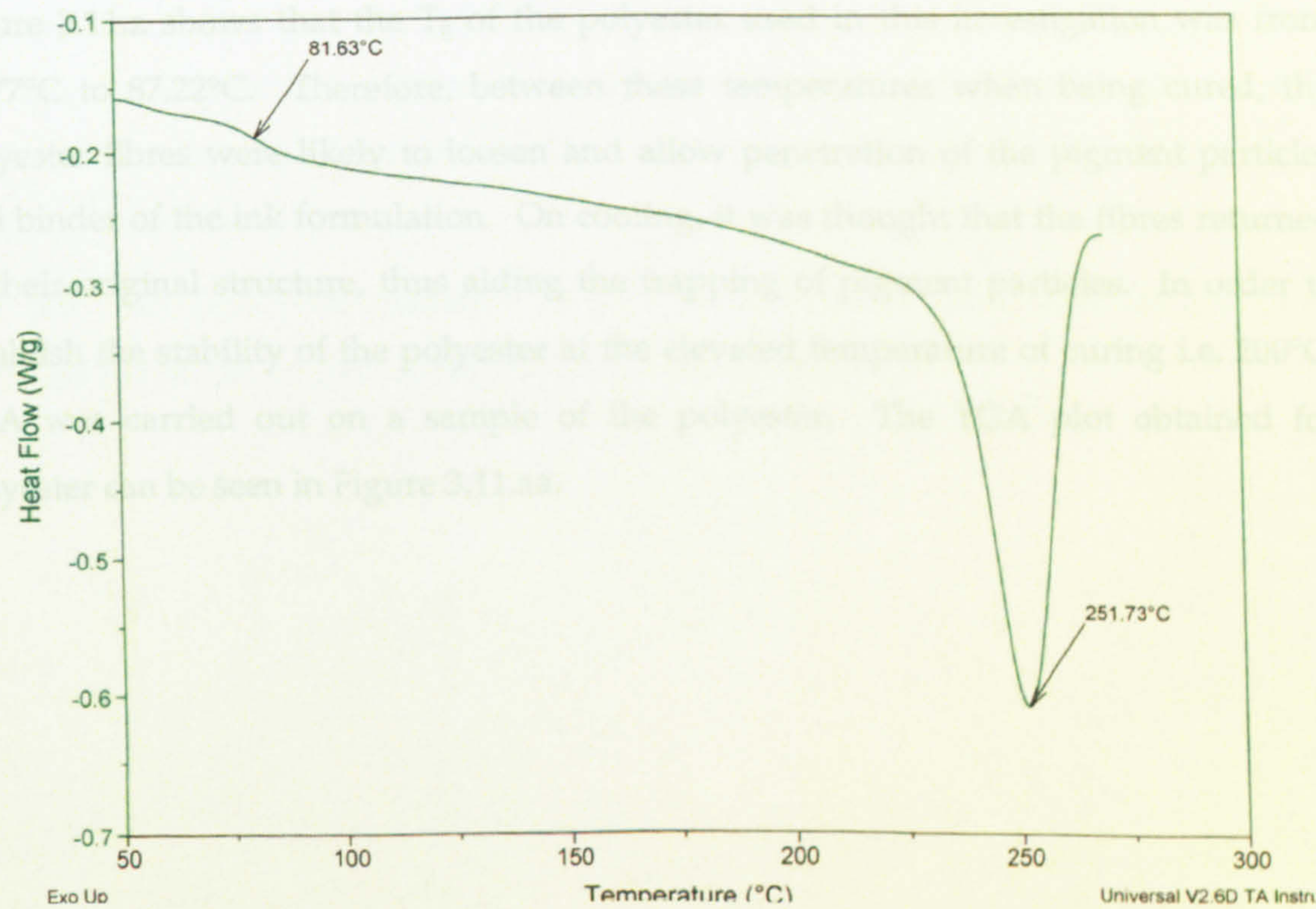


Figure 3.11.y DSC plot for re-heated polyester fibres

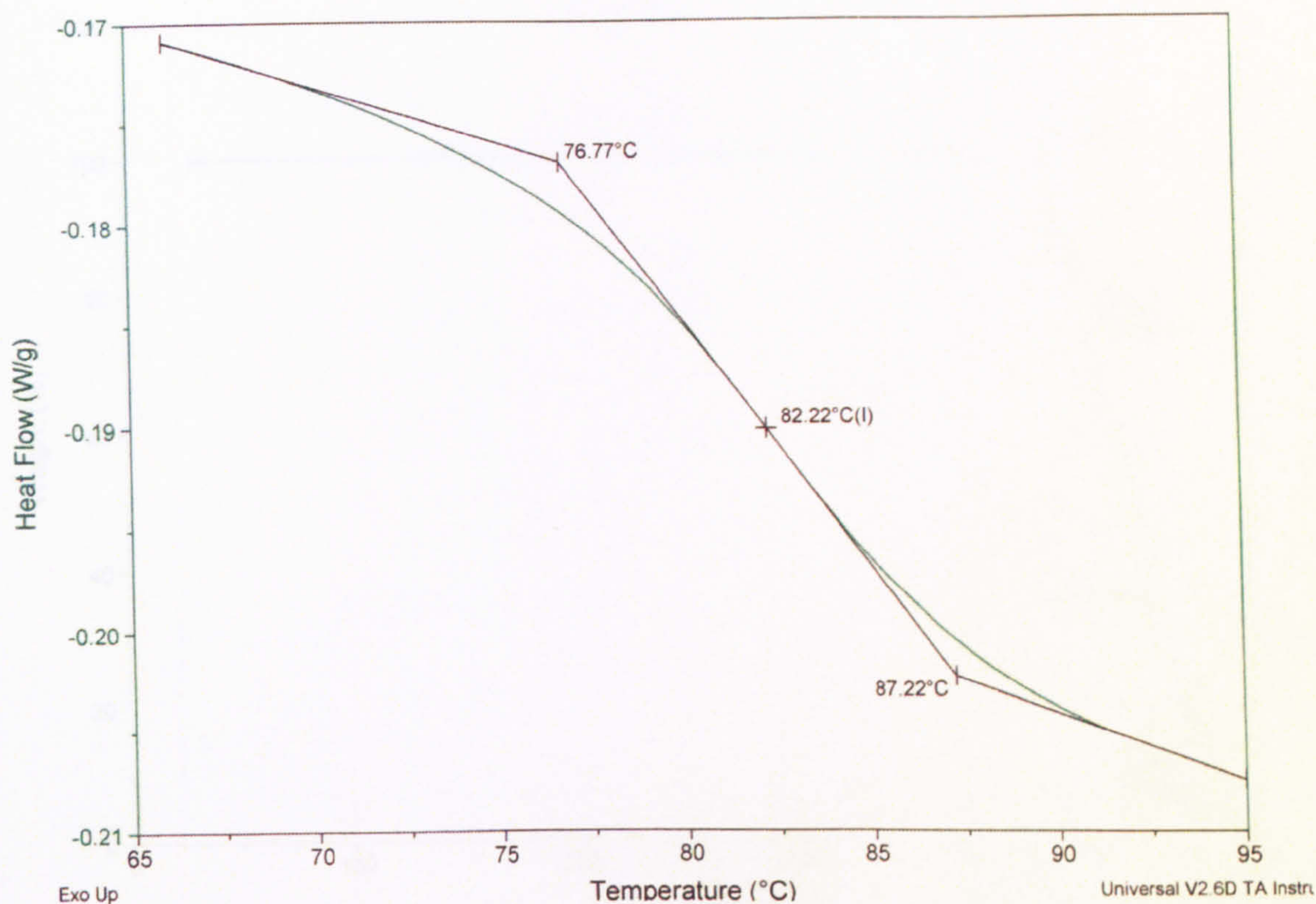


Figure 3.11.z Close up of DSC plot of reheated polyester fibres to highlight T_g

Figure 3.11.z shows that the T_g of the polyester used in this investigation was from 76.77°C to 87.22°C. Therefore, between these temperatures when being cured, the polyester fibres were likely to loosen and allow penetration of the pigment particles and binder of the ink formulation. On cooling, it was thought that the fibres returned to their original structure, thus aiding the trapping of pigment particles. In order to establish the stability of the polyester at the elevated temperature of curing i.e. 200°C, TGA was carried out on a sample of the polyester. The TGA plot obtained for polyester can be seen in Figure 3.11.aa.

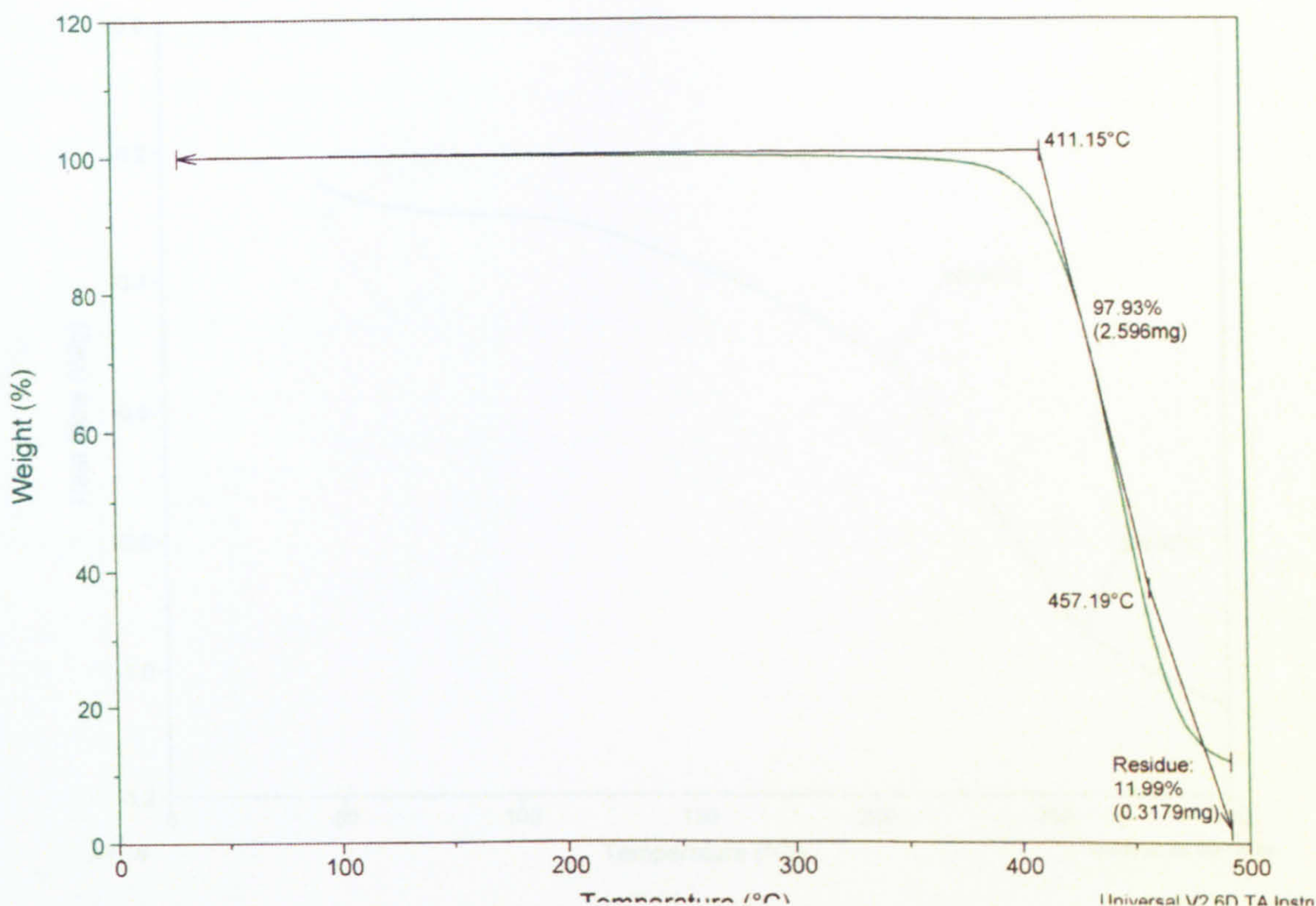


Figure 3.11.aa TGA plot of polyester fibres at the required curing temperature

It can be seen from Figure 3.11.aa that there was no weight loss from the polyester over the range of temperatures it was subjected to under curing conditions. It was only when extreme temperatures above 400°C were reached that any decomposition of the polyester was seen.

The DSC and TGA plots obtained for the Cab-O-Jet Cyan 250 C and the Cab-O-Jet Magenta 260 M can be seen in Figure 3.11.bb to Figure 3.1.ee.

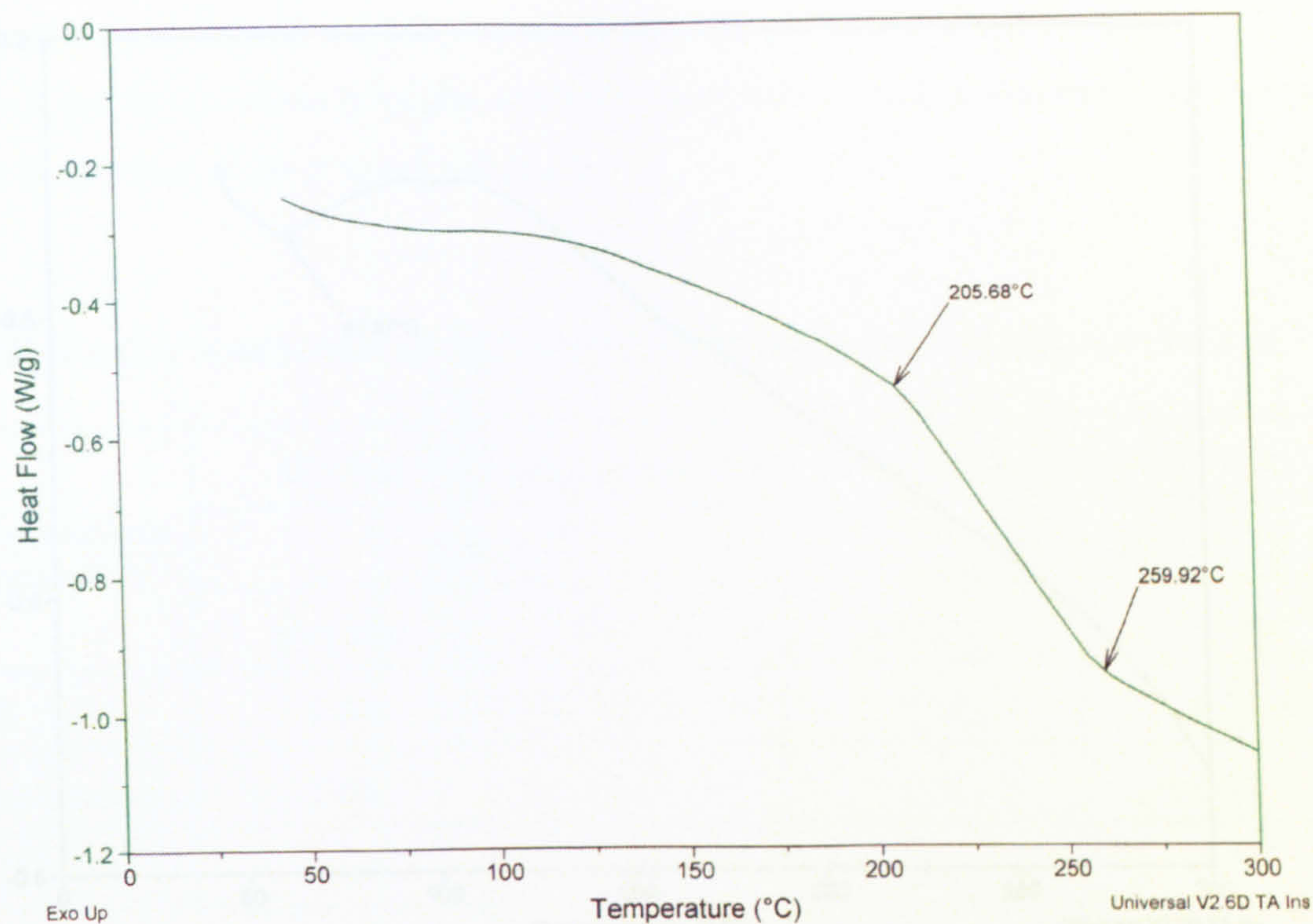


Figure 3.11.bb DSC plot of Cab-O-Jet Cyan 250 C

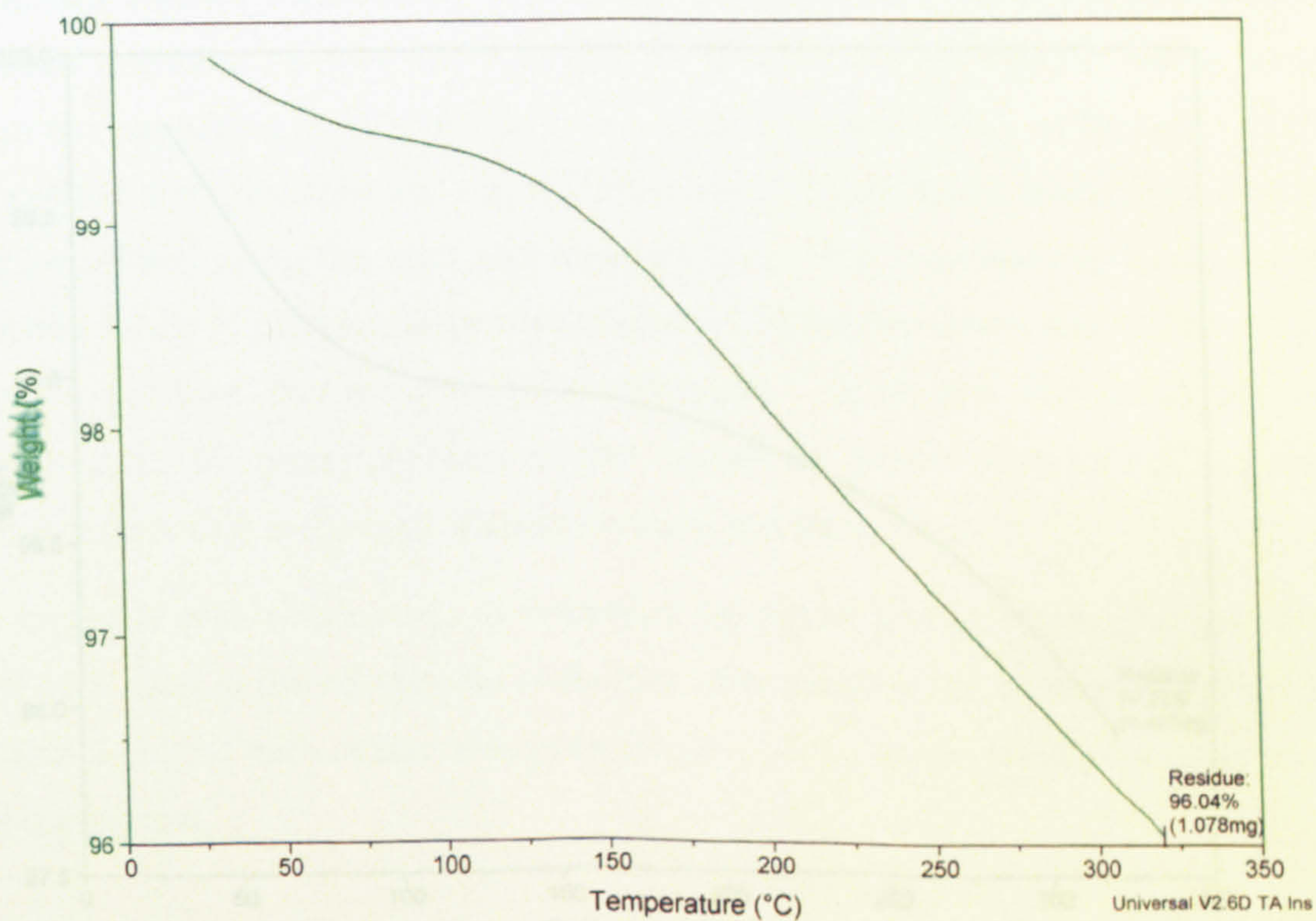


Figure 3.11.cc TGA plot of Cab-O-Jet Cyan 250 C

Rubbing Cycles	Weight (%)
0	~99.8
20	~99.4
40	~99.1
60	~98.9
80	~98.6
100	97.93

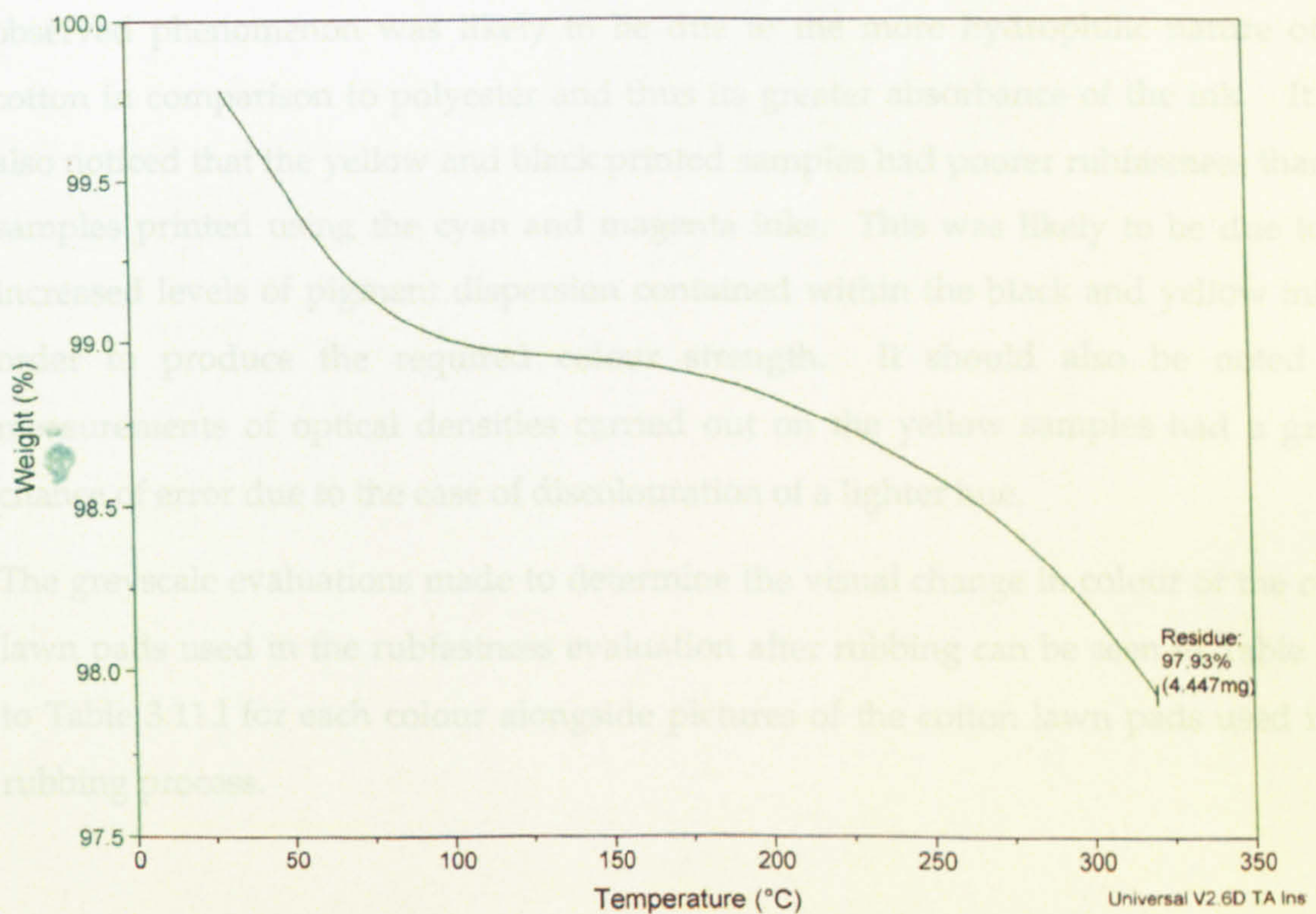


Figure 3.11.ee TGA plot of Cab-O-Jet Magenta 260 M

The results obtained for the rub resistance of the prints can be seen in Table 3.11.h in terms of the optical density of the area of the cotton lawn pad that had been rubbed across the surface of the printed substrate.

Table 3.11.h Assessment of rubfastness of printed cotton and polyester fabrics

Pigmented ink formulation	Optical density of cotton lawn rubbing fabric after rub test			
	Cotton		Polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
FCS Yellow	0.09	0.25	0.15	0.32
FCS Magenta	0.08	0.12	0.11	0.13
FCS Cyan	0.09	0.14	0.12	0.16
FCS Black	0.13	0.36	0.24	0.38

It can be seen from Table 3.11.h that from the optical densities measured, the printed cotton had a better rubfastness than the printed polyester. It was thought that this observed phenomenon was likely to be due to the more hydrophilic nature of the cotton in comparison to polyester and thus its greater absorbance of the ink. It was also noticed that the yellow and black printed samples had poorer rubfastness than the samples printed using the cyan and magenta inks. This was likely to be due to the increased levels of pigment dispersion contained within the black and yellow inks in order to produce the required colour strength. It should also be noted that measurements of optical densities carried out on the yellow samples had a greater chance of error due to the ease of discolouration of a lighter hue.

The greyscale evaluations made to determine the visual change in colour of the cotton lawn pads used in the rubfastness evaluation after rubbing can be seen in Table 3.11.i to Table 3.11.l for each colour alongside pictures of the cotton lawn pads used in the rubbing process.

Table 3.11.i Visual assessment of the rubfastness of cotton and polyester fabrics printed with FCS Yellow




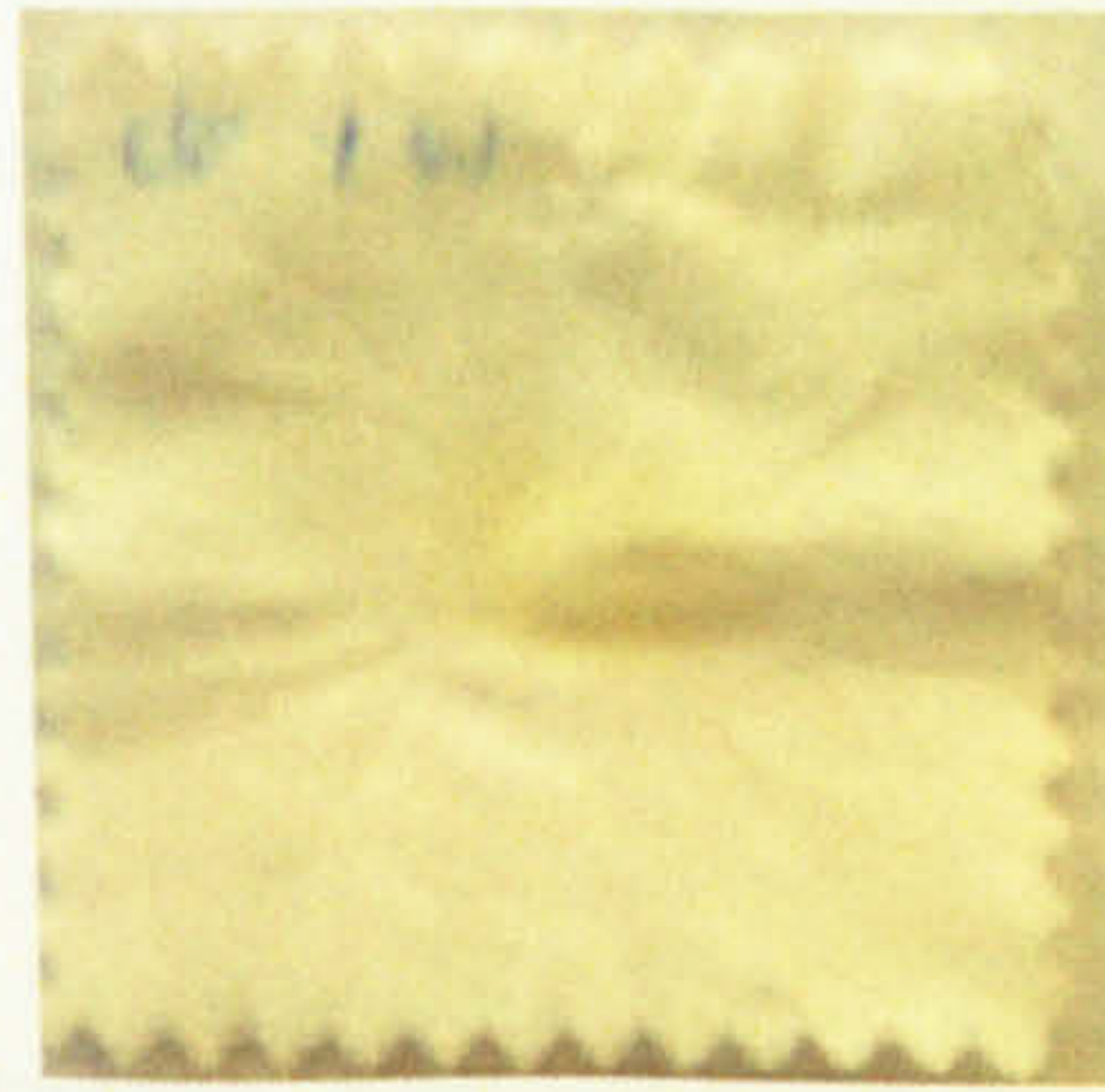
	Substrate printed and rubbed	
	Cotton	Polyester
Dry rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	4	3
Wet rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	3/4	3

Table 3.11.j Visual assessment of the rubfastness of cotton and polyester fabrics printed with FCS Magenta



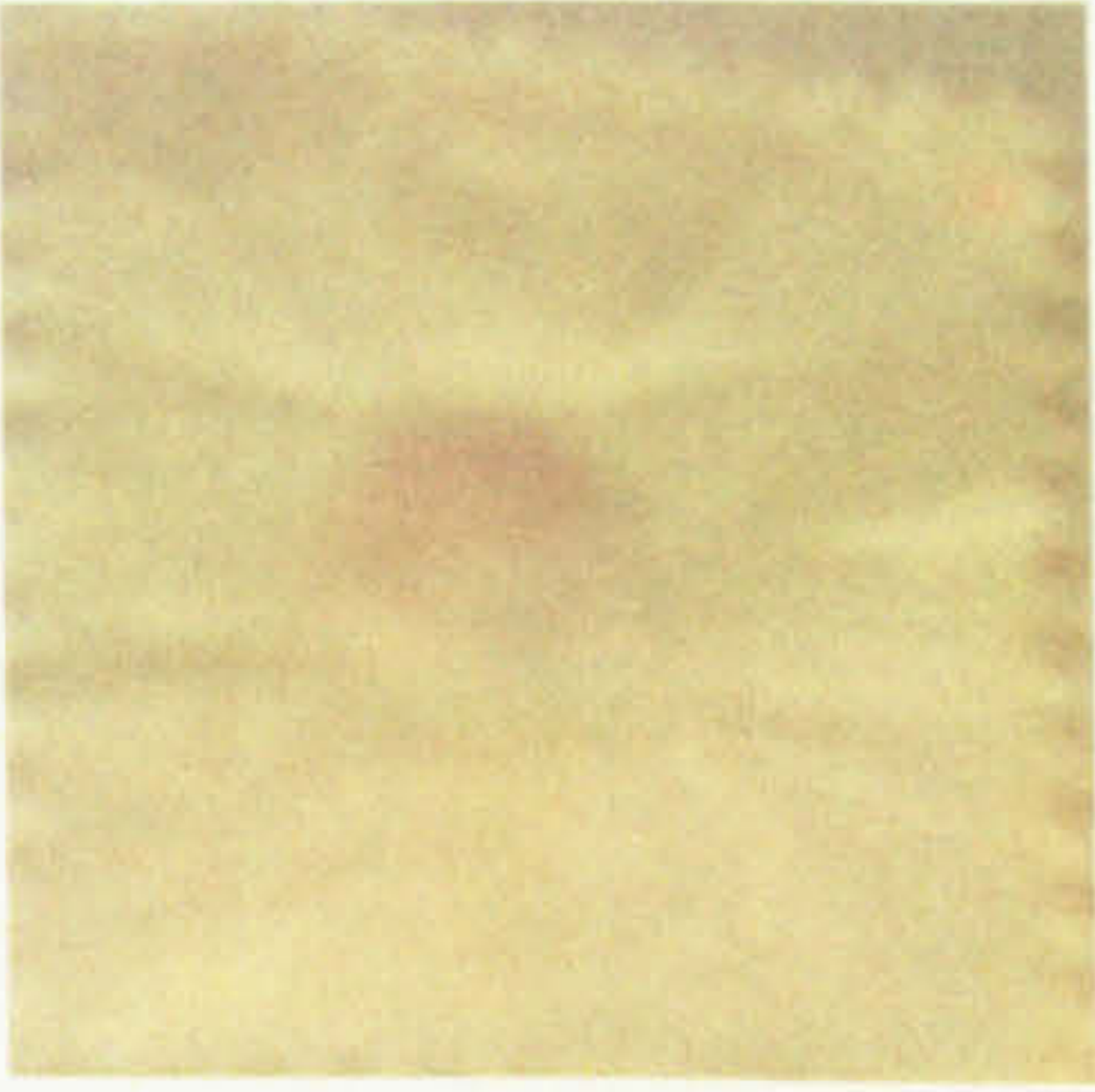





	Substrate printed and rubbed	
	Cotton	Polyester
Dry rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	4/5	4
Wet rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	4	4





Table 3.11.k Visual assessment of the rubfastness of cotton and polyester fabrics printed with FCS Cyan

	Substrate printed and rubbed	
	Cotton	Polyester
Dry rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	4	4
Wet rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	4	3/4

It can be seen from Table 3.11.i to Table 3.11.j that the results obtained for the visual assessments of the cotton lawn pads after rubbing correlated with the results obtained for the colour density measurements. Thus, good rubfastness results were obtained for the cyan and magenta-based inks, whilst slightly poorer rubfastness results were achieved for the black and yellow inks. However, in each case, the rubfastness results were seen to be within acceptable limits for industrial standards.

The SEM's of unwashed polyester prints showed some evidence of particles on the surface of the fibres. It was thought that these might be pigment particles and this contributed to the fact that the rub results for the printed polyester were poorer than that for printed cotton. In order to establish whether these particles were

Table 3.11.1 Visual assessment of the rubfastness of cotton and polyester fabrics printed with FCS Black

	Substrate printed and rubbed	
	Cotton	Polyester
Dry rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	4	3
Wet rub		
Assessment of colour difference of cotton lawn pads before and after rubbing	3	3

It can be seen from Table 3.11.i to Table 3.11.l that the results obtained for the visual assessments of the cotton lawn pads after rubbing concurred with the results obtained for the colour density measurements. Thus, good rubfastness results were obtained for the cyan and magenta based inks, whilst slightly poorer rubfastness results were achieved for the black and yellow inks. However, in each case the rubfastness results were seen to be within acceptable limits for industrial standards.

The SEM's of unwashed polyester prints showed some evidence of particles on the surface of the fibres. It was thought that these fibres may be pigment particles and thus contribute to the fact that the rub resistance of the printed polyester was poorer than that for printed cotton. In order to ascertain whether these particles were

pigment, EDX was carried out on the polyester printed with the ink containing Cab-O-Jet Cyan 250 C. EDX was used to analyse the particles on the surface of the polyester for the presence of copper from the copper phthalocyanine pigment present within the ink formulation. The plot obtained can be seen in Figure 3.11.ff.

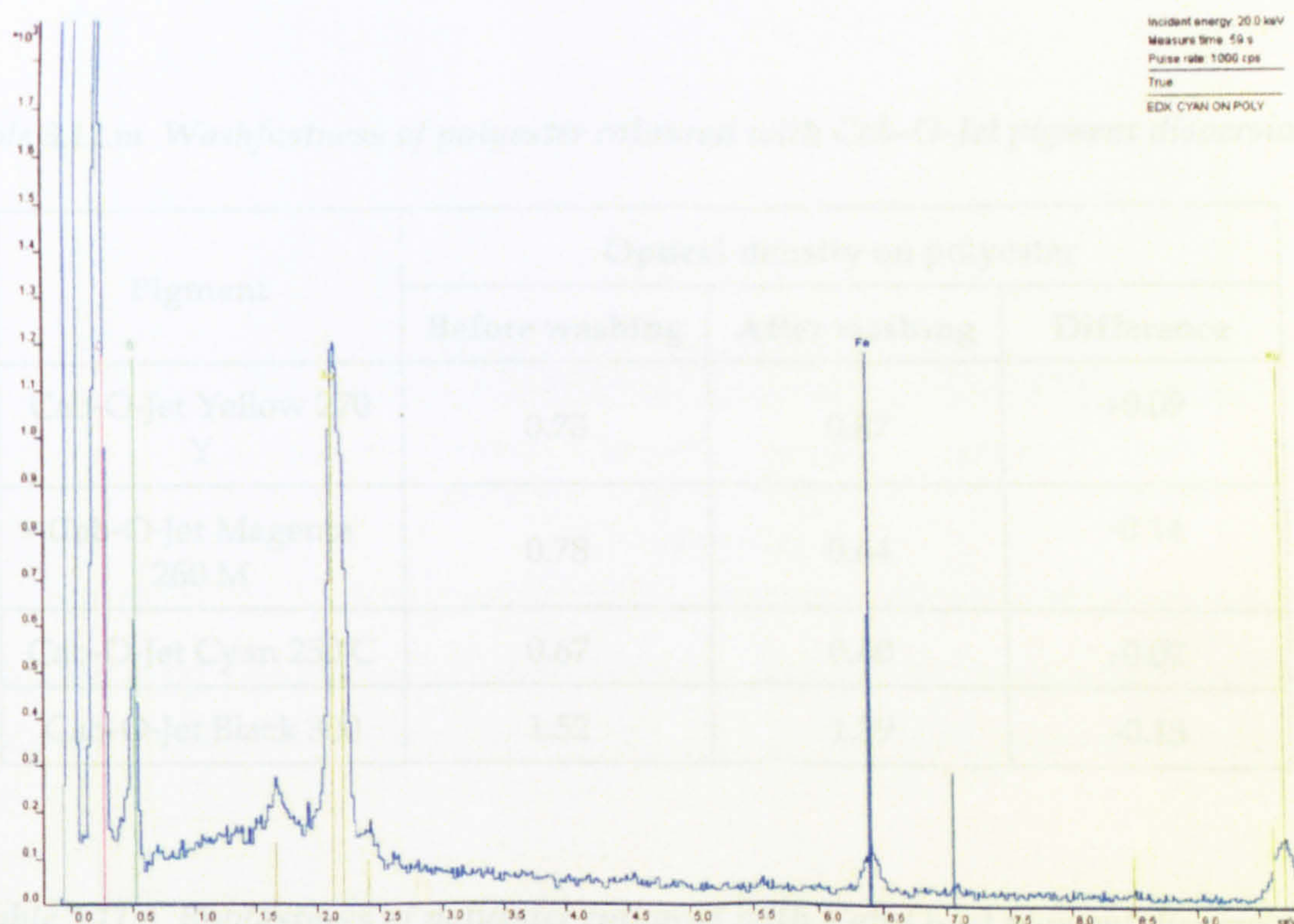


Figure 3.11.ff EDX of particles on the polyester fibres printed with FCS Cyan

It can be seen from Figure 3.11.ff that no copper was found to be present in the particles seen on the surface of the polyester fibres. As such, it was very unlikely that any of the particles seen were pigments. Elements found using EDX were iron, calcium, sodium, zinc and chlorine. This would suggest the presence of metals and their salts which were likely to be found in water. This analysis also acted as confirmation of the likelihood that the Cab-O-Jet pigments contained within the ink formulations had penetrated the fibres of the polyester.

In order to prove that the Synthappret BAP was assisting in the pigment trapping and thus acting to increase the wash and rub resistance of the print, it was decided to test the effect of colouring polyester with simply pigment dispersion. Thus, Cab-O-Jet

pigment dispersions were applied to polyester and then dried under the same conditions as the inks, i.e. at 200°C for 2 minutes using a Werner Mathis KTF 4099 curing oven. Once subjected to these conditions, the coloured samples were assessed for their washfastness and rubfastness according to the methods outlined in Section 2.3.10 and Section 2.3.11. The results obtained can be seen in Table 3.11.m and Table 3.11.n.

Table 3.11.m Washfastness of polyester coloured with Cab-O-Jet pigment dispersions

Pigment	Optical density on polyester		
	Before washing	After washing	Difference
Cab-O-Jet Yellow 270 Y	0.78	0.87	+0.09
Cab-O-Jet Magenta 260 M	0.78	0.64	-0.14
Cab-O-Jet Cyan 250 C	0.67	0.60	-0.07
Cab-O-Jet Black 300	1.52	1.39	-0.13

Table 3.11.n Rubfastness of polyester coloured with Cab-O-Jet pigment dispersions

Pigment	Optical density of cotton lawn rubbing fabric after rub test	
	Dry rub	Wet rub
Cab-O-Jet Yellow 270 Y	0.50	0.28
Cab-O-Jet Magenta 260 M	0.42	0.30
Cab-O-Jet Cyan 250 C	0.46	0.60
Cab-O-Jet Black 300	0.56	0.71

It can be seen from Table 3.11.m and Table 3.11.n that the wash and rub resistance of the pigments were significantly poorer than when Synthappret BAP was applied in conjunction with the pigment (Table 3.11.b and Table 3.11.c). It is therefore likely that the mechanical trapping of the pigment by the polyester fibres alone will not provide the required fastness properties for a textile print. As such, it can be said that the

presence of Synthappret BAP within the ink formulation provided a significant effect on the wash and rub resistance properties of the printed substrate. A comparison in the difference seen in the optical density of the coloured samples after being washed can be seen in Figure 3.11.gg.

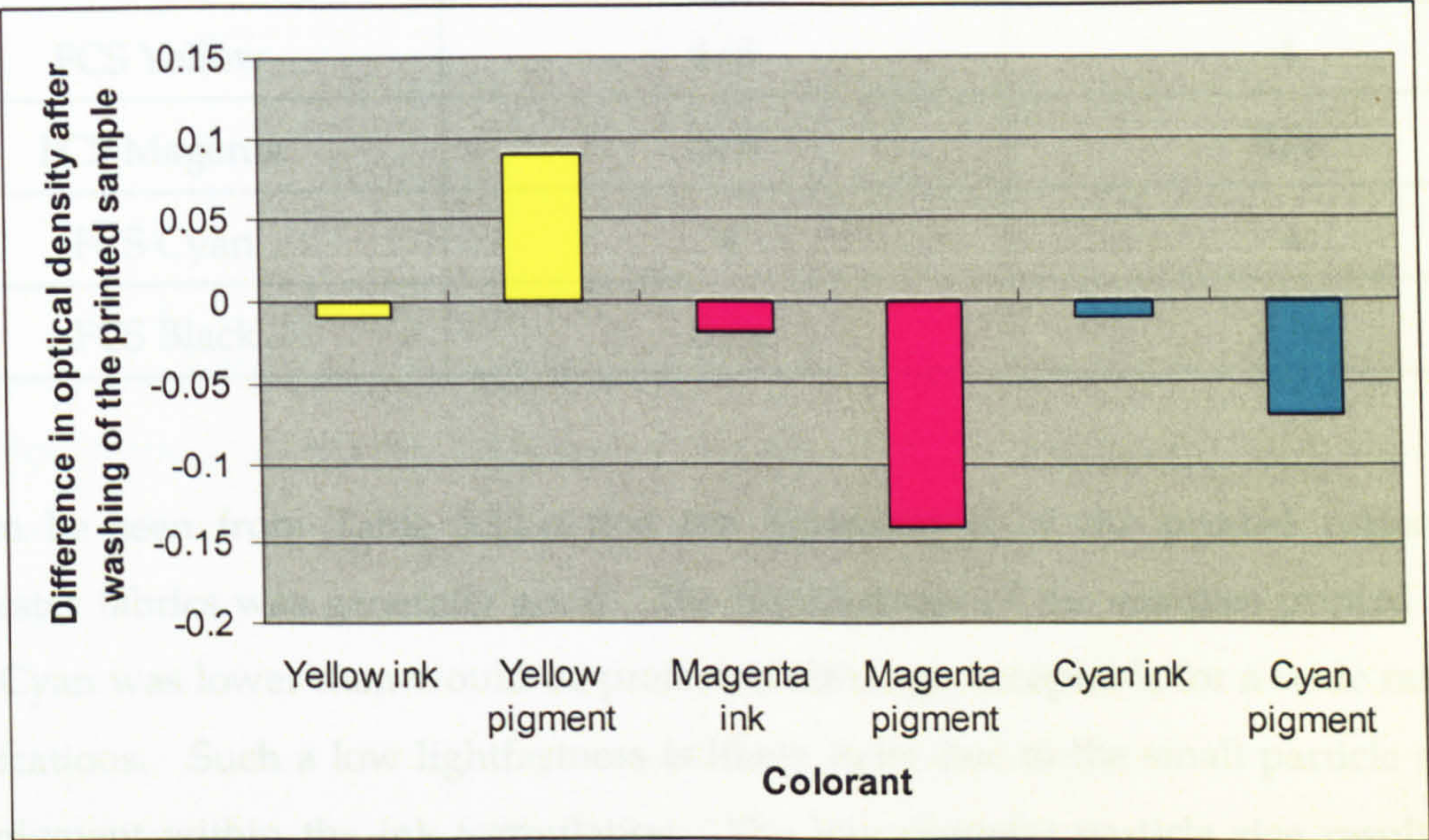


Figure 3.11.gg Comparison of colour difference observed on washfastness tests on polyester fabric coloured with the FCS inks and the Cab-O-Jet pigment dispersions

It can be seen from Figure 3.11.gg that the change in optical density of the coloured substrate after the washing process was significantly greater in the substrate coloured purely with the pigment dispersion. It should also be noted that a far greater amount of coloured material was applied in the case of the pigment dispersion and as such any change in the optical density would be less apparent. It was noticed that, the substrate coloured purely with yellow pigment, increased in optical density after washing. This may be attributed to the fact that the washing process may have disrupted the fibres of the polyester, thus, releasing some of the colour that had penetrated the fibres. As such this data confirms the fact that in order to achieve the required washfastness of printed polyester fabric, it was necessary to include Synthappret BAP within the ink formulation.

3.11.1 Assessments made on the Lightfastness of FCS Inks

The results obtained from the evaluation of the lightfastness of the printed substrates can be seen in Table 3.11.o.

Table 3.11.o Assessment of the lightfastness of the printed substrates

Ink formulation	Assessment of the lightfastness of the printed substrate according to the blue wool scale	
	Cotton	Polyester
FCS Yellow	4/5	4
FCS Magenta	5/6	5/6
FCS Cyan	4	4
FCS Black	5/6	5/6

It can be seen from Table 3.11.o that the lightfastness of the printed cotton and polyester fabrics was generally good. The lightfastness of the samples printed using FCS Cyan was lower than would be preferred although acceptable for a wide range of applications. Such a low lightfastness is likely to be due to the small particle size of the pigment within the ink formulation. The low pigment particle size results in a smaller surface area of each particle and as such may cause a more rapid dissipation of energy, supplied by photofading agents through the pigment, thus causing a more rapid breakdown of the particles. The presence of diazonium ions on the surface of the pigment may also have acted to lower the lightfastness. Such groups may have acted to interrupt the crystalline structure of the pigment and as such allow for easier breakdown of the pigment particles on exposure to photofading agents. However, it should be noted that for applications where a moderate to high lightfastness is required the inks formulated acted in accordance with the required specifications. Therefore, whilst not suitable for applications such as billboards, the formulated inks would be ideal for applications such as indoor furnishings, T-shirts and bed sheets where a high lightfastness is not required.

3.11.2 Assessments made on the Thermal Stability of FCS Inks

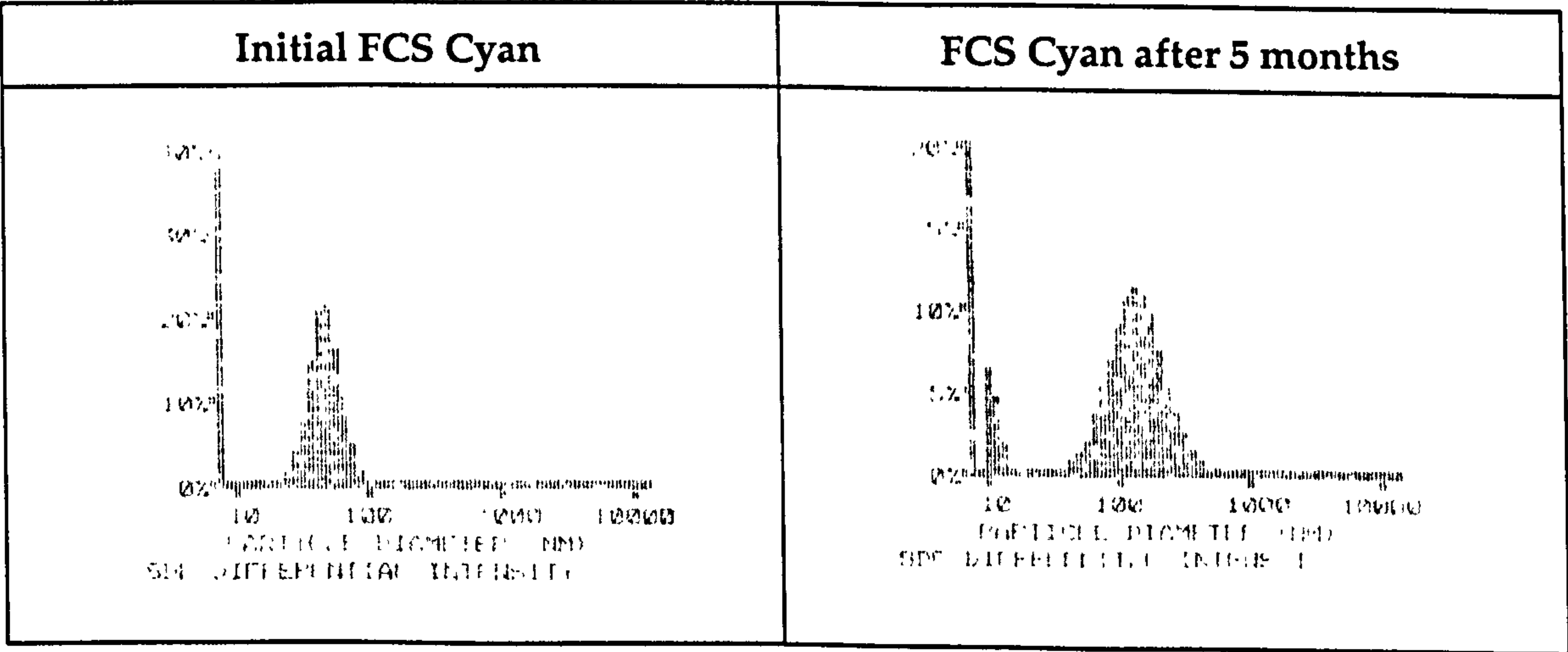
The results obtained from thermal stability tests are detailed in this section. The tests were carried out on FCS Cyan. The results of any change in particle size of the pigment within FCS Cyan stored at 40°C for 5 months can be seen in Table 3.11.p.

Table 3.11.p Effect of storage of FCS Cyan at elevated temperatures on the particle size of the pigment

Time kept at 40°C	Particle Size 95% limit (nm)
1 day	90.5
4 weeks	92
5 months	80.6

It can be seen from Table 3.11.p that storing at a high temperature did not have any significant effect on the particle size of the pigment. The sample left for 5 months showed a reduction in the average particle size when compared to the original ink. This was likely to be due to a small amount of agglomeration and settling of larger particles. This was backed up by the fact that the distribution curve was broader for the sample kept for 5 months. A comparison of the distribution curves obtained for these three samples can be seen in Table 3.11.q.

Table 3.11.q Comparison of particle size distributions of FCS Cyan after a settling period of 5 months at 40 °C



The effect of the holding of FCS Cyan at 40°C on its viscosity can be seen in Table 3.11.r.

Table 3.11.r Effect of storage of FCS Cyan at elevated temperatures on viscosity

Time kept at 40°C	Viscosity (mPas) at 60 rpm and 25°C
1 day	3.65
4 weeks	3.60
5 months	3.62

It can be seen from Table 3.11.r that storing the inks at a temperature of 40°C over a period of 5 months did not have a significant effect on the viscosity of the ink. This would suggest that the formulation was stable over this period of time. It is likely that, if any degree of settlement of the pigment particles within the ink formulation had occurred, that the viscosity would have increased slightly. Any agglomerates or large particles would have acted to resist the flow of the liquid ink to a greater extent to smaller primary particles. Such an effect on the viscosity of the ink is shown in Figure 3.11.hh.

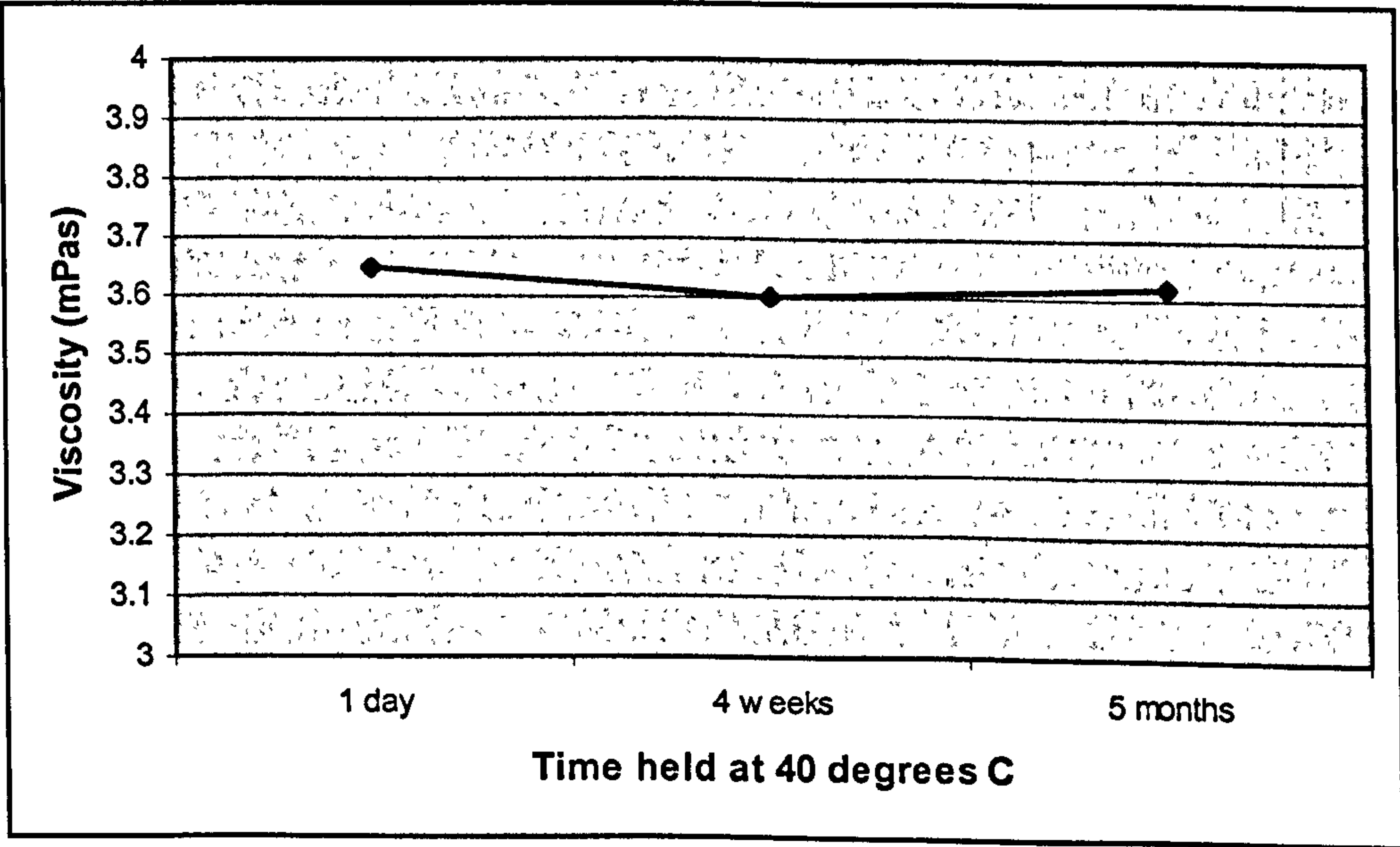


Figure 3.11.hh Graph showing the change in viscosity of FCS Cyan held at an elevated temperature

The effect of the application of a temperature of 40°C over a period of 5 months on the

surface tension of the ink formulation can be seen in Table 3.11.s.

Table 3.11.s Effect of storage of FCS Cyan at elevated temperatures on surface tension

Time kept at 40°C	Surface tension (mNm ⁻¹)
1 day	36.56
4 weeks	37
5 months	36.5

It can be seen from Table 3.11.s that there was no real effect on the surface tension of the ink when stored at a temperature of 40°C over a period of 5 months. This was expected as the samples were held in sealed containers and as such no solvent or humectants could evaporate from the ink. As such components provide the main contribution to the surface tension of the ink, no change would be seen at this temperature.

It should also be noted that as well as the pigment being stable within the ink, the Synthappret BAP was also stable under the conditions applied. This would suggest that the Synthappret BAP was unaffected by extended periods of time at an elevated temperature. However, it should be noted that higher temperatures might cause some cross-linking of the Synthappret BAP.

4 Conclusions

During this investigation, a novel binder system for incorporation within a printing ink for the printing of textile materials was identified. Such a binder was unique in its application for such a use, as it had previously only been used as a shrink resist treatment for wool. The novelty of the binder lay in it being both self cross-linkable and water soluble. Traditionally screen printing inks contain polyester resins, epoxy resins or polyurethanes as their print binder. Such products are limited due to their poor stability in water based systems and in their need for a second component within the ink to promote cross-linking. Once cross-linked onto a textile substrate it is usual for such binders to create a stiff handle to the fabric due to the hard polymer films produced. The novel binder used in this investigation, Synthappret BAP, provided printed fabrics with an extremely soft handle that was barely perceptible when compared to a control sample of fabric. Another significant advantage in the use of Synthappret BAP was in its water solubility. Such solubility allowed for excellent stability within an aqueous ink. Binders such as polyurethanes are extremely unstable in water and often need the presence of blocking agents to prevent reaction with water. Such blocking agent may be removed upon curing. Other binders, such as polyester resins and epoxy resins, for water based inks, are usually supplied as emulsions or dispersions within water. Such emulsions or dispersions are often unstable and sensitive to other components of the ink. A further component within a potential ink is also required when considering traditional binders in the cross-linking agent which is often a necessity. Emulsions and dispersions therefore often cause stability problems within low viscosity ink jet inks.

The following section details the conclusions which may be drawn from the results obtained throughout the investigation into the development of inks for printing onto textile materials, via screen printing and ink jet printing formulations.

4.1 Screen Printing Inks for Application to Textile Materials

This section summarises the findings of the investigation into the use of Synthappret BAP as a binder within a screen ink for printing onto textiles.

- A screen ink incorporating Synthappret BAP printed successfully onto cotton via a flatbed screen printing process.
- An initial printing ink containing 15% Synthappret BAP was cured at 120°C for

2 minutes to produce a printed substrate with the required fastness properties.

- A cure temperature of 200°C and a cure time of 2 minutes were required to cure an ink containing 15% Synthappret BAP printed onto cotton fabric, in order to attain a print with the required fastness properties.
- Incorporation of ethanol within the screen ink formulation in an attempt to increasing drying rate did not reduce the required cure time.
- Incorporation of sodium hydroxide (1M) within the ink formulation to give a pH of 11 had a detrimental effect on print quality. Such an effect was likely to be due to possible cross-linking of the Synthappret BAP at ambient temperatures.
- Reduction in the film thickness of ink applied by means of reducing the thickener concentration and thus the viscosity of the ink formulation did not have a significant effect on cure time and had a negative effect on print quality.
- An increase in the concentration of Synthappret BAP to 30% within the ink formulation caused a reduction in the cure time to 60 s whilst maintaining the required fastness properties.
- Increasing the Synthappret BAP concentration to 50% reduced the required cure time to 30 s.
- For a 50% concentration of Synthappret BAP, incorporation of sodium bicarbonate to give a pH of 8, immediately prior to printing the substrate, resulted in the reduction in the cure time to 20 s.

The investigation into the use of Synthappret BAP as a binder within a screen ink formulation was successful. It was found that an optimised formulation printed well and gave a cotton substrate with excellent washfastness and rubfastness whilst maintaining a soft fabric handle, after curing at 200°C for 20 s. Morphological evaluation of printed cotton showed strong evidence for the presence of binder and pigment on the surface fibres before and after application of a washfastness test. The results obtained showed a consistency in line with the expectations of such inks within the printing industry.

4.2 Ink Jet Printing Inks for Application onto Textile Materials

This section details the conclusions obtained from the investigation into the suitability of Synthappret BAP as a binder system within an ink jet printing process.

4.2.1 Efficiency of Synthappret BAP as a Shrink Resist Treatment for Wool via Ink Jet Printing

- An ink formulation without colorant, containing 25% Synthappret BAP, was ink jet printed successfully onto wool.
- A small sculpting effect was observed when the printed wool was subjected to shrinkage treatment.
- An ink formulation containing 30% Synthappret BAP also ink jet printed successfully onto wool.
 - On printing two layers of such an ink onto wool a significant sculpting effect was observed upon application of the shrinkage treatment.
 - Morphological evaluation of the printed wool indicated that in the areas where Synthappret BAP had been printed, the wool fibres appeared smooth. Such observations indicated the likelihood of the wool fibres being coated by the applied Synthappret BAP.
- An ink incorporating 5% of a pigment dispersion containing 11% solids and 30% Synthappret BAP was successfully ink jet printed.
- On application of a shrinkage treatment, a sculpted effect was observed on the wool. The pigment applied in conjunction with the Synthappret BAP was found to remain on the fibres after application of the shrinkage treatment, thus suggesting that the Synthappret BAP had acted to trap and bind the pigment to the wool fibres.

The results obtained showed that an ink containing Synthappret BAP could be successfully printed using thermal ink jet technology. The retention of colour after application of a shrinkage treatment indicated that Synthappret BAP could be used as a binder system within an ink used for printing onto textile materials. Such a conclusion can be drawn due to the fact that the shrinkage treatment involved a heavy milling of the fabric in hot water and soap concentrate.

4.3 Investigation into the Crosslinking Mechanism of Synthappret BAP

- From the results of FTIR analysis carried out on cured and uncured Synthappret BAP, it was concluded that the cross-linking mechanism of Synthappret BAP involved a shift in position of the C=O absorption peak from 1645.4 cm^{-1} to 1714.4 cm^{-1} within the spectra. Such a shift was associated with a change in nature of the C=O group from a primary amide to a ketone. An extra peak absorbing at 1243.9 cm^{-1} within the cured Synthappret BAP was also observed. Such a peak corresponded to a S=O stretch in SO_3H , a known bi-product of the cross-linking reaction.
- Investigation into cure times indicated that for cross-linking to occur in a short period of time, a cure temperature of 200°C was required.

Investigation into the cross-linking mechanism of Synthappret BAP showed that application of an elevated temperature (200°C) induced cross-linking without the presence of an alkali component.

4.4 Pigmented Ink Jet Inks for Printing Textile Materials

The conclusions drawn from the results of the incorporation of Synthappret BAP within a pigmented ink jet ink for printing onto textile materials are described in this section.

4.4.1 Ink Jet Inks containing Toner Pigments

- Ink formulations containing Toner pigments and Synthappret BAP had the physical properties (viscosity, surface tension and particle size) required for application via ink jet printing.
- Ink formulations containing Toner pigments and Synthappret BAP printed successfully using a desktop ink jet printer in initial trials.
- Printed cotton and printed polyester substrates had excellent washfastness and acceptable rubfastness.
- Ink formulations containing Toner pigments were successfully prepared via either a two step process involving a pigment concentrate or via a one step process.
- After a period of time, Toner pigment was found to form aggregates in the ink and settle out from the bulk medium. Such pigment settling may cause problems in terms of blocking of print-head nozzles over a period of time. The

phenomenon of pigment settling also lead to an increase in viscosity and an increase in average particle size of the pigment in the formulation.

- Incorporation of a slip additive (Lubrisil CR 200) in the ink formulations was found to slightly improve the rubfastness of the resulting printed cotton and printed polyester fabrics. However, some separation of the silicone based emulsion was observed.

Inks containing Toner pigments were successfully ink jet printed onto cotton and polyester resulting in prints of satisfactory fastness properties. Pigment settling caused a problem in terms of the long term stability of the ink formulations. However, due to the successful printing on two very different textiles, it is likely that an ink with such fastness properties would find applications in the textile printing market. The stability issues may mean that such ink formulations are restricted to applications where a large volume of material is printed and as such requires frequent replenishment of the ink supply. Alternatively further optimisation of the formulation may be carried out in order to improve the stability of the system. Such optimisation may include a detailed investigation into further dispersants and additives, use of alternative toner grade pigments and humectants.

4.5 Ink Jet Inks containing Microlith™ Pigments

- Ink formulations containing Microlith pigments and Synthappret BAP had suitable physical properties (viscosity, surface tension and particle size distributions) for application via ink jet printing.
- Morphological studies showed that the Microlith pigments became highly dispersed in alkali conditions. Such findings were confirmed by results obtained for the particle size characterisation of the pigment within the ink formulation.
- Ink formulations containing Microlith pigments ink jet printed successfully onto cotton fabric via a desktop ink jet printer during initial studies.
- Cotton samples printed with inks containing Microlith pigments and Synthappret BAP were found to have excellent fastness properties.
- Morphological studies of cotton fabric printed with ink containing Microlith pigment showed no evidence of the presence of pigment particles on the surface of the cotton fibres. Such findings indicate that it is likely that the

pigment particles had been absorbed into the cotton fibres as part of the ink formulation.

- Microlith pigments dispersed equally well using sodium hydroxide at a pH of 11-12 as the alkaline component of the paste as using ammonia at the same pH.
- Morphological studies highlighted the greater friction generated by the printed substrate during wet rubfastness tests as opposed to dry rubfastness tests. Such friction gave rise to a greater destruction and flattening of the fibres of the cotton lawn pads. Such fibre destruction may allow for any pigment that had penetrated the fabric to come into contact with the rub pads and thus cause a greater removal of said pigment.
- The presence of alkali $\geq 9-10$ caused a degree of cross-linking of the Synthappret BAP at ambient temperatures. Such cross-linking led to formation of a spongy solid and as such would cause problems within a print-head.

Inks containing Microlith pigments were successfully ink jet printed onto cotton fabric giving prints of excellent fastness properties after curing. The presence of an alkali within the ink formulation caused cross-linking of the Synthappret BAP at ambient temperatures over a period of time. However, due to the successful printing of cotton fabric and the excellent fastness properties obtained, it is likely that such an ink may find applications within the textile printing market. The stability issues may mean that such ink formulations are restricted to applications in which a large volume of material is printed and as such, requires frequent replenishment of the ink supply.

4.6 Ink Jet Inks containing Cabot™ Pigments

- Ink formulations containing Cab-O-Jet pigment dispersions and Synthappret BAP achieved suitable physical properties (viscosity, surface tension and particle size) for application via ink jet printing. The mean particle size of the pigments was found to be very small, below 150 nm.
- Ink formulations containing Cab-O-Jet pigment dispersions printed successfully onto cotton fabric using a desktop ink jet printer.
- Inks containing Cab-O-Jet pigment dispersions conferred excellent washfastness and good rubfastness to printed cotton fabric.
- Pre-treatment of the cotton substrate with a 2% solution of sodium bicarbonate, an alkaline component known to aid the cross-linking reaction of Synthappret

BAP, did not improve cure speed or fastness properties.

- Incorporation of anti-slip additives within the ink formulations in order to improve the rub resistance of the printed cotton fabric did not improve the fastness significantly. As such, it was concluded that on application of such an abrasive test, some removal of colour from the substrate was inevitable at low binder concentrations (15% binder solution).
- The colour removed from the printed substrate during rubfastness testing did not have an adverse effect on the visual appearance of the printed sample as a whole.

Inks containing Cab-O-Jet pigment dispersions were found to print successfully onto cotton fabric and confer the required fastness properties. No stability issues were encountered and as such these inks would be successful for a number of applications in the textile printing industry.

4.7 The Effect of Increased Amounts of Synthappret BAP within an Ink Jet Ink

- As the concentration of Synthappret BAP within an ink formulation was increased, the viscosity of that formulation increased. The viscosity increase was nearly linear to the concentration of Synthappret BAP up to 15% Synthappret BAP. Further increase in concentration of Synthappret BAP thereafter saw a greater increase in viscosity each time.
- Increasing the concentration of Synthappret BAP within the given ink formulation did not significantly influence the surface tension of the ink.
- The pH of the ink formulation was found to decrease on increasing the concentration of Synthappret BAP due to the acidity of the Synthappret BAP. The pH became constant beyond 20% Synthappret BAP. Such a low pH did not affect the stability of the Cab-O-Jet pigment dispersion.
- The increase in concentration of Synthappret BAP within the ink formulation only affected the particle size of the pigment to a very minor extent.
- As the concentration of Synthappret BAP was increased, the washfastness of printed cotton was unaffected, however, slight improvement in the rubfastness was noted.

The investigation into the effects of the increased concentration of Synthapret BAP within an ink jet ink formulation showed that, in order to achieve the required physical properties, stability, printability and fastness properties, 15% Synthapret BAP was the optimum amount.

4.8 Suitability of Pigments for Ink Jet Printing

- Particle size analysis on the three magenta pigments showed that each was affected by a period of settling. The order of particle size was Cab-O-Jet Magenta 260M < Microlith Magenta B-WA < Toner Magenta E02.
- Freeze-thaw was seen to approximately double the particle size of each pigment with Microlith Magenta B-WA being affected the most.
- Each pigment used as part of an ink, had no effect on the surface tension of the ink.
- The viscosity was affected by particle size of the pigments and as such Cab-O-Jet Magenta 260M had the lowest viscosity. This was thought to be because of the surface modification of the Cab-O-Jet pigment providing it with some degree of solubility in terms of the attached diazinium group containing SO_3^- .
- Cab-O-Jet Magenta 260M was stable at both low, neutral and high pHs with Microlith Magenta B-WA flocculating at low pH and Toner Magenta E02 only being stable at neutral pH.
- Inks containing Cab-O-Jet Magenta 260M and Microlith Magenta B-WA gave prints of very good quality whereas ink containing Toner Magenta E02 offered very poor print quality.
- Dot quality of the prints produced using the inks was found to be far better on cotton fabric than on polyester fabric. This was likely to be due to the greater absorbency of the cotton, thus reducing the possibility of wicking of the ink along surface fibres.
- Inks containing all the pigments in the presence of Synthaprat BAP were seen to confer excellent washfastness to the printed cotton and printed polyester.
- Inks containing Cab-O-Jet Magenta 260M and Microlith Magenta B-WA in the presence of Synthaprat BAP gave good rubfastness results for printed cotton and printed polyester fabrics.

- Cab-O-Jet Magenta 260M offered a greater colour strength than Microlith Magenta B-WA and Toner Magenta E02.

It was apparent that stable pigment based inks for ink jet printing of textiles could be formulated. This study suggested that of the three pigment types investigated, Cab-O-Jet Magenta 260M was most suitable for application to textiles via ink jet printing due to its smaller particle size, lower intrinsic viscosity, greater stability to freeze-thaw cycles and greater stability to changes in pH. Whilst Toner Magenta E02 and Microlith Magenta B-WA could also be useful for ink jet applications, their relatively lower stabilities may give rise to problems such as nozzle blocking. In addition, Cab-O-Jet Magenta 260M was found to offer the best colour strength, when applied in equal concentrations of pigment solids, and excellent printability. This again was likely to be due to the small average particle size offered by the Cab-O-Jet pigment dispersions.

4.9 pH Stability of Synthappret BAP

- Investigation into pH stability of Synthappret BAP highlighted that at high pH values cross-linking of Synthappret BAP occurred at ambient temperatures over a period of time. A spongy solid was formed trapping the pigment and separating out from the bulk solvent.
- More vigorous mixing of the ink during formulation led to a greater instability of the Synthappret BAP at high pH values i.e. >9.

It can be concluded that for an ink containing Synthappret BAP to be stable over an extended period of time, the pH of the system may be slightly alkaline but must not exceed 8.5; ideally, a neutral pH would be preferred.

4.10 Comparison of Cabot Ink Formulations to an Alternative Commercially Available Set of Inks

- Commercially available Irgaphor pigmented ink jet inks were found to have a larger mean particle size than inks formulated using Cab-O-Jet pigment dispersions.
- Irgaphor inks did not successfully ink jet print using a desktop ink jet printer.
- Fastness properties offered by inks containing Cab-O-Jet pigment dispersions were found to be comparable to those offered by the Irgaphor inks whilst conferring a softer handle to the printed substrate.

It can be concluded that the inks formulated using the Cab-O-Jet pigment dispersions were comparable in all respects with the commercially available Irgaphor ink jet inks. Ideally comparisons would have been made with printed samples and with other commercially available inks. However this was not possible due to the sensitivity of the companies involved as many of their products were in their infancy.

4.11 Four Colour Set of Inks for the Ink Jet Printing of Textiles

- A four colour set of inks for ink jet printing onto textile materials were successfully prepared.
- Each ink had physical properties (viscosity, surface tension and particle size) suitable for application via ink jet printing. The mean particle size was very small, typically below 150 nm.
- Each ink formulation was printed successfully onto cotton and onto polyester fabrics and once cured offered excellent washfastness, very good rubfastness and very good lightfastness properties.
- Morphological evaluation showed little or no difference between washed and unwashed printed cotton fibres. There was no evidence of the presence of pigment particles on the surface of the fibres thus suggesting the penetration of the cotton fibres.
- Optical microscopy confirmed penetration of each ink through the surface layer of the cotton fibres.
- Morphological evaluation showed little or no difference between washed and unwashed printed polyester fibres. There was, however, evidence of crystalline structures on the surface of the fibres.
- Evaluation of such crystalline structures on the fibres printed with cyan ink using EDX showed no evidence for the presence of copper ions. As such, it is extremely unlikely that the crystalline structures were pigment particles. It is thought that such crystals came from water or treatments used on the polyester prior to any printing. Such a conclusion was backed up by the analysis of a washed sample of unprinted fabric which showed the same crystalline structures. It was therefore likely that the ink and thus the pigment particles had penetrated the polyester.

- Optical microscopy confirmed the penetration of the ink through the layers of polyester fibres. This phenomenon was unexpected as such penetration of the polyester is usually only seen when disperse dyes are used for colouration.
- Thermal analysis of the pigments confirmed that they bore no resemblance to disperse dyes in terms of possible sublimation. Thus, it is likely that the ink has penetrated the polyester due to the small particle size of the pigment.
- Thermal analysis of the polyester showed that it had a T_g from 76.77°C to 87.22°C. As such it is likely that some relaxation of the polyester fibres occurs at the T_g and this phenomenon aided the penetration of the ink containing pigment particles into the polyester.
- Assessment of the fastness properties of substrates coloured with just pigment dispersions were significantly poorer than the inks. Such a result indicates the importance of the Synthappret BAP as a binder within the ink formulations.
- The ink containing Cab-O-Jet Cyan 150C and 15% Synthappret BAP was found to be very stable at a temperature of 40°C for 5 months. Such stability confirms that inks containing Cab-O-Jet pigments are likely to be highly stable within an ink jet cartridge over extended periods of time. The storage at an elevated temperature also proved the stability of Synthappret BAP within such an ink formulation.

The four colour set of inks printed well onto cotton and also onto polyester fabrics and gave excellent washfastness, good rubfastness and lightfastness whilst conferring a soft handle to the fabrics. The inks penetrated both cotton and polyester fibres with no pigment particles visible on surface fibres when morphological evaluation was undertaken.

4.12 Final Conclusions

This investigation has shown that Synthappret BAP was an excellent binder system for use in both screen inks and ink jet printing inks. Inks that when applied to cotton and to polyester gave excellent fastness properties whilst maintaining a soft fabric handle were formulated. The objectives of the investigation were to produce screen printing inks that required a short cure time (< 1 minute) and also an ink jet printing ink system that could be applied to textiles in a one-pack printing process. Each of these objectives was achieved successfully. Such success in laboratory trials should transfer to

commercial applications within the textile printing industry with relative ease. In terms of ink jet printing, Cab-O-Jet pigment dispersions provided very stable inks with the required fastness properties and good colour characteristics. The fact that a four colour set of inks were successfully printed onto such differing substrates as cotton and polyester indicated that the systems could be employed for ink jet printing on a wide range of textile materials. The retention of a soft fabric handle whilst achieving the required fastness properties indicated that such printing inks were a potential rival for any commercially available inks for jet printing onto textiles.

5 Opportunities for Further Work

The following sections detail areas where there is potential for further work to be carried out on some aspects of the investigation.

5.1 Screen Printing Inks

There is scope for the optimised screen ink formulation to be scaled up and an industrial print trial carried out. Such a trial would affirm the suitability of such an ink formulation for a large scale print process.

5.2 Ink Jet Printing of Shrink Resist Treatments

The investigation proved that ink jet printing of Synthappret BAP as a shrink resist treatment was successful when two layers of the ink formulation were applied. There is scope for attempting to print the same ink using a print-head with larger nozzles, thus applying a greater amount of ink to the substrate. A greater volume of ink may result in the required sculpting effect of the wool after one pass through a printer.

5.3 Ink Jet Inks containing Toner Pigments

- Further investigation into dispersants and other additives.
- Application of a microfluidiser would act to reduce the mean pigment particle size to a far greater extent than application of a bead mill. A smaller mean particle size would allow for greater stability of the pigment within the ink formulation and as such give greater long term stability in terms of its time within a print-head and print cartridge.
- Possible stability tests in terms of shelf life could be carried out by application of a Lumifuge. A Lumifuge system is an adapted centrifuge with a light

attachment that is able to simulate shelf life aging of 2 years in a period of 2 weeks.

- Possible scale-up and industrial print trial.
- Further optimisation of the formulation may be carried out in order to improve the stability of the system. Such optimisation may include a detailed investigation into further dispersants and additives, use of alternative toner grade pigments and humectants.

5.4 Ink Jet Printing using Microlith Pigments

- Possible investigation into alkali components that provide pigment dispersion without interfering with the cross-linking mechanism of the Synthappret BAP.
- Possible stability tests in terms of shelf life could be carried out by application of a Lumifuge.
- Possible scale-up and industrial print trial.

5.5 Ink Jet Printing using Cab-O-Jet Pigment Dispersions

- Possible stability tests in terms of shelf life could be carried out by application of a Lumifuge.
- Scale-up of ink formulation and application of an industrial print trial using thermal or piezo print-heads.
- Application of ink formulations to a wide range of textile materials and subsequent fastness testing.

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8 Appendix

Contributed paper

Evaluation of pigmented ink formulations for jet printing onto textile fabrics

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Keywords

Ink jet printers, Inks, Pigments, Textiles

Abstract

Recent years have seen a significant increase in the use of inkjet technology for printing on textile fabrics. Typical inkjet printed textile products included curtains, large advertising posters, flags and banners. As a result of the need for such inkjet printed products to have a greater durability, especially for outdoor applications, inks containing pigments as the colourants are gaining more interests. However, pigments may give rise to logistical problems in terms of their dispersion stability within the ink formulation, consequently blocking the nozzles within the inkjet print head. This paper reports methods for the preparation of pigment dispersions and of inkjet printing ink formulations and the methods for the evaluation of the suitability of pigmented ink formulations for jet printing on textile materials. In particular, the suitability of three magenta pigments for inkjet inks were assessed and reported.

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Introduction

Inkjet printing is an ever evolving technology with a rapidly increasing number of applications. This is mainly due to the significant, worldwide research and development interest since the first commercialisation of the inkjet printing technology by Hewlett Packard in 1984. At present, inkjet printing is a fairly mature technology. This is true particularly in the areas of inkjet printing on paper, desktop inkjet printing, wide format (poster size) inkjet printing and industrial scale, high-speed (usually continuous stream) but relatively low-resolution inkjet printing.

Although being a fairly mature technology, inkjet printing still attracts an increasing amount of research and development interests. In fact, such interests have grown steadily throughout the last decade. Figure 1 shows the number of patents granted each year from 1990 to 2002 (Lin, 2003a).

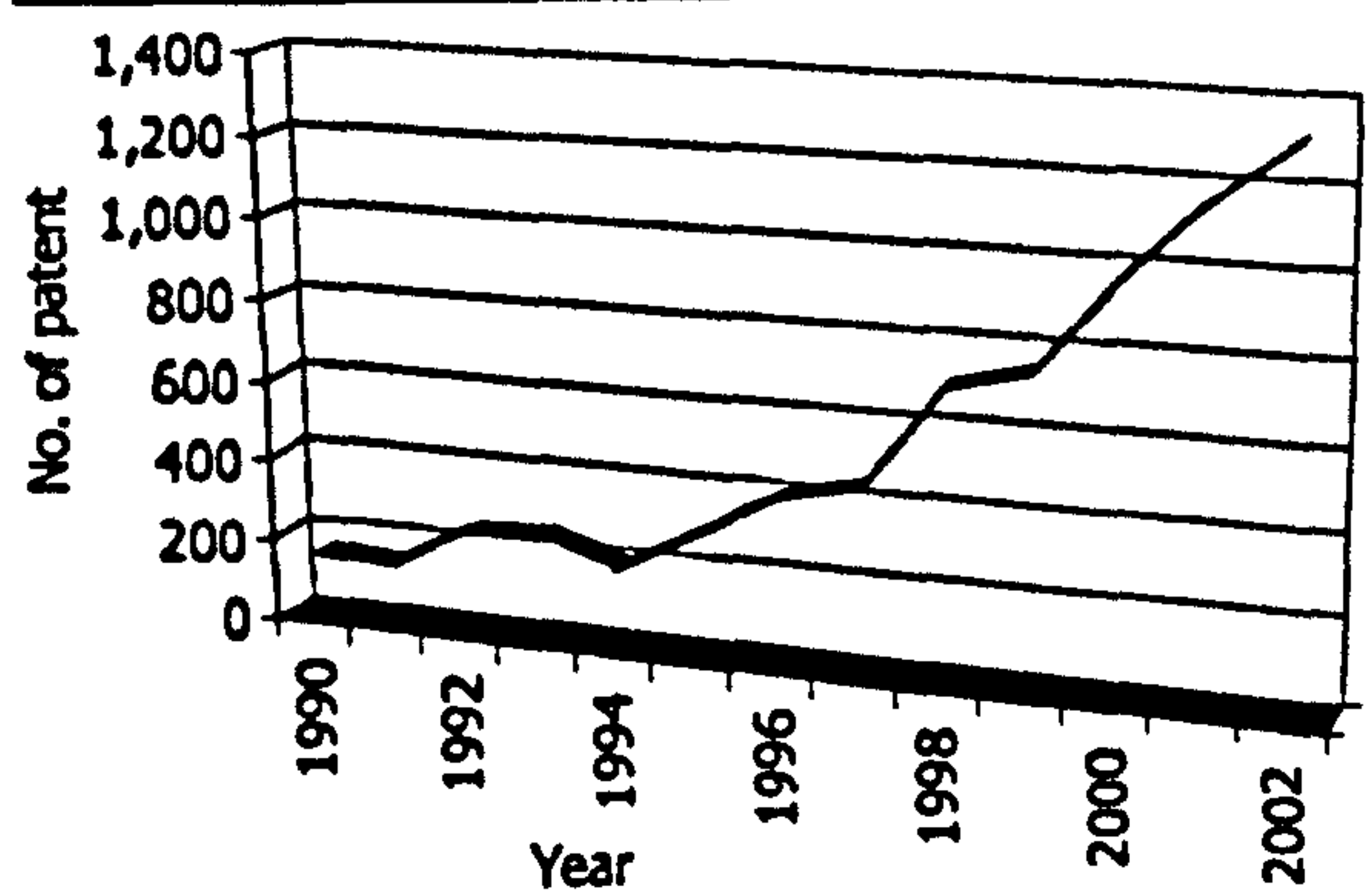
Comparing with conventional printing processes, inkjet printing has significant advantages. Such advantages include the following (Lin and Guthrie, 2001).

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

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

- Inkjet printing allows very high degree of reproducibility. There is usually very little variation in image quality of prints from one batch to another.
- Inkjet printing also allows very high degree of printing stability. In other words, there is virtually no variation of image quality of prints from the beginning to the end of a print run. As such, the cost

Figure 1 Number of patent applications relevant to inkjet printing



caused by starting, stopping and re-starting print runs can be eliminated.

- As ink-droplets are created only when required (in drop-on-demand inkjet printing), there is very low ink wastage associated with inkjet printing. Even continuous inkjet printing allows low ink wastage as ink droplets not reaching the substrate are collected, replenished and reused.
- As the whole printing operation is relatively simple, inkjet printers do not usually require any monitoring, provided that adequate fault correction mechanism is incorporated, which is the case for most wide format inkjet printers.

Inkjet printing technology is particularly suitable for printing of inks that contain high value-added ingredients. Typical examples of expensive ingredients include photochromic colourants, thermochromic colourants for anti-counterfeit applications (Lin, 2003a) and biochemicals.

The high level of automation of inkjet printing technology compares very favourably with most conventional printing processes, which invariably requires the attention of experienced operator throughout the print-production.

Due to it being a non-impact process, inkjet printing offers great versatility in terms of the variety of printable substrates. Emerging markets for inkjet printing include printing of plastics, circuit boards and electronic displays. For industrial applications, inkjet printing is currently used for graphics, signs, labels, textiles and flags and banners (Tanaka *et al.*, 1999). While continuous inkjet is used for fast, quick change processes such as printing use by dates on produce, it is generally accepted that for most other applications,

drop-on-demand inkjet printing is preferred. Two major types of drop-on-demand print heads namely, thermal and piezo jet exist. Piezo inkjet print heads are more widely used in wide format industrial applications (Dante *et al.*, 1999).

Recent years have also seen a significant increase in the research and development activities into inkjet printing on textiles. It is apparent to the authors that large, industrial scale inkjet printing facilities will soon be available to textile printers. There are two ink types which can be chosen from depending on the application. Traditionally, dye-based inks have been used due to their high colour quality (Bugner and Bermel, 1997; Dante *et al.*, 1999). However, most dye-based inkjet printing inks suffer from poor water-fastness when printed on common office printing paper. As such, various attempts to develop colourants capable of improved water-fastness when printed on various substrates had been made, some of which are successful (Lewis *et al.*, 2001).

However, in general, where good durability and light fastness are required, pigmented systems are preferred. This is borne out by the fact that 48 per cent of the textile printing sector is concerned with pigment printing (Hees *et al.*, 2002). Recently, there has been significant progress in the development of pigmented inks for inkjet applications (Dante *et al.*, 1999).

There are several drawbacks in the use of pigments for inkjet applications due to the relatively low dispersion stability of the pigments within the generally low viscosity inkjet ink formulations. Such a low dispersion stability is mainly due to the lack of polymeric binder at an adequate concentration (Lin, 2003b). Thus, the pigment particles may flocculate or agglomerate leading to the blocking of the jet nozzles within the print head. A significant factor that has been widely used for the assessment of the status of pigment dispersion is the particle size within the ink formulation. Ideally, for inkjet applications, a particle size of 0.5 μm or below is required. Smaller particles allow for improved stability, optical density, colour gamut, gloss and light fastness (Bugner and Bermel, 1997). To be suitable for inkjet printing, an ink must also have the required viscosity profile for a specific print head (Hees *et al.*, 2002). Although affected by pigment loading, the viscosity profile of an ink

is largely governed by polymeric components of the ink such as binders and humectants. Other factors affecting the suitability of an ink for jet printing include pH, surface tension and thermal stability.

From the image quality point of view, the inks are also required to produce images that have good resolution, colour characteristics and light-fastness. Inks designed for jet printing on textile materials need to satisfy further criteria, such as the wash-fastness and rub-fastness. A series of methods designed for the evaluation of the inkjet printing inks and the inkjet-printed images on non-woven cellulose substrates have been reported by Kang (1990). The study reported here attempted to establish a complete range of analyses required for the qualitative evaluation of the inks for jet-printing on textile fabrics and the jet printed images on textile fabrics. Such analyses include the measurement of viscosity, surface tension, particle size, print qualities including the roundness and the linearity of the print, of wash fastness and rub fastness. In particular, analyses of various pigmented ink formulations are detailed in support of the test methods introduced.

Experimental

Typically, pigmented inks are produced via a step of formulation of a pigment concentrate. Preparation of a pigment concentrate usually involves a process of mechanical shearing of the pigment within a liquid medium containing a dispersing agent. The aim of this step is to produce a pigment paste in which most agglomerates and aggregates are broken up into smaller particle units. Such smaller particles are kept apart in suspension due to the effect of the dispersing agent providing stability usually sterically or electrostatically (Lin, 2003b). The pigment concentrate can then be blended with other necessary components such as humectants, binder(s) and surfactants to form an ink formulation.

As such, various pigment concentrates/dispersions were prepared and their jettability evaluated. This was followed by blending the pigment dispersions with other suitable ingredients to give ink formulations. The printability of such ink formulations and the quality of the printed

and cured images on textile fabrics were assessed.

Materials, equipments and instruments

Materials

Currently, a large array of pigments and pigment pre-dispersions are commercially available, some of which are specifically tailored for use in inkjet ink systems. In this study, three magenta pigments were investigated. These included:

- (1) a pigment powder, Toner Magenta E02, supplied by Clariant Ltd, Horseforth, Leeds, UK;
- (2) a pigment, partially soluble in dilute alkali, Microlith Magenta B-WA, supplied by Ciba Special Chemicals, Clayton, Lancashire, UK; and
- (3) a pigment pre-dispersion, IJX 266 Magenta, supplied by Cabot Carbon Ltd, Stanlow, Ellesmere Port, South Wirral, UK.

A commercially available, thermal curing binder was used within the ink formulations. Laboratory grade isopropanol (IPA), ammonia, ethylene glycol, sodium carbonate, hydrochloric acid, sodium hydroxide, supplied by Sigma-Aldrich, Gillingham, Dorset, UK were also used within the ink formulations or in the experiments relevant to the investigation of pH resistance or to the wash-fastness testing. Solsperse 27000, supplied by Avecia, Blackley, Manchester, UK, was used as a dispersing agent in formulations containing Clariant Toner Magenta E02. Cotton/polyester fabrics supplied by Brook International, Bradford, West Yorkshire, UK were used as substrates for printing. Multifibre and standard wash soap supplied by the Society of Dyers and Colourists, Bradford, West Yorkshire, UK were used for the wash-fastness test of the prints.

Equipments and instruments

An MK11 Eiger Torrance bead mill (50 ml chamber) supplied by Eiger Torrance Ltd, Warrington, Cheshire, UK was used for the dispersion of the ink formulations prepared.

A Coulter N135 particle size analyser supplied by Beckman Coulter Ltd, High Wycombe, Buckinghamshire, UK was used for the analysis of the particle size of the pigment dispersions prepared.

A Jenway 350 pH meter supplied by BDH Ltd, Poole, Dorset, UK was used for measuring the pH in the pH stability tests carried out on the pigment dispersions.

A Brookfield DV-II+ viscometer, supplied by Brookfield Viscometers Ltd, Harlow, Essex, UK was used to measure the viscosity of the pigment dispersions and of the ink formulations prepared. A TBS Torsion Balance supplied by Torsion Balance Supplies, Malvern Wells, Worcestershire, UK was used to measure the surface tension of the pigment dispersions and of the ink formulations prepared.

A Hewlett Packard Deskjet 660 C inkjet printer, was used to print the ink formulations onto textiles while a laserjet printer, a Hewlett Packard LaserJet 4P, was used for printing images for comparative analysis using ImageXpert software.

A Mathis KTF 4099 dryer and a Mathis WT wash-fastness tester supplied by Werner Mathis AG, Zurich, Switzerland were used for curing the printed samples and for wash-fastness testing of the printed samples, respectively. A Roaches Crockmeter supplied by Roaches International Ltd, Staffordshire, UK was used to assess the rub-fastness of the printed samples.

A Gretag D183 densitometer, supplied by Colour Data Systems Ltd, Eastham Village, Wirral, UK was used to measure the optical density of the printed samples. An X-Rite SP68 spectrophotometer, supplied by X-Rite Ltd, Poynton, Cheshire, UK was used to measure the colour properties of the printed samples.

The quality of the printed and cured images on fabric samples was assessed using an ImageXpert supplied by VisonJet Ltd, Lumen House, Royston, Hertfordshire, UK. The ImageXpert provided objective and repeatable quality analyses including dot quality, dot position, line quality, mottle, text quality, and registration.

Methods

Methods for the preparation of the pigment dispersions, of the ink formulation, for the evaluation of the properties of the inks, printing of the inks, curing of the prints and for the evaluation of the printed images are detailed in this section.

Preparation of pigment dispersions

All percentages concerned are percentages by weight. Each of the pigments was dispersed in deionised water to give a 1 per cent formulation. In particular,

- The Toner Magenta E02 dispersion was prepared by mixing the pigment (1 per cent) with 2 per cent of dispersing agent (Solsperse 27000) and 97 per cent of deionised water for 1 h using the Eiger-Torrance bead mill.
- The Microlith Magenta B-WA dispersion was prepared initially by making a paste consisting of pigment (25 per cent), deionised water (54 per cent), isopropanol (IPA) (20 per cent) and ammonia (1 per cent). Such a paste was then used to make a dispersion containing 1 per cent pigment and 99 per cent deionised water, which was mechanically stirred for 1 h to achieve uniformity.
- The IJX 266 Magenta dispersion was prepared by blending 1 per cent of the pigment pre-dispersion in 99 per cent of the deionised water followed by mechanical stirring for 1 h.

Preparation of inkjet ink formulations

Design and optimisation of ink formulations for inkjet printing have been of significant research and development interest in the past few decades. Most inkjet printing inks involve multiple components making the design and optimisation of the formulations a challenging task. For more details of formulation and formulation optimisation, readers are referred to a series of studies reported elsewhere (Lin and Guthrie, 1993, 1998; Lin *et al.*, 1992, 2000, 2001, 2003). For the purpose of the current investigation, a general formulation was employed. Thus, each of the pigments was used in the formulation of an inkjet ink to the following specification using the same methods as for the preparation of the pigment dispersions (Table I):

It should be pointed out that the ink formulation containing Toner Magenta E02

Table I Preparation of the pigment dispersions

	Per cent
Pigment	2
Binder	15
Ethylene glycol	5
IPA	5
Water	73

included 2 per cent Solsperse 27000 as a dispersing agent, thus reducing the content of the deionised water to 71 per cent.

Characterisation of particle size and particle size distribution

Particle size and particle size distribution of the pigment dispersions prepared were measured using the Coulter N135 particle size analyser immediately, 1 week and 4 weeks after the preparation of the dispersion.

Freeze/thaw cycling was carried out as described by Bugner and Bermel (1997).

Thus, the dispersions were allowed to stand for 24 h at -20°C followed by standing for 24 h at 60°C . This process formed one cycle which was repeated four times. The dispersions were also monitored visually for any signs of pigment sedimentation.

Characterisation of ink stability

As mentioned earlier, the stability of the pigment dispersion is of significant importance for inkjet printing inks. A widely accepted method for the evaluation of the stability of a pigment dispersion is the monitoring of the relevant properties of the pigment dispersion over a period of time. In this study, the viscosity, the surface tension and the stability against pH variation of the pigment dispersions prepared were monitored over a period of 4 weeks.

The pH of the pigment dispersion was varied at 2, 3, 7 and 12, by the addition of either a diluted hydrochloric acid solution (1 molar solution) or a diluted sodium hydroxide solution (1 per cent). Visual assessments of the subsequent effect of the pH variation on the pigment suspension were made.

Surface tensions of the pigment dispersions were measured using the TBS torsion balance and the viscosities using the Brookfield DV-II+ viscometer at 25°C and 60 rpm. The inkjet ink formulations prepared were assessed for their viscosity and surface tension using the same methods.

Printing of the inks

Each ink prepared was jet printed onto both cotton and polyester fabric samples of size 25×18 cm using the HP Deskjet 660 C printer. In order to ensure adequate printing quality, the fabric samples were held on a piece of A4 office printing paper with a conventional adhesive.

For the evaluation of the colour characteristics of the prints on textile fabrics, a solid 20×15 cm rectangle was printed.

For the evaluation of the print quality, a standard ImageXpert test image, as shown in Figure 2, was printed.

Curing of the printed images

All prints were thermally cured in the Werner Mathis KTF 4099 dryer at 150°C for 2 min.

Measurement of the colour characteristics

The colour characteristics of both the pigment dispersions and the ink formulations were assessed. For the pigment dispersions, optical density of the drawdown samples, prepared using a No. 2 K-bar and standard white photocopy paper, was measured. For the ink formulations, optical density of the prints on both cotton and polyester fabrics was measured. All measurements of optical density and chroma were taken using both the Gretag D183 optical densitometer and the X-Rite SP68 spectrophotometer.

Evaluation of wash and rub-fastness of printed textile samples

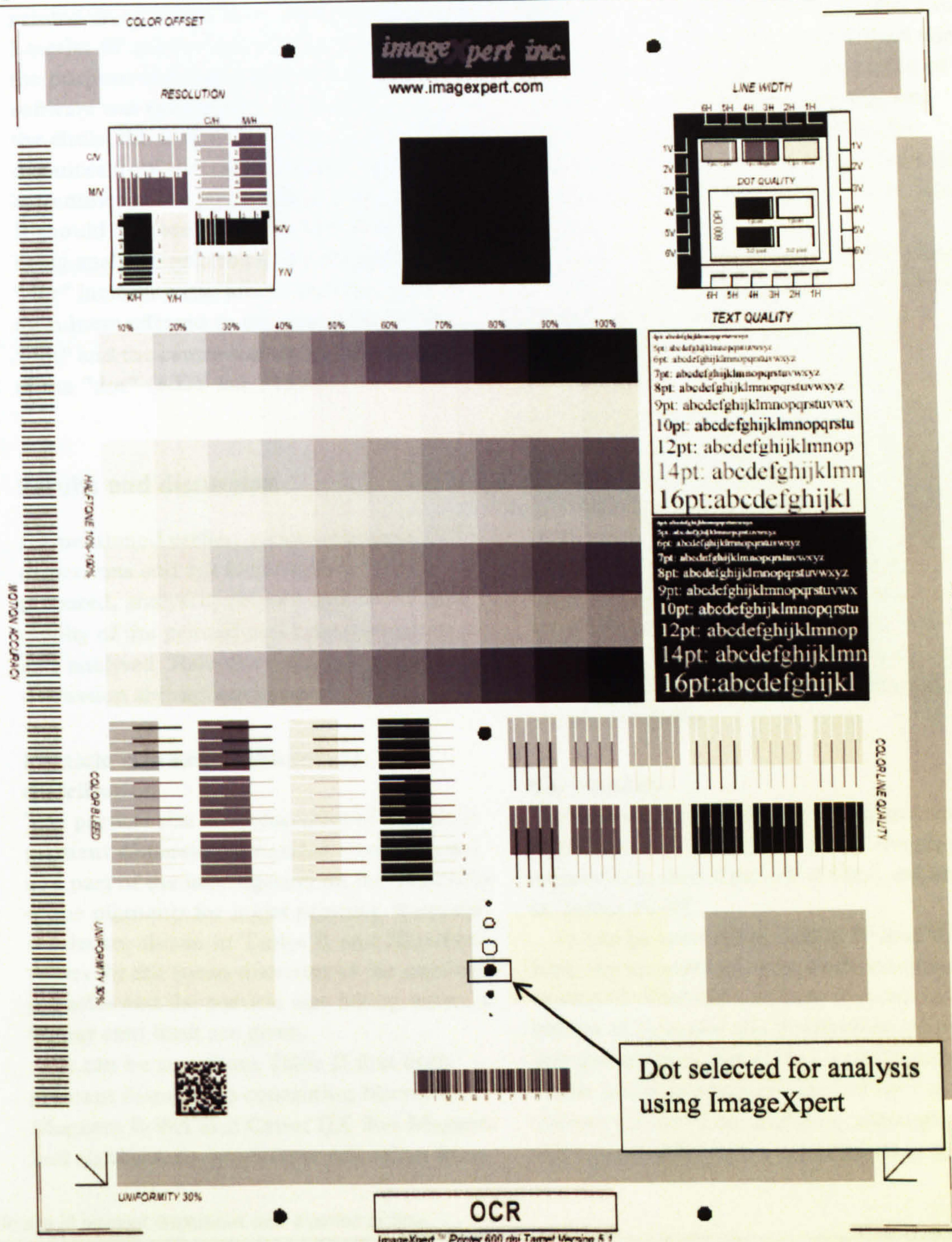
Both the wash-fastness and the rub-fastness of the printed and cured fabric (cotton and polyester) samples were assessed. The assessment of the wash-fastness was carried out using the Mathis WT wash-fastness tester detailed earlier. Each printed and cured fabric sample, along with a multifibre strip, was washed at 60°C for 30 min in liquor containing 4 g standard soap and 1 g sodium carbonate per litre of water at a liquor ratio of 50:1.

The tests of rub-fastness were carried out using the Roaches crockmeter. Each printed and cured fabric sample was subjected to a standard rub-fastness test of ten back and forth rubs with both dry and wet cotton lawn rubbing fabric.

Assessment of jettability and print image quality

Jettability is one of the more important properties of the inkjet printing ink formulations. Jettability could be assessed using high-speed digital video systems that are capable of capturing the emergence of the individual droplet from the nozzle and the motion of the individual droplet ejected from the nozzle. There exists several commercially

Figure 2 Standard ImageXpert test image



available high-speed digital video systems specially designed for the evaluation of the jettability of inks, including the VisonJet systems available from Xennia Technology Limited, Lumen House, Lumen Road, Royston, Hertfordshire, UK. A more widely accepted method for the evaluation of the jettability is by visual assessment, which was adapted for this study. Thus, the jettability of each of the inks prepared was assessed through the visual assessment of the coverage of the solid blocks on the printed and cured fabric samples.

Image qualities such as the dot quality, dot position, line quality, the mottle, text quality and the registration all make a significant contribution to the visual effect of the image. All these image qualities could be measured using the ImageXpert image analysis system. In this paper, dot qualities such as the dot area, dot roundness, centre-to-left distance, centre-to-right distance, centre-to-top distance and the centre-to-bottom distance obtained through the ImageXpert system are reported. Thus, the marked area shown in Figure 2 was chosen for analysis, this being

a solid circle of colour. The same image printed on standard copy paper using the HP LaserJet 4P printer was used as a standard for the purpose of comparison. The ImageXpert software was then used to measure the area of the circle, the roundness of the circle and the distances from the centre of the circle to its extremities at the left, right, top and bottom. It should be noted that the area of the image being analysed referred to the total area of the "dot" including any joined satellites, the roundness referred to the roundness of the "dot" and the centre was the geometric centre of the "dot" (KDY Inc., 1999).

Results and discussion

As mentioned earlier, various pigment dispersions and ink formulations were prepared, analysed, printed and cured. The quality of the printed and cured images was also analysed. Relevant results, together with discussion are reported here.

Particle size and particle size distribution

The particle size characteristics of the three pigment dispersions prepared were assessed as a part of the investigation on the suitability of the pigments for inkjet printing. Relevant results are shown in Tables II and III, where values for the mean diameter of the pigment particles and the particle size falling within a 95 per cent limit are given.

It can be seen from Table II that both pigment dispersions containing Microlith Magenta B-WA and Cabot IJX 266 Magenta had significantly smaller particles than that

containing the Clariant Toner Magenta E02. It can also be seen, from Table II, that such a characteristic of particle size remained fairly constant throughout the storage period of 4 weeks. However, all the three pigment dispersions appeared to be suitable for application in inkjet printing inks, indicated by their particle size being close to or below 500 nm.

The effect of freeze-thaw cycling on the particle size of each pigment dispersion was significant, indicated by the considerable increase of the particle size after four freeze-thaw cycles (Table III). Such increases in particle size are likely to be due to the flocculation of the pigment particles caused by the dramatic change in temperature. The pigment dispersion containing the Microlith Magenta B-WA had the greatest increase in particle size after four freeze-thaw cycles. Such a drastic increase was considered to be due to the evaporation of ammonia at 60°C resulting in the lowering of the pH causing a reduction in the affinity between the pigment and the medium.

Ink stability

The viscosity, the surface tension and the dispersion stability against pH of the pigment dispersions, over a period of time, are shown in Tables IV–VI.

It can be seen, from Tables IV and V, that both the viscosity and the surface tension remained relatively constant over the relevant period of time and the freeze-thaw cycles. It was generally accepted that a commercially viable inkjet printing ink should have a viscosity lower than 20 mPa s, although it is not uncommon for an inkjet printing ink to

Table II Particle size of pigment dispersions over a period of time

Storage time	Particle size characteristics of pigment dispersions (nm)					
	Clariant Toner Magenta E02		Ciba Microlith Magenta B-WA		Cabot IJX 266 Magenta	
	Mean diameter	95 Per cent limit	Mean diameter	95 Per cent limit	Mean diameter	95 Per cent limit
1 day	597	644	177	184	92.5	95.5
1 week	322	341	183	192	98.6	102
4 weeks	247	260	157	164	84.1	86.6

Table III Effect of freeze-thaw cycling on particle size of the pigment dispersion

Number of cycles	Mean particle size of pigment after freeze-thaw cycle (nm)		
	Clariant Toner Magenta E02	Ciba Microlith Magenta B-WA	Cabot IJX 266 Magenta
1	206	200	109
4	400	442	229

Table IV Viscosity of the pigment dispersions over a period of time

Storage time (days)	Viscosity of pigment dispersion (mPa s) at 60 rpm		
	Clariant Toner Magenta E02	Ciba Microlith Magenta B-WA	Cabot IJX 266 Magenta
1	1.15	1.19	1.09
2	1.21	1.20	1.11
7	1.22	1.21	1.11
14	1.19	1.14	1.06

Table V Effect of storage on the surface tension of the pigment dispersions

Storage time	Surface tension of pigment dispersions (mNm)		
	Clariant Toner Magenta E02	Ciba Microlith Magenta B-WA	Cabot IJX 266 Magenta
1 day	53	49.5	74
1 week	51.5	48.5	73
2 weeks	53	50	73.5
4 weeks	53	50	73.5

Table VI Effect of pH on the stability of the pigment dispersions

Storage time	Stability of pigment dispersion								
	Clariant Toner Magenta E02			Ciba Microlith Magenta B-WA			Cabot IJX 266 Magenta		
	pH 2	pH 3	pH 12	pH 2	pH 3	pH 12	pH 2	pH 3	pH 12
1 day	No	No	Yes	No	Yes	Yes	Yes	Yes	Yes
2 days	No	No	No	No	Yes	Yes	Yes	Yes	Yes
1 week	No	No	No	No	Yes	Yes	Yes	Yes	Yes
4 weeks	No	No	No	No	Yes	Yes	Yes	Yes	Yes

have a viscosity up to 30 mPa s (Kipphan, 2001). Thus, it can be seen, from Table IV, that all pigment dispersions are suitable for inkjet printing indicated by low viscosity values.

Ideally, inks for application via inkjet printing should have a surface tension in the range of 25–60 dynes cm⁻¹ (MacFaul, 2003). It can be seen, from Table V, that both the pigment dispersion containing Clariant Toner Magenta E02 and the pigment dispersion containing Ciba Microlith Magenta B-WA had a surface tension within the operational range. The pigment dispersion containing the Cabot Magenta IJX 266 had a surface tension higher than 60 dynes cm⁻¹. However, on completion of a full ink formulation, the surface tension would be lower due to the inclusion of the humectants and the isopropyl alcohol.

Table VI shows that the pH had a significant effect on the stability of the pigment dispersions containing the Clariant Toner Magenta E02 or the Ciba Microlith Magenta B-WA. Both pigment dispersions containing Ciba Microlith Magenta B-WA and Cabot Magenta IJX 266 were stable over

the storage time at high pH. The pigment dispersion containing Clariant Toner Magenta E02 was unstable at extreme acidity or extreme alkalinity.

The viscosity and the surface tension of the three ink formulations prepared are given in Table VII. From Table VII, it can be seen that all the three ink formulation had satisfactory viscosity and surface tension for inkjet printing.

Colour characteristics

The colour characteristics (optical density and chroma) of the pigment dispersion are shown in Table VIII. It can be seen from Table VIII that the pigment dispersion containing Cabot Magenta IJX 266 had a higher optical density and a higher chroma than the pigment dispersions containing either of the other two pigments.

The colour characteristics of the printed and cured textile fabrics are shown in Table IX. It can be seen, from Table IX, that the optical density of the images on textile fabrics obtained followed the similar order as that of the pigment dispersions, with the

Table VII Viscosity and surface tension of inkjet ink formulations

Ink formulation	Viscosity (mPa s) at 60 rpm	Surface tension (mNm)
Clariant Toner Magenta E02	3.0	36
Ciba Microlith Magenta B-WA	2.8	35
Cabot IJX 266 Magenta	2.5	35

Table VIII Colour characteristics of the pigment dispersions

Pigment	Optical density	Chroma
Clariant Toner Magenta E02	0.47	40.18
Ciba Microlith Magenta B-WA	0.44	33.68
Cabot IJX 266 Magenta	0.65	43.19

exception that the print derived from Ciba Microlith Magenta B-WA appeared to have a greater optical density than the print derived from Clariant Toner Magenta E02. This is likely due to the fact that the ink formulation containing the Ciba Microlith Magenta B-WA had a lower viscosity and a lower surface tension (Table VII), giving it a greater printability than the ink formulation containing Clariant Toner Magenta E02.

Wash and rub-fastness

In order to assess the effect of wash-fastness of the images printed and cured on the textile fabrics, the optical densities of the images were measured before and after washing. Relevant optical density results are given in Table IX.

It can be seen from Table IX that all printed and cured images had a good wash-fastness, indicated by the negligible changes of the optical densities before and after wash. Such a good wash-fastness was not unexpected as the binder included in the ink formulations was known to have a good affinity with textile fibres and to give a high degree of crosslinking.

However, it is also noticeable that images on cotton fabrics had a better wash-fastness than those on polyester fabrics. This is likely due to the greater absorbance of the ink offered by cotton.

The results of the rub-fastness tests are shown in Figure 3. In each case, the top pair of cotton lawn pads is after rubbing cotton and bottom pair after rubbing polyester with dry rub on the left and wet rub on the right.

Rub-fastness was also more scientifically assessed, by measuring the optical density of the cotton lawn rubbing fabric after rubbing the substrate. Relevant results are shown in Table X.

It should be noted that due to the poor print quality of the ink containing Clariant Toner Magenta E02 and the lack of ink reaching substrate, no rub test for the print derived from this ink was carried out.

It can be seen, from Table X, that the ink formulation containing Ciba Microlith Magenta B-WA gave prints of better rub-fastness than did the ink formulation containing Cabot Magenta IJX 266. It can also be noticed that both inks gave prints of better rub-fastness on cotton fabrics than on polyester fabrics, probably due to the greater absorbency offered by cotton.

Jettability and quality of the printed image

The dot area, dot roundness and the centre-to-extremity distances data obtained through measurement using the ImageXpert are shown in Tables XI–XIII. The ImageXpert software measures roundness on a scale of 0 to 1 with 1 being perfectly round. It should be noted that due to the poor image quality, no image analysis was made on the prints produced using the ink containing Clariant Toner Magenta E02. The profiles of the typical printed dots on both the cotton and the polyester are shown in Figure 4.

It can be seen from the data given in Tables XI–XIII and Figure 4 that the structure and the type of the textile fabrics have an effect on the interaction between the ink and the substrate. Thus, the printed dot on cotton has a greater roundness and a smaller dot gain. This is likely due to the lower degree of

Table IX Optical density of prints before and after washing

Ink formulations	Optical density			
	On cotton		On polyester	
	Before washing	After washing	Before washing	After washing
Clariant Toner Magenta E02	0.30	0.30	0.37	0.35
Ciba Microlith Magenta B-WA	0.43	0.43	0.52	0.49
Cabot IJX 266 Magenta	0.61	0.61	0.56	0.54

Figure 3 Rub-fastness of printed fabric samples

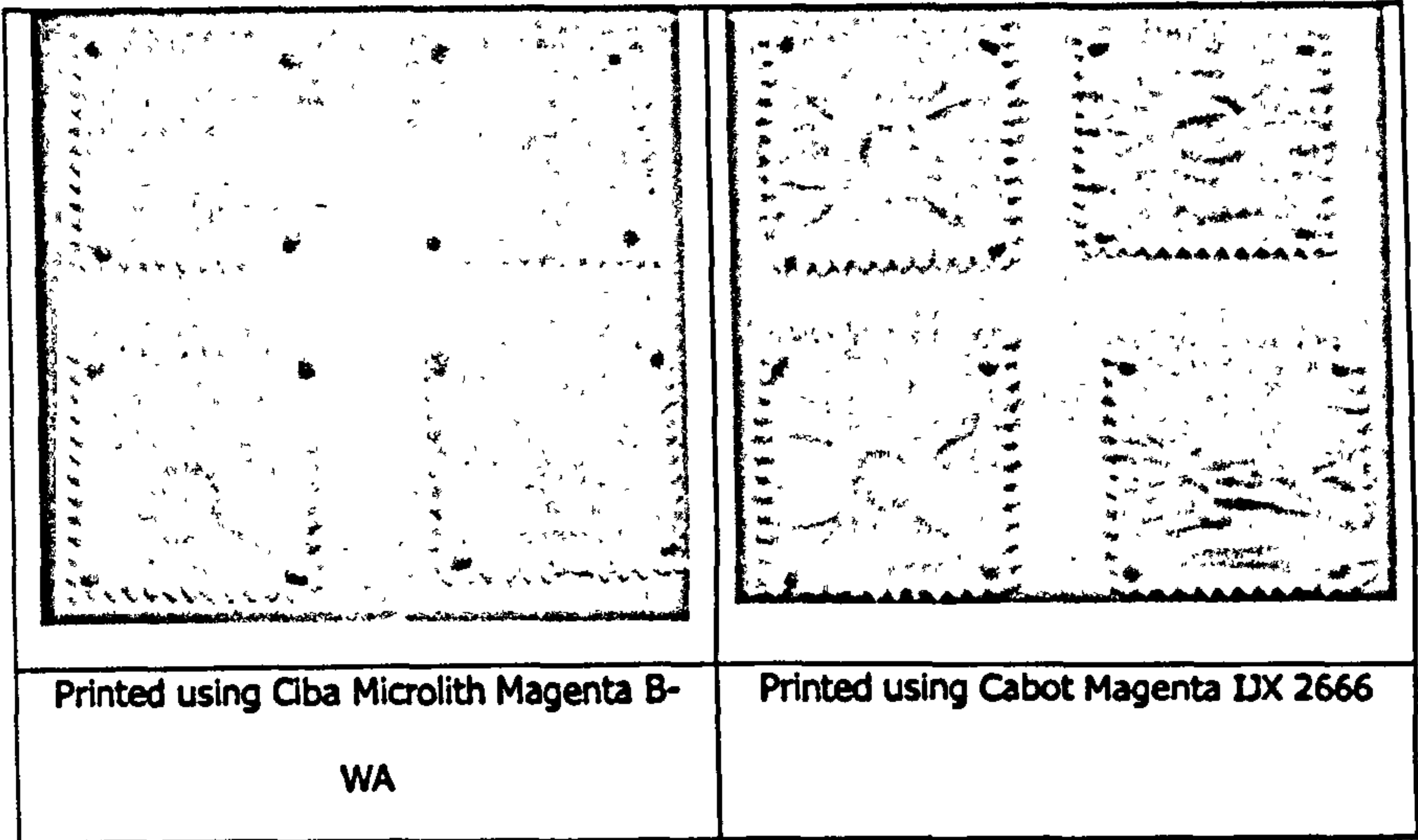


Table X Optical density of cotton lawn pads after rub test

Ink formulations	Optical density of cotton lawn rubbing fabric after rub test			
	On cotton		On polyester	
	Dry rub	Wet rub	Dry rub	Wet rub
Ciba Microlith Magenta B-WA	0.01	0.02	0.04	0.05
Cabot IJX 266 Magenta	0.07	0.02	0.15	0.16

Table XI Areas of the same dot print on various substrates

Ink/toner formulation	On paper	Area of dot (mm ²)	
		On cotton	On polyester
Laserjet black	3.50	–	–
Ciba Microlith Magenta B-WA	–	4.10	3.78
Cabot IJX 266 Magenta	–	4.21	3.90

Table XII Roundness of the circular image area

Ink/toner formulations	On paper	Roundness	
		On cotton	On polyester
Laserjet black	0.91	–	–
Ciba Microlith Magenta B-WA	–	0.26	0.12
Cabot IJX 266 Magenta	–	0.35	0.12

Table XIII Centre to point measurements of the image area

Ink/toner formulations		Point to point measurements (mm)			
		Centre to left	Centre to right	Centre to bottom	Centre to top
Laserjet black	On paper	2.86	2.86	2.80	2.82
Ciba Microlith Magenta B-WA	On cotton	3.34	3.19	3.18	3.10
	On polyester	4.28	4.24	4.04	3.93
Ciba Microlith Magenta B-WA	On cotton	3.30	3.30	3.22	3.30
	On polyester	4.85	4.10	3.46	3.54

Figure 3 Rub-fastness of printed fabric samples

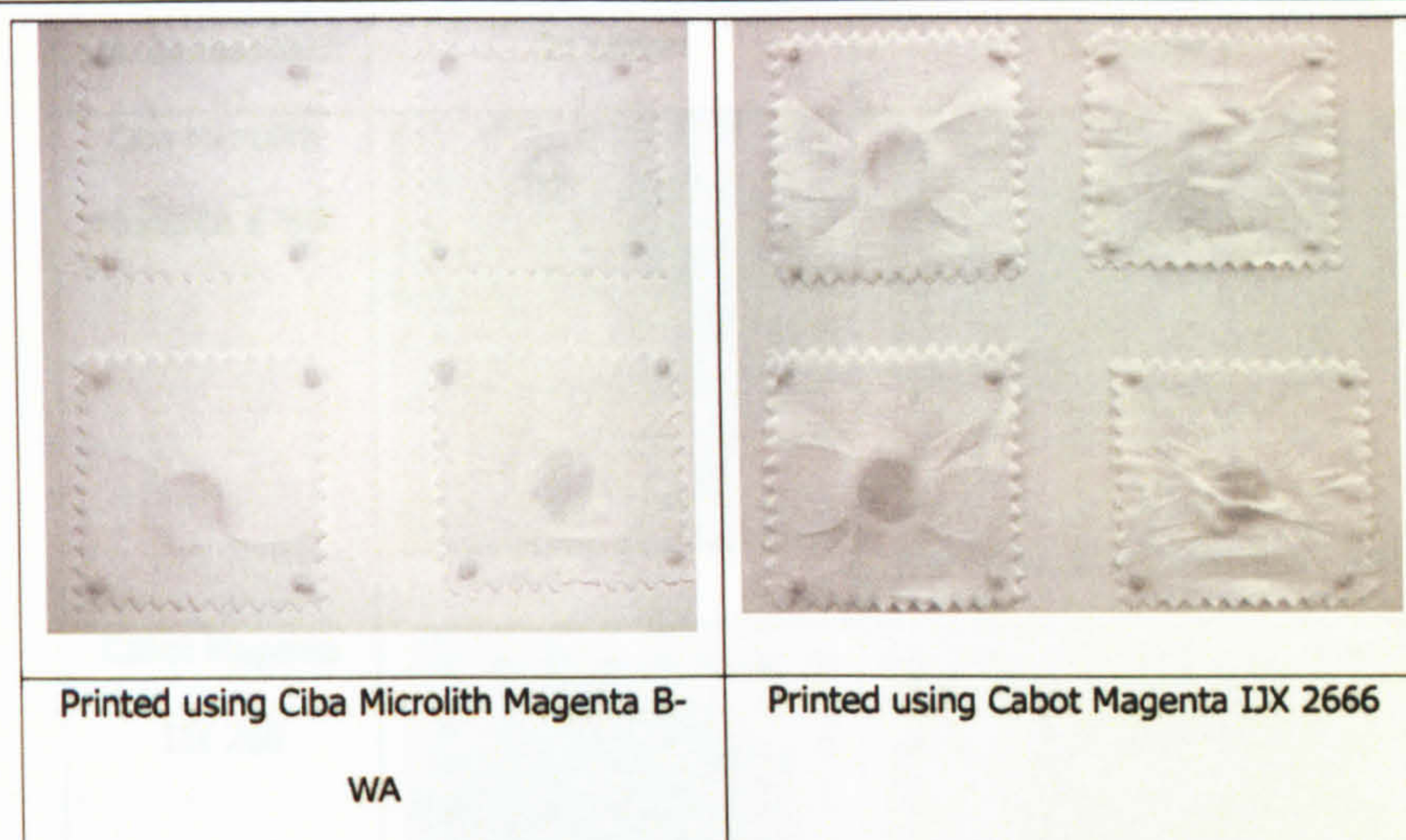


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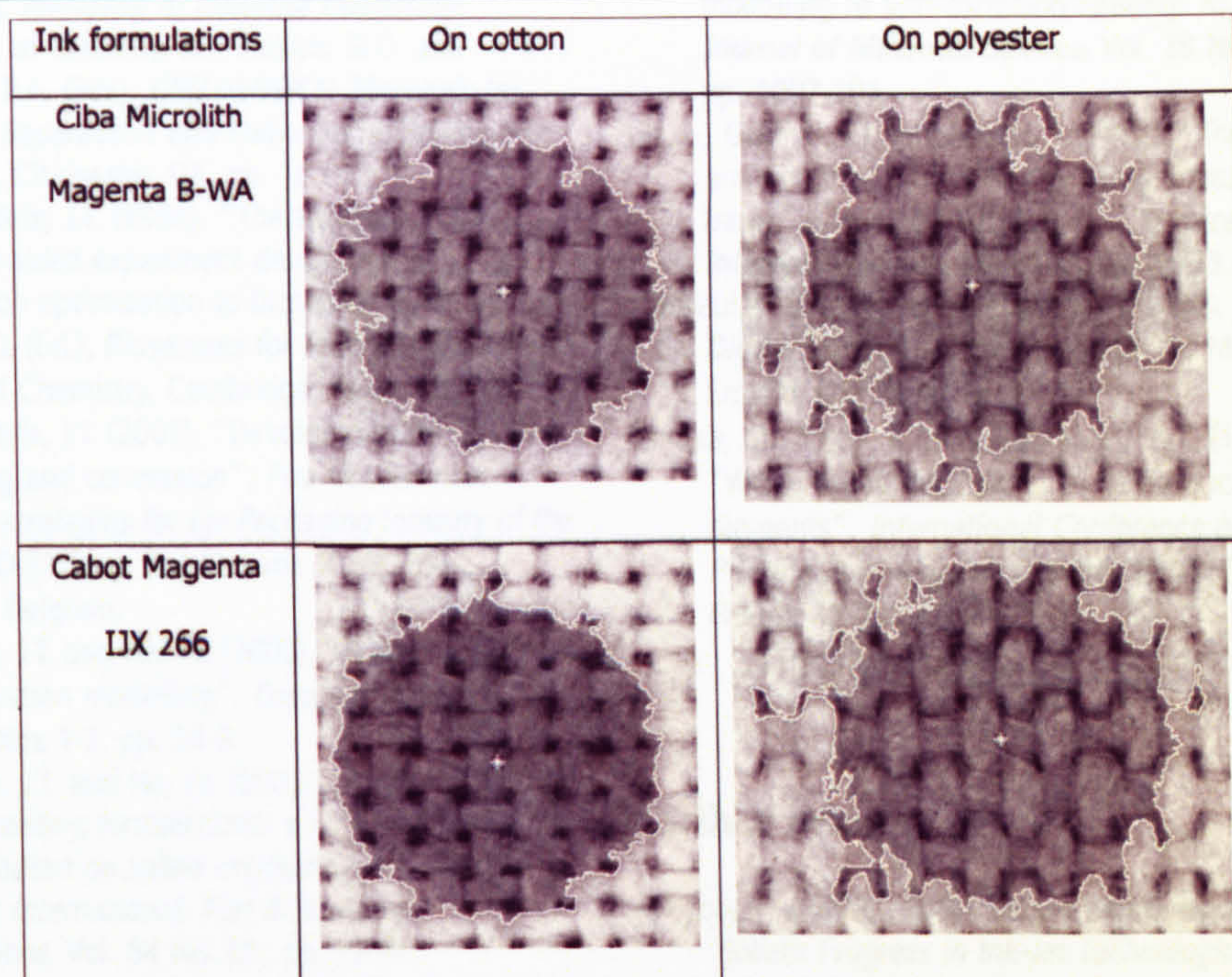
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	On polyester	4.85	4.10	3.46	3.54

Figure 4 Micrographs of printed dots on textile fabrics



wicking of the ink on cotton fibre as a result of the significant absorbency offered by the cotton fabrics.

Conclusion

It is apparent that the stable pigment-based inks for inkjet printing on textile fabrics could be formulated. The results of this study suggested that of the three pigments investigated, Cabot Magenta IJX 266 was the most suitable for application via inkjet printing due to its smaller particle size, lower intrinsic viscosity and stability to freeze-thaw cycles and pH changes. Whilst the Clariant Toner Magenta E02 and the Microlith Magenta B-WA could also be used for inkjet ink application, their relatively lower stabilities may give rise to problems especially in terms of blocking of print head nozzles.

On visual assessment, the ink containing Cabot Magenta IJX 266 gave the best performance followed by Microlith Magenta B-WA. The formulation containing the Clariant Toner Magenta E02 as the colourant did not have a good printability, probably due to its larger particle size as indicated by the results of particle size analysis. It was also found that prints on cotton fabrics had better image qualities than those on polyester fabrics, mainly due to the greater absorbency offered by the cotton fibres. The use of ImageXpert software enabled an accurate,

quantitative assessment of the image quality of the prints on both paper and textile substrates.

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Further reading

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