Part III

Digital printing coloration

Substrate preparation for ink-jet printing

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12.1 Introduction

Pre-treatment of textiles in preparation for ink-jet printing is carried out because inclusion of auxiliary chemicals and thickeners into the low viscosity ink has proved troublesome. Thus the methodology is akin to 'two-phase' conventional printing as opposed to the 'all-in' approach. In the latter case all the dyes, chemicals and thickeners required are included in the print paste, whereas in the former some of the ingredients, particularly chemicals, are applied before, or after, printing.

Although ink-jet printing of textiles has been established since about 1987, it has yet to account for a significant proportion of the total volume of printed textile production. The main reason for this is the low productivity of the printing equipment that has been available, but the expense and complexity of having to pre-treat the fabric prior to printing is also a stumbling block. Having applied thickening agents and chemicals to the fabric to aid fixation of dyes and prevent undue wicking and penetration, these, along with unfixed dye, have to be removed after the fixation step. This is in contrast to transfer or sublimation printing, where the thickener and chemicals remain on the paper after the volatile disperse dyes have diffused into the textile during printing. Consequently no further fixation or wash-off is required. Jet printers for printing directly onto fabric can also be used to print transfer paper, as the machines were originally designed for the graphics industry. Transfer of the design onto rolls of fabric may then be carried out in a continuous manner using a cylinder and blanket-type machine, known as a transfer calender. The graphics printers, which have been adapted for ink-jet printing of textiles, are discontinuous. This point will be elaborated on later.

While transfer printing is an attractive alternative to ink-jet printing for polyester substrates it is not viable for natural fabrics such as cotton, wool or silk, as disperse dyes are not substantive to them. Historically there have been attempts to transfer print these fibres, particularly by Dawson International and Tootals. Substantive dyes, such as reactive or acid dyes, were printed onto paper,

but thickener and chemicals were applied to the substrate. Some moisture was also required to ensure the dyes dissolved. The Fastran Process[1] was developed by Dawson International. It was a batchwise process used mainly for printing pre-treated woollen garments with acid dyes. Tootals built the DewPrint machine to carry out the damp transfer process on a continuous basis.[2] The machine never gained any commercial acceptance, however, as printing a damp substrate was difficult.

Ink-jet printing of textiles has generally been carried out using pre-treated materials, with the exception of carpets. The Millitron carpet printer[3] enables nylon or wool carpets to be printed on a continuous basis using low viscosity acid dye inks. The carpet is often pre-treated with an aqueous solution of surfactant which is hydro-extracted with a suction slot prior to printing. This process has been successfully used for over 30 years, and is still the best example of continuous jet printing on a commercial scale. On a smaller scale, the Zimmer Chromojet machine, used mainly for printing carpet tiles, and the more recent Chromotex fabric printer have also met with some success. Zimmer now have a continuous 'beam' Chromotex printer for carpets. Once more, the ink contains dyes, thickener and chemicals in the 'all-in' style.

When printing cotton the choice has generally been between reactive dyes and pigments. The pigment printing process is simpler, as it involves three main stages (print, dry, bake/cure), whereas reactive printing has two extra processes (print, dry, steam, wash-off, dry). Pigment printing is therefore a more economical procedure, and for that reason is favoured in most countries. Polyester/cotton presents more difficult technical problems than 100% cotton when printing with dyes, and although these have been overcome,[4] pigment printing is overwhelmingly the choice for this blend. However, when ink-jet printing emerged, reactive dye inks were made available in the first instance. Jet printing with pigments has proved to be technically difficult and the development of systems has taken much longer. The problems for pigment systems were exacerbated because the graphics printing machines first adapted for jet printing were of the thermal drop-on-demand type, the Encad machine being the most popular. In this type of printer the ink is heated and a bubble of vapour forces the droplet out of the nozzle. Pigment inks, especially if they contained the binder, were not compatible with this type of machine.

Reactive printing by the 'all-in' method is the normal approach for screen printing, but for jet printing it has certain dangers. These will be dealt with later. As a result the jet printing of cotton, wool and silk has generally been carried out by the 'two-phase' method, the ink containing only purified dyes, the thickener and chemicals being applied to the substrate in a pre-treatment. Although the quality of the resulting prints is excellent, the extra expense of pre-treating the fabric by a pad/dry process makes the process uneconomical for anything but short runs. Accountants also frown on the concept of holding stocks of expensive pre-treated fabric.

Over the past few years one of the barriers to successful ink-jet printing of pigments has disappeared with the introduction of the piezo type of printer, since no heating of the ink takes place. It was clear from the start that it would be of great commercial benefit if a pigment-based printing system, which did not require a fabric pre-treatment, were to become available. Early attempts were unsuccessful as the pigments produced much duller shades than could be achieved with dyes, and there was a tendency for nozzles to block, in other words the 'runnability' was poor. The inks tended to dry out in the nozzle, and in an attempt to avoid this happening, some producers installed air humidifiers in the vicinity of the printer. Companies such as Ciba and BASF have improved their pigment inks over a long development cycle, and these drawbacks have been corrected to a considerable extent.

12.1.1   Reasons for pre-treatment

The main reasons for separating the dyes from thickeners and other chemicals and applying them separately to the fabric are as follows.

- 'All-in' inks are less stable and have lower storage stability, e.g. reactive dyes are more likely to hydrolyse when alkali is present in the ink.
- Chemicals in the ink cause corrosion of jet nozzles; the deleterious effect of sodium chloride on steel surfaces is well known, for instance; inks for use in 'charged drop' continuous printers should have low electrical conductivity.
- Thickeners in the ink often do not have the desired rheological properties.
- Some chemicals can be utilised in pre-treated fabric but would cause stability problems in the ink; e.g. sodium carbonate as alkali for reactive dye fixation is acceptable on the fabric but not in the ink.
- The presence of large amounts of salts in aqueous inks reduces the solubility of the dyes; concentrated inks are required in jet printing due to the small droplet size.

The point about the rheology of the ink requires amplification. Generally low viscosity inks are required at the printing stage, but once the ink is deposited on the substrate, higher viscosity is necessary to prevent lateral spread. This suggests the use of highly pseudoplastic thickeners.[5] Unfortunately, this can cause 'tailing' and satellite formation during printing.[6] During printing, inks with Newtonian flow properties perform better.

A further advantage of applying thickeners and chemicals separately from the dyes is that it allows the wettability and penetration properties of the fabric to be adjusted. Wettability is the lateral spread of liquid when it impinges on a fibrous matrix, and is caused by the capillary forces that are present in the narrow interstices between fibres and yarns. In the past this was assessed with the aid of a burette containing the liquid (water or sugar solution) and stopwatch.[7] The fabric was held in an embroidery ring and the time taken for a drop of liquid to

spread out on the surface was measured manually. More recently this procedure has been automated.[8]

12.2   Ink systems

12.2.1 Reactive dyes

Reactive inks are generally used for cellulosic substrates, where they produce bright shades with good fastness to washing and light. The dyes form stable, covalent bonds with the fibre under alkaline conditions. Wool, silk and nylon may also be printed with them. There are several types of reactive dye, not all of which are suitable for printing purposes. The factors involved are (i) reactivity and (ii) substantivity.

1. Reactivity. The main classes of reactive dye[9] are shown in Table 12.1. Dichlorotriazines are the most reactive, and cannot be used in printing because their storage stability in inks and print pastes is too low. Monochlorotriazine (MCT) dyes are less reactive and are the most common choice for ink-jet printing inks.
2. Substantivity. Dyes intended for printing should have low substantivity to the substrate. In this respect they are akin to dyes used for continuous dyeing, as opposed to those used in exhaustion dyeing, which should have high substantivity. The way low substantivity is achieved is to build into the dye structure bulky side groups, which sterically hinder the dye molecules from approaching dye sites on the fibre.

Reactive dyes in liquid form, as supplied for conventional screen printing, are not suitable for ink-jet printing. Commercial dyes contain quite high levels of salt (sodium sulphate or sodium chloride) and this can cause corrosion of jet nozzles. The water solubility of the dyes is also reduced. Therefore, the majority of the salt has to be removed in reactive dye ink formulations. This is generally achieved by the process of reverse osmosis (RO), in which a semi-permeable membrane is employed to separate the ionic species.

Table 12.1 Major types of reactive dyes[9]

Reactive group	Relative reactivity*
Dichlorotriazine	1
Difluorochloropyrimidine	2
Dichloroquinoxaline	3
Monofluorotriazine	3
Vinyl sulphone	4
Monochlorotriazine (MCT)	5
Dichloro- and trichloro-pyrimidine	6

* 1 – most reactive, 6 – least reactive.

Even with reduced salt levels, dye solubility in reactive dye inks can be a problem. As a result, manufacturers have turned to the use of lithium as a partial replacement for sodium as the cation associated with the anionic, sulphonated dyes.[10] Apart from the dye, the inks contain hygroscopic (or hydrotropic) agents such as diethylene glycol, propylene glycol, and diethyleneglycol monobutyl ether, to avoid drying out of the ink in the nozzles, surfactants and phosphoric acid-based buffers.[11] These modifications partly explain the high cost of the inks, which, weight for weight, are more expensive than gold. Fixation of reactive prints on cellulosic substrates is by atmospheric steaming for 10 minutes at 102ºC, followed by a wash-off.

12.2.2   Acid dyes

These water-soluble anionic dyes are the common choice for printing wool, silk and nylon. They do not react with the fibre to form covalent bonds, but instead are attracted to positively charged dye sites on the fibre. The shades are often deeper and brighter than are achievable with reactive dyes. Similar measures have to be taken to purify the dyes in ink formulations as are mentioned above for reactive inks. Hygroscopic agents, such as glycerine, diethylene glycol and triethylene glycol monobutyl ether, and a surfactant are also commonly included in the ink.[12] Fixation after printing is by atmospheric steaming at 101–103ºC for 30–40 minutes, followed by washing and drying.

12.2.3   Disperse dyes

These dyes are applied to synthetic-fibre textiles as finely dispersed particles as they have very limited water-solubility. Inks were developed later than the water-soluble dye inks because of difficulties experienced in producing stable dispersions.[13] Ink manufacturers tend to produce two sets of disperse dye inks, one for direct printing onto polyester, and the other for transfer printing. The latter contain lower molecular weight, more volatile, dyes than the former. Fastness requirements may dictate the use of higher molecular weight dyes, such as in certain apparel end-uses and for automotive seat-cover materials, where light-fastness is critical. However, the transfer printing inks can be printed directly onto polyester fabric rather than paper, and there are advantages in doing this, as the dyes require less time or a lower temperature for the subsequent fixation step than the higher molecular weight ones. The high definition and tonework made possible in transfer printing is matched by the results achieved when jet printing directly onto fabric, and the extra expense of the paper and a second printing operation is avoided.

Once again, the ink formulations have reduced salt content. Fixation of prints is achieved by high temperature (HT) steaming at 170–180ºC, or by dry heat at 190–200ºC, and is followed by a wash-off cycle, including a reduction clear.

12.2.4   Pigments

Pigments are insoluble in water and are applied to textiles as finely divided dispersions, in a similar manner to disperse dyes. Methods of producing sub-micron particle size have been developed over recent years. They have no affinity for textile substrates, and are adhered to their outer surfaces by means of a polymeric, self-cross-linking binder. The fixation step after printing is by dry heat curing. Jet printing with pigments contained in the ink is fraught with difficulties, due to the risk of the particles aggregating and causing nozzle blockages. When the binder is also included in the ink, the risk of blockages can only increase. This also increases the viscosity of the ink to levels that may be too high for some printing machines.[14] Under these circumstances it has been found necessary to apply the binder as a post-treatment (after printing). It is for these reasons that jet printing with pigments has taken such a long time to develop. A detailed study involving four different types of pigment dispersion (polymer dispersion, surfactant dispersion, microencapsulation and surface modification by hydrophilic functional groups) has been carried out.[15] Binder was included in the inks and the optimum ratio of pigment to binder determined (1:2 for all inks). The inks formulated on surfactant dispersion showed good compatibility, printability and textile properties.

Pigment systems require a dry-heat curing or fixation stage after printing. There has been much speculation, however, on the potential for ultraviolet-curable systems in textile jet printing. These solvent-based inks have been in use in the graphics industry for some time. One such system, which does not require a pre-treatment for the cloth being printed, has recently been patented.[16]

12.2.5   Inks for paper printing

Water-soluble dyes such as direct dyes and food dyes are usually used in ink-jet inks for paper printers. In the early days this meant that the prints were subject to smudging during later handling. The problem was solved by making modifications to the dye structure. Sodium sulphonate ($-SO_3^-$ Na^+) groups, which provide water-solubility, were initially converted to sodium carboxylate ($-COO^-$ Na^+) groups. These interact with the acidic size on the paper to produce $-COOH$ groups which cause the dye to become insoluble.[17] It was later found that the ammonium salt of the acid produced even better results, since on warming ammonia is released and conversion to the insoluble carboxylic acid is virtually complete.

12.3   Fabric pre-treatments

All textile substrates destined for colouration, whether by dyeing or printing, require preparation to make them clean and receptive to aqueous treatments. This is the case whether the fibres involved are natural or synthetic, although

natural fibre substrates require a more thorough and expensive processing route. For example, a typical sequence for woven cotton fabric is as follows:

Singe > desize > scour > bleach > mercerise > dry > weft-straighten > batch

The order of these processes may vary slightly and some of the processes can be combined. It is during the hot alkaline scouring stage that the hydrophobic outer layer of the cotton fibres is removed. Mercerisation with concentrated caustic soda solution improves dye yield and lustre for cotton fabrics. A less severe causticisation process is used for viscose rayon and lyocell fabrics.

The batched fabric should then be checked for wettability. If this is satisfactory it is ready for dyeing or printing (if printing, the fabric is often labelled 'P for P' – prepared for print). Fabric absorbency is important in screen printing because, if the fabric is water-repellent, the first colour printed will not be absorbed before the fabric reaches the second screen, where the first colour will be smudged. However, should the fabric be very absorbent the print paste may penetrate too far through to the back, resulting in poor colour yield and subdued colours. A compromise is therefore required. The same applies to fabric intended for jet printing.

Woven fabrics contain size, knitted ones have knitting oils, non-wovens contain lubricants as do carpets, and all these must be removed.

12.4   Pre-treatments for ink-jet printing

12.4.1 Cotton and cellulosics

Cotton, viscose rayon and lyocell fabrics are normally jet printed with reactive dyes by the two-phase method, i.e. the fabric is pre-treated with thickener and alkali, while the ink contains the dye. The pre-treatment liquor is normally applied with the aid of a pad mangle, though it could be screen printed. In either case the fabric must be dried to about 5–7% moisture content before printing. The main constituents of the aqueous liquor are usually thickener, alkali and urea. A typical formulation is given in Table 12.2. The nature and role of each of these constituents will be discussed.

Table 12.2 Pre-treatment for reactive dyes (MCT type) on cotton

100 g/L	Medium viscosity sodium alginate, e.g. 6% Lamitex M5
100 g/L	Urea
20–30 g/L	Sodium carbonate

Pad (approx. 75% pick-up) – Dry at 120°C or below*
For viscose rayon increase urea to 200 g/L and add 10 g/L Lyoprint RG (Ciba)

* The reason for the low drying temperature is that urea is unstable at higher temperatures and these cause high levels of fumes at the stenter exit.

Thickener

Thickeners are employed in printing to preserve the sharpness of edges and outlines by countering the natural wicking effect of the substrate. In addition they hold moisture to enable dyes and chemicals to dissolve and enter the fibres during the steaming stage after printing and drying. They also modify the flow properties (rheology) of the ink or print paste. The thickening agent should not react with either the dye or other chemicals present because, if they do, an insoluble product usually results. This does not wash off and the fabric becomes stiff.

Natural product-based thickeners are carbohydrates and contain many hydroxyl groups, which is why they absorb moisture so well. However, this also means that they react with reactive dyes in a similar fashion to their reaction with cellulose, another polysaccharide. In practice this restricts the choice of thickener to one type only, sodium alginate. This product is derived from brown seaweed and is polyanionic. It is this property that prevents the anionic reactive dyes from reacting with the thickener, since both have negative charges and so repel each other. Various grades of sodium alginate are produced, ranging from low to high molecular weight. The low molecular weight grades produce high solids content thickener solutions with fairly Newtonian flow properties, whereas the high molecular weight grades produce low solids content pastes or inks with highly pseudoplastic (shear thinning) flow properties. When the thickening agent is being applied to fabric prior to printing, as in this case, the flow properties are not as important as the solids content. A higher weight of thickener on the fabric assists the preservation of edges and outlines in the printed design during drying and steaming.

When the thickener is included in the aqueous component of an oil-in-water emulsion and then dried the thickener layer takes on a microporous, sponge-like structure.[18] This produces jet prints with superior definition.[19] There will clearly be environmental implications, however, as the hydrocarbon phase of the emulsion will evaporate into the atmosphere.

Alkali

Reactive dyes react with cellulose under alkaline conditions to form covalent bonds between fibre and dye. There are various classes of reactive dyes, monochlorotriazine (MCT), vinyl sulphone etc., and these require different strengths of alkali for optimum fixation. Sodium bicarbonate is generally recommended for 'all-in' pastes and inks, as it causes least hydrolysis of the dye on storage, but the stronger (and cheaper) alkali, sodium carbonate, is satisfactory for most pre-treatment purposes. Some padding formulation recommendations replace the sodium carbonate in Table 12.2 with 25 g/L sodium bicarbonate.

Urea

Urea is a very common constituent of print pastes as it acts as both dye solvent and hygroscopic agent (or humectant). Concerns have been expressed about the detrimental environmental effect of discharging high levels of nitrogen into waste water,[20] but despite this urea remains the common choice. Many padding recipes for viscose rayon increase the level of urea to 200 g/L.

Other auxiliaries

Another commonly incorporated constituent of the pad liquor is sodium meta nitrobenzene sulphonate (Ludigol, BASF, 25 g/L), a mild oxidising agent, which is included to avoid the risk of reduction, and hence decolourisation, of the dye during steaming.

The inclusion of hydrophilic non-ionic polymers, such as polyoxyethylene diisopropyl ether,[21] ethylene oxide/propylene oxide random copolymers[22] or polyoxyethylene lauryl ether[23] to replace the alginate thickener, has been mentioned in patents, as has the use of hydroxyalkyl imine derivatives.[24] Fluorine-containing water repellents are also claimed to improve colour yields.[25]

Coating formulations for paper intended for ink-jet printing often contain fillers such as silica gel, and this has proved to increase colour yield and reduce bleeding when applied to cellulosic textiles.[26,27]

Some references in the patent literature mention the use of cationic agents, such as polyvinyl pyrrolidone derivatives, in the pre-treatment formulation,[28,29] but this must be viewed with caution. Such agents may increase the colour yield of reactive prints, but there is a danger that, during the wash-off, unfixed anionic dye and hydrolysed dye will stain unprinted grounds.

The requirement of a pre-treatment for cellulosic fabrics has been avoided by including in the ink a durable press finishing agent.[30] Both reactive and acid dyes were examined. An alkaline catalyst was not required for reactive printing.

Cationisation of cotton

There has been a great deal of research into the cationisation of cotton and other cellulosics,[31] and Chapter 16 of this book is dedicated to the subject. This process, which enhances the dyeability of the fibre with anionic dyes, involves the chemical reaction of cationic reactive agents with cellulose. Typically these are quaternary ammonium compounds with reactive groups such as epoxy groups attached.[32] Among the factors which should be considered before such a process is carried out are:

- The cost of the cationic reagent
- The toxicity of the reagent
- The total cost of the process, including drying

Table 12.3 Pre-treatment for silk prior to reactive ink-jet printing

10 g/L	Lyoprint RG (Ciba)
100 g/L	Alginate medium viscosity, e.g. 6% Lamitex M5
100 g/L	Urea
30 g/L	Sodium bicarbonate

Pad (approx. 75% pick-up) – dry at low temperature, 100–120ºC.

- Whether the higher dye fixation level normally achieved is sufficient to prevent staining of the print during the wash-off phase.

12.4.2   Wool and silk

There is a choice to make when printing wool or silk, as either acid dye or reactive dye inks may be used. As explained above, acid dyes provide colours of greater depth and chroma, but reactive prints are perfectly acceptable for most purposes. When a company is printing mainly cellulosic materials with reactive dyes it would make economic sense to use them on silk too, in order to save holding stocks of two ranges of inks. It is very unusual, though, to print wool with reactive dyes. The pre-treatment formulation for reactive dyes on silk is similar to the recommendations for cotton, except that it is safer to use sodium bicarbonate than sodium carbonate (Table 12.3).

The pre-treatment for acid dyes on wool and silk is quite different from that shown in Table 12.3, and there are a number of alternatives suggested by the ink manufacturers. The three main constituents are thickener, urea and an acid or latent acid (a substance that breaks down during fixation of the print to release acid): see below. A typical padding recipe is shown in Table 12.4.

Thickener

The preferred thickening agents for printing with acid dyes are of the manno-galactan type. These are stable to the acidic conditions which are required at the fixation stage. Sodium alginate should not be used, as insoluble alginic acid is formed in the presence of acids. The two main sources of these thickeners are guar gum and locust bean gum. They differ only in the ratio of mannose to galactose units in the polysaccharide structure.[33]

Table 12.4 Pre-treatment for wool and silk prior to acid dye ink-jet printing

150 g/L	Guar gum thickener, e.g. Meyprogum NP 8 (8% solution)
100 g/L	Urea
50 g/L	Ammonium tartrate solution (1 part water to 2 parts ammonium tartrate)

Pad (approx. 75% pick-up) – dry at low temperature, 100ºC or below.

Acid or latent acid

Acidic conditions during the steaming of the printed fabric are necessary to protonate amino groups in the wool or silk. The incorporation of mineral acids such as sulphuric or hydrochloric acid is not recommended, as these will damage the fabric, but organic acids such as citric acid (20 g/L) have been recommended for silk and polyamide substrates. Most formulations, however, include a latent acid. These are generally ammonium salts which decompose during steaming to release ammonia and leave the parent acid. The cheapest option is ammonium sulphate (20 g/L), but there is a small risk, as sulphuric acid may attack some dyes or damage the fabric. The ammonium salt of an organic acid is safer, hence the inclusion of ammonium tartrate in Table 12.4.

12.4.3   Nylon

This is usually printed with acid dyes, using a similar pre-treatment to that shown in Table 12.4. Some experimentation with varying amounts of urea and acid may be necessary to achieve optimum results. A novel approach, in which polyamide substrates are treated with a solution of a bisphenol derivative[34] for 30 minutes at 90ºC, washed, dried, and then jet printed with acid dye ink, is claimed to provide high colour yield and good colour fastness. The incorporation of cationic compounds in a pre-treatment for polyamide substrates has also been patented.[35] Another patent mentions the inclusion of a reagent, *N*-aziridinyl-*N*′-stearyl urea, to reduce bleeding of the subsequent print.[36]

Wool, silk and nylon can also be jet printed with inks containing reactive dyes.[37] In that case sodium alginate is preferred as migration inhibitor/hydrotropic agent rather than mannogalactan types for the reasons previously given.

12.4.4   Polyester

Polyester is printed with disperse dye inks. Disperse dyes require temperatures above the glass transition of the polymer for them to diffuse inside the fibre. There is no great risk of reaction between the dye and the thickening agent, but the latter should be stable to the high fixation temperatures. The usual choice is sodium alginate. This acts as a migration inhibitor during drying and steaming. Synthetic thickeners have also been included as alternatives to sodium alginate. The same bleeding preventer mentioned above for nylon has also been included in a pre-treatment for polyester textiles.[36] For once, urea does not appear in many pre-treatment formulation recommendations, although there are exceptions.[38,39] The inclusion of urea is likely to cause fumes and pollution problems during the high temperature, dye fixation stage. Instead, the ink manufacturers have developed their own formulations, and they should be asked for their latest recommendations. Table 12.5 provides a guide.

Table 12.5 Pre-treatment for polyester printed with disperse dye ink

| 10 g/L | Cibatex AR (Ciba) |
| 100 g/L | Sodium alginate medium viscosity, e.g. 6% Lamitex M5 |

Pad (70% pick-up) – dry.

Other thickeners may be used instead of sodium alginate. One patent[40] includes a mixture of polyacrylic acid, sodium salt (1%) and polyvinyl alcohol (2%) in a pre-treatment formulation; another includes α-tocopherol.[41] A further Japanese patent describes a different pre-treatment for polyester.[42] The formulation contains carboxymethyl starch, sodium chlorate and polyoxyethylene alkyl ether.

Cationic polymers have also been patented for use in pre-treatment formulations for polyester fabrics.[43] In this case there will be an attraction for the anionic dispersing agent in the disperse dye ink. An interesting variation in this approach has also been patented.[44] In this method a polyester fabric is pre-treated with barium chloride solution and dried. The ink contains disperse dye with an anionic dispersing agent with the structure shown in Fig. 12.1. The divalent barium cation presumably replaces the monovalent sodium ion to produce a less hydrophilic, insoluble compound. It is claimed that this procedure reduced the spread of printed drops considerably.

12.4.5   Polyester/cellulose blends

The Japanese company Seiren have patented a method for printing polyester cotton blend fabrics with ink containing disperse and reactive dyes.[45] A pre-treatment formulation including a cellulose-reactive compound, such as isonicotinic acid, a water-soluble polymer and an inactive non-water-soluble oil is mentioned.

12.4.6   Pre-treatments for pigment printing

Some pigment systems for ink-jet printing require a fabric pre-treatment. The binder may be applied to the fabric and dried before it is printed instead of being included in the ink.[46] Another system involves pre-treating fabric with a solution containing multivalent metal salts (e.g. magnesium nitrate). The ink contains
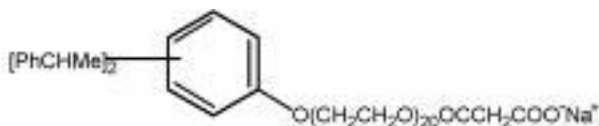
12.1 Anionic dispersing agent.

pigments that are coated (or encapsulated) with resins (e.g. styrene acrylic resins) coloured by oil-soluble dyes.[47]

12.4.7   Paper for transfer printing

The paper for transfer printing is used simply as a carrier for the printed image, and has little or no use after transfer of the design onto the substrate. Therefore the less it costs the better, but it should not be so thin that dye vapour easily passes through it onto the heated surface behind it during transfer. Highly calendered paper based on a kraft pulp is generally favoured.[48] Inorganic fillers, such as finely divided calcium carbonate, china clay or titanium dioxide, are also likely ingredients.

It is also advisable to apply a coating or size to the side to be printed. This serves to provide a smoother printing surface, and one which is impermeable to disperse dye vapour. Sodium alginate, for example, is impermeable[18] and so is a good choice as a size for transfer paper. Starch products, such as sodium carboxymethyl starch, on the other hand, have a granular structure, which allows free passage of disperse dye vapour.

12.5   Post-treatments

When the pre-treated fabric has been dried and then jet printed there is usually little need to provide a drying station to dry the print, as the printing process is so slow. By the time the fabric is batched on a roll it has dried by exposure to the warm atmosphere in the room. If necessary supplementary heating is applied. Sometimes the printed fabric is only required for photographs in a catalogue, in which case it may not be necessary to fix the print. However, in most instances fixation and washing will be necessary. This not only ensures that the full fastness properties of the dyes are realised, but also brightens and alters the colours significantly.

12.5.1   Fixation

Steaming is the process normally used to fix printed textiles. Reactive and acid dyes are steamed under atmospheric pressure at just over 100ºC. During the process steam condenses on the fabric and is absorbed by the thickener and hygroscopic agents in the printed areas. Dyes and chemicals dissolve and form extremely concentrated dyebaths within the thickener film. As a result of the extremely low liquor ratio (approximately 1:1) fixation is much more rapid than in exhaustion dyeing. High temperature steam is necessary for the fixation of disperse dyes on polyester. The T_g of polyester in steam is lower than it is in dry air, and fixation is more efficient. Usually the steam is heated to 170–180ºC at atmospheric pressure, but sometimes pressure steaming at 130–150ºC is used. Pigment prints are cured using hot air in a stenter or a roller baker.

12.5.2   Washing-off

Washing the fixed jet printed fabric is likely to be carried out on a batchwise basis, since the lengths printed are usually quite short. The process, whether batchwise or continuous, takes place in several stages, the first of which should be a cold rinse. The reason for this is that thickener, auxiliaries and loose dye should be removed under conditions where the dye is unlikely to stain white or unprinted ground shade areas. The risk of this happening may be reduced further by the inclusion of reagents that hold the unfixed dye in the bath. For instance, inclusion of 1 g/L sodium carbonate in the first bath when washing off acid dyes prevents protonation of amino groups on nylon, wool or silk, thus removing any potential dye sites.

The main requirement after the first cold rinse when washing off reactive dye prints is to ensure that the temperature of the hot wash reaches a minimum of 95ºC, otherwise hydrolysed dye may not be removed. Fabrics printed with disperse dyes may require a reduction clear with alkali and sodium dithionite ($Na_2S_2O_4$) in order to remove surface dye. The temperature of the bath for this process should not exceed 70ºC as sodium dithionite (also known as sodium hydrosulphite or 'hydros') is unstable at higher temperatures.

12.6   Jet printing machines

These have been discussed in Part I of this book, and reviewed by Dawson.[49] A survey of the machines exhibited at the 2003 ITMA show in Birmingham has also been published.[50] Most of the machines sold for printing textiles are modifications of graphics printers. In the early days the most popular machines were bubble jet (thermal drop on demand) printers, but more recently piezo printers, many of them made by the Japanese company Mimaki, have taken over. Stork also introduced a machine based on the continuous (charged drop) principle,[51] but the high cost of the machine reduced its appeal.

12.7   Limitations

Nearly all the fabric jet printing machines marketed up to the present use a print head that scans across the fabric while it is stationary. The fabric then indexes forward while the head is stationary at the side. In this respect they resemble desk-top paper printers and flat-screen fabric printing machines. Jet printers would be much more productive if they utilised print heads which were stationary, but covered the full width of the substrate.[52] Printing would then be fully continuous, i.e. the fabric would move steadily while it was being printed, as is the case with the Millitron and Chromotex carpet printers, and in rotary screen printing. Productivity could be still further enhanced if a machine were designed that included an applicator for the pre-treatment formulation coupled

with a drying station, in line with the print heads. This design was suggested in 1997 by Hawkyard,[52] and has been the subject of a patent application more recently.[53]

12.8   Future trends

The breakthrough for jet printing textiles on a large scale is likely to be as a result of the introduction of a pigment printing system that is superior to those presently available, and one that is lower in price. However, the use of multi-functional dispersing agents (MFDA) in pigment ink formulations [14] may herald the long-awaited breakthrough. These dispersing agents contain polymeric segments within their structure, and so obviate the use of traditional binders. The fact that pigment printing does not require a fabric pre-treatment is a massive incentive, as is the simple fixation step and the lack of a wash-off. The cost of reactive dye inks is also prohibitive.

While the trend for shorter and shorter run lengths continues,[54] the prospects for jet printing improve. When run lengths are short it would probably be better to employ a bank of several graphics-style printers, as have been used by the Japanese company Seiren, rather than one large and expensive continuous printer.

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13
Pigmented ink formulation

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13.1   Introduction

Ink jet digital printing of textiles is an emerging market that presents both tremendous opportunities and significant challenges. The worldwide production of printed fabric is approximately 34 billion square yards and is dominated by rotary screen printing. During the past eight years or so the textile industry, the printer OEMs, designers, entrepreneurs and the raw material and ink suppliers have expressed great interest in digital printing technologies for design, sampling, and short run production.

In other chapters of this book textile ink, particularly dye-based, ink jet print head, color management software, fabric handling equipment and fabric pre- and post-processing technologies have been discussed in detail. In this chapter, I will be focusing on polymer binder containing pigmented aqueous textile inks. I will provide general guidance on pigmented ink jet ink formulation for digital textile printing, including overall considerations, pigment dispersion selection, binder selection, surfactant selection, co-solvent and humectant selection and rheology modifier selection. I will also provide the relevant properties to test and test methods for pigmented ink development, including (1) basic physical properties, (2) ink and print head interaction properties, such as ink and print head compatibility, start-up, jetting and printing, (3) ink and media interaction properties and image quality, (4) durability and permanence of printed images such as cure conditions, wash, crock and dry cleaning, and (5) safety for both the handling of the ink itself and the printed fabric and garments.

I will briefly discuss some optional pre- and post-treatments for pigmented digital textile printing and emphasize the importance of white ink for dark color T-shirt printing.

I will conclude the chapter with further information and advice on some books to consult, major trade/professional bodies, research and interest groups and websites.

13.2   Overview

Initial development in ink jet textile printing focused primarily on dye-based inks such as acid dyes for silk, nylon, and wool, disperse dyes for polyester, and reactive dyes for cotton and rayon. In order to achieve adequate wash properties, they all require complicated and somewhat environmental unfriendly pre- and post-treatments. To some degree, these pre- and post-treatments defeat the original purpose of digital printing in term of ease and fast customization. On the other hand, pigment-based inks are more versatile in terms of fiber types and require only simple dry heat post-treatment (Table 13.1).

Traditional pigment textile printing with emulsion-based textile binders enjoys more than 50% of the total printed textile market. However, development of textile pigment inks with emulsion-based textile binders for ink jet printing is extremely challenging due to ink stability and jetting reliability (drying and nozzle clogging) issues, especially for low viscosity print-heads. Table 13.2 summarizes a view held by some key players in the industry. The unconventional textile binder on the third row in Table 13.2 can be any new polymeric binder developed for pigmented ink jet inks, which may include ink medium soluble but water insoluble random and block copolymers or dispersant, binder and other property combined cross-linkable multi-functional agents.

Table 13.1 Comparisons of ink chemistry

Ink type	Fiber types	Pre-treatment	Post-treatment
Acid	Silk, nylon, wool	Acid donor	Steam and wash
Disperse	Polyester	Thickener	High-temperature steam and wash
Reactive	Cotton, rayon	Alkali	Steam and wash
Pigment	All, best on cotton, polyblends	Not required	Dry heat

Table 13.2 Print head type and viscosity versus ink formulation

	Piezo head, low viscosity	Piezo head, high viscosity	Thermal print head
Pigment ink without textile binder	Yes	Yes	Yes
Pigment ink with conventional textile binder	No	Yes	No
Pigment ink with unconventional textile binder	Yes	Yes	No

Pigment inks for digital textile printing present different challenges than dye-based textile inks. Pigment inks contain 50 to 150 nm crystalline particles as a colloidal system while dye inks are uniform dye molecule solutions. The permanence properties such as wash and crock come from acid (on the dye molecule) and base (on the fabric) interaction for acid dyes, from the dye solubilization in the polyester fibers for dispersed dyes and chemical reaction between the dye and the fabric for the reactive dyes. On the other hand, for pigment inks, the acid–base interaction and/or chemical reaction between pigment particle and the fabric, if any, are simply not enough and a soft, low glass transition temperature (T_g) polymeric binder is required to achieve adequate permanence properties such as wash and crock. The challenges associated with formulating soft low T_g polymeric binder containing pigmented textile ink are as follows:

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

The above difficulties and relatively lower color density, less vibrant colors and smaller color gamut than dyes are probably the reasons for the slow development and relatively low percentage usage of pigmented textile inks for ink jet printing. This may also be associated with the choice of fabric type in current digital textile printing. Since the end use of digitally printed fabrics or assembled garments should not be very different from that of conventionally printed, there is no reason to believe that the pigmented inks for digital textile printing will not reach the same percentage (50%) as in the conventional textile printing industry. I would predict the percentage may be even higher due to the fact that it does not require pre-treatment or complicated post-treatment, which has great synergy with digital printing for simple, easy and fast customization. Easy set-up, fast customization and photographic image quality are the major advantages for digital textile printing, and slow speed and relatively high cost per unit printed area are the major disadvantages. Pre-assembled garments such as T-shirts and ready and easy to assemble items such as flags, scarves, banners, backdrops, etc., are the best places to take advantage of digital printing while minimizing the impact of the above disadvantages of digital printing. These niches will lead the evolution of textile printing from conventional to digital.

The key components in digital textile printing systems are the printer, especially the fabric handling and the garment mounting system, the software, including printing, color management and workflow management, and the ink. Among these three key components, the ink, especially the pigment ink, requires the most advancement to approach the same level as traditional printing in terms

of color strength, permanence, speed and reliability. Some of the leading developers in pigment textile inks for digital printing are Rohm and Haas, DuPont, BASF, Ciba, Trident and Sensient.

13.3   Pigmented ink formulation for digital textile printing

This section will focus on the ingredient selection for a typical pigment ink for digital textile inkjet printing and the function(s) of each ingredient will also be discussed.

13.3.1   Overall considerations

A typical pigment ink formulation for ink jet digital textile printing includes:

- A pigment dispersion for color
- A polymeric binder, a solution polymer or latex for image durability
- Water, for aqueous inkjet inks – a medium to carry other components
- A co-solvent, helping water to carry other ingredients through solubility and compatibility and enhancing the performance of other ingredients in terms of wetting and adhesion to the substrates and jetting properties
- Surfactants, for nozzle and substrate wetting and jetting reliability and also for stabilizing the key ingredients such as binder and pigment particles from coagulation
- Humectants, to prevent drying when not printing
- An antifoam agent to reduce foaming
- A viscosity control agent for damping control and droplet formation
- A penetrant to speed drying on porous media such as paper and textile
- A biocide to prevent spoilage.

Aqueous pigmented ink jet inks have existed for some time. But the challenge for textile printing is to incorporate enough binder in the ink for washability and at the same time to maintain low viscosity, ink stability and jettability. To maintain low viscosity, ink stability and reliable jetting, solids level and formulation space are limited. It is important and sometimes critical for an ingredient to serve multiple functions. For example, a nonionic surfactant of long chain polyethylene glycol with a hydrophobe serves as a surfactant to aid stability and to control wetting and surface tension, as a humectant to slow water evaporation and therefore preventing the ink drying near the nozzle, and as a rheology modifier to control the viscosity profile and therefore jetting and drop formation. A cross-linkable and ink medium soluble but water insoluble polymer could serve as a dispersant to disperse the pigment, as a binder to bind the pigment particles to the fabric for wash and rub resistance, and as a rheology modifier and possibly as a humectant. The key ingredient selection, their

functions and interaction and synergy, will be discussed in detail in the following sub-sections.

13.3.2   Pigment dispersion selection

Pigment dispersion is probably the most important ingredient, and the rest of the ingredients in the ink jet textile ink formulation either serve to position the pigment particles to the right place on the substrate through a given print head in order to generate beautiful images, or to bind the pigment particles to the substrate so that the image can last a long time with respect to different types of resistance such wash and rub.

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

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

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

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

Typically pigment dispersions with low viscosity and high surface tension are more preferable. Low viscosity in pigment dispersion means leaving more room

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

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

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

13.3.3   Binder selection

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

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

To overcome these difficulties, leading companies in this field such as DuPont, Rohm and Haas, and BASF have developed proprietary polymer and formulation technology, which may include ink medium soluble, but water insoluble random or block copolymers with or without cross-linking functionality, dispersants, binders and other property combined cross-linkable multi-functional

agents and protected cross-linkable latex polymers. For example, in the case of protected latex polymers, the soft and sticky binders are protected by a thin layer of shell, like an egg; it is not sticky in the ink before the protective shell is broken, and becomes sticky glue only when the protective shell is broken in the later curing stage.

13.3.4   Co-solvent and humectants

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

13.3.5   Surfactant selection

Surfactants are another key ingredient in terms of delivering the pigment and the binder from the ink to the substrate through the print head. High HLB (hydrophilic and lipophilic balance) surfactants are used typically for aiding the colloidal stability of the systems, and low HLB surfactants are used to lower the surface tension, so the ink can wet the nozzle capillary to establish and maintain the meniscus at the nozzle tip. The importance of maintaining the meniscus at the nozzle tip both in the steady state and in the dynamic state during jetting cannot be overemphasized because it is so critical for start-up, reducing latency (defined as number of firings needed before the ink establishes the first stable drop of jetting), increasing the elapsed time between jetting without refreshing and ultimately long-term reliable continuous printing. For some print heads, reliable jetting or printing can be achieved even when the nozzle plate is wetted. This low HLB surfactant is also a major factor which determines the interaction between the ink and the substrate and therefore controls or affects wetting,

bleeding, dot-gain, dot-quality and ultimately the image quality. Surfactants affect these properties through a physical parameter, namely surface tension (both static and dynamic). The most popular surfactants used for this purpose are relatively short-chain ethylene glycol nonionic surfactants such as the Air Products Surfynol^{TM} line of products like Surfynol^{TM} 465. Anionic surfactants such as Aerosol^{TM} OT are also used.

13.3.6   Rheology modifier selection

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

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

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

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

13.3.7   Other miscellaneous ingredients selection

Pigments, along with dispersants, binders, co-solvents, humectants, surfactants and rheology modifiers (viscosity adjusters), are the main functional ingredients of pigment ink jet ink formulation for textile printing. Other ingredients such as de-foamers, penetrants and biocides may be added as needed. The defoamer is for defoaming as its name suggests. The penetrant helps the ink vehicle to be absorbed into the substrate faster and therefore may make the print touchable sooner. Biocide is for preventing bacteria growth and maintaining ink shelf lifetime. It is always a good rule to keep the formulation simple; if not needed, do not put it in or take it out. When possible, use one ingredient to serve multiple functions.

13.3.8   Putting them together – synergies among all the ingredients

In the previous sections, the function and selection of each ingredient were discussed. In this section, I will briefly talk about how to put them together and the synergy among all the key ingredients.

As stated in the previous sections, pigment is to provide the image, binder is to keep the image permanent, water along with co-solvents is the vehicle to carry the pigment and binder, and surfactants and rheology modifiers are to provide the right surface tension and rheology for reliable jetting through the nozzle and for the proper interaction with the substrate to create a high quality image. Each ingredient needs to do its own job and at the same time to work together in harmony.

If the binder is polymeric latex particles, the binder particles and pigment particles need to have the right energy balance so that they will not be so attractive to each other to create stability problems and at the same time they should not repulse each other in a way to create pigment and latex particle phase separation. Co-solvents such as 2-pyrrolidone along with water are not only a carrier for pigments and binders, but also help to dissolve the low HLB surfactant to make it more effective and to transport it quickly through the medium to ensure low dynamic surface tension. Co-solvents and low HLB surfactants work together to create better wetting condition for both the nozzle and the substrate. Co-solvents often soften the binder and substrate to enhance adhesion. Long EO chain high HLB surfactants can serve as stabilizers, humectants and also rheology modifiers. They can also emulsify the low HLB surfactant to prevent it from forming an oily layer on top. The low and high HLB surfactants together with the co-solvent may form a good cleaning solution for metal and semiconductor surfaces, so the ink is self-cleaning. Polyethylene glycols (PEG) serve as both humectants and rheology modifiers.

13.4   Tests and test methods for pigmented textile inks

As in any field, in aqueous pigment ink jet textile ink formulation, knowing the ingredients and their functions is not enough; we also need to know the important properties and how to test these properties.

13.4.1   Overview of tests and test methods

The following 22 properties/test methods are important in developing pigmented textile ink jet inks.

1. Viscosity
2. Surface tension
3. pH
4. Particle size (PS) and PS distribution
5. Total solids
6. Ink mass density

7. Ink filterability
8. Foaming
9. Air content in the ink and degassing.
10. Drying rate at controlled temperature and humidity and re-dispersability

11. Heat-aging stability (3 days, 10 days and 28 days by PS, ST, viscosity, pH, total solid at 60ºC)
12. Settling rate at regular or accelerated gravity
13. Phase separation

14. Ink fill-up
15. Continuous jetting reliability (x number of square meters of continuous printing without defect)

16. OD or color density
17. L.a.b.
18. Printability (resolution, inter-color bleeding, and color uniformity)

19. 3A wash fastness
20. Dry and wet crocks
21. Dry cleaning fastness

22. Regulatory and safety (wet ink and dry printed sample).

These 22 properties and test methods are separated into seven groups, which consist of a basic property group (1 to 6), a jetting reliability property group (7 to 10), a shelf lifetime property group (11 to 13), actual jetting reliability tests (14 and 15), an image quality related property group (16 to 18), an image permanence property group (19 to 21) and a regulatory and safety group (22).

13.4.2   Basic physical properties

The first six properties (1 to 6) are the basic physical properties. The required value may be unique, but the properties themselves are not. These properties, especially the first three, are specified for a given design of print head. The viscosity (or more precisely the rheology) determines the fluid dynamics for the specific design of the print head geometry, e.g. the sufficient supply of the ink for starting the jetting and during jetting and the drop formation. Otherwise, start-up, latency and ink-starvation massive nozzle dropout can occur. The simple low shear rate Brookfield^{TM} viscosity is far from enough to know the rheology profile of the ink. Even if the rheology profile is known, it is still difficult to predict the fluid dynamics and drop formation due to the complicated geometry of the ink pathway and the driving waveform. One thing print head manufacturers have done is to do computer-based simulations using finite element analysis methods. Nonetheless, the simple Brookfield viscosity provides a starting point and gives the formulators something to think about.

The optimum surface tension for jetting is determined by the surface energy of the channel of the nozzles vs. that of the front face of the print head in such a way that the ink does not ooze out and wet or dirty the front face, but has the maximum force to wet the channel to maintain the proper meniscus at the orifice of the nozzle. The proper meniscus at the orifice of the nozzle must be maintained both when it starts to jet and during the jetting, which means both the static and dynamic meniscus needs to be right. This requires both static and dynamic surface tension to be right. Again the simple static surface tension only provides a starting point and gives the formulators something to think about. In some situations, stable jetting can be achieved even when the front face is maintained wet during jetting. In this case, the ink has to be slow-drying, otherwise nozzle clogging or partial clogging could be a major issue. It is also important to understand that even when the static surface tension of the ink is lower than the surface energy for the front face of the nozzle, the front face may not be wet during the jetting because the dynamic surface tension may be higher than the surface energy of the front face. The optimum surface tension for jetting is not likely to be the optimum surface tension for wetting or controlling the bleeding or coalescence on the substrate of interest. Compromise is unavoidable.

The pH and other chemical characteristics of the ink are important in terms of its compatibility with the construction materials of the print head. The compatibility means that the ink should damage neither the print head materials nor the adhesive bond between different head parts and also that the print head materials should not leach out any material to change the ink composition or properties in any way affecting the stability, jetting or ink performance on the substrate. The particle size and distribution, total solids and mass density of the ink are properties affecting jetting in very subtle ways.

13.4.3   Ink and print head interaction properties

Beside the chemical compatibility between ink and print head mentioned in the previous section, the next four properties (7 to 10) are particularly important in terms of jetting reliability, especially for piezo-based print heads. The ink flow from the ink supply to the substrate during the ink jet jetting process is indeed a series of filtering processes through very small (micron size) orifices such as filters in the damper and the nozzles themselves at very high shear rate (~1 million s^{-1}). The filterability is related to both the content of large particles and shear stability to some degree. It is highly important in ink jet inks because it could shorten the lifetime of the print head. The air content can be measured using an oxygen meter. Typical water contains about 7–8 mg oxygen per gram or 7–8 ppm. For piezo print head, less than 4 mg/g or ppm may be desirable. This is because the high air content in the ink (foam or dissolved) makes the compressibility of the ink high, and when the compressibility is high, the periodically pulsed jetting force or energy is converted to thermal energy and is wasted, instead of being used for ejecting the ink drop. This is particularly important for piezo heads because the jetting push for piezo is relatively high force, short duration and low volume capacity. When the bubbles are big (foam), they could clog the nozzles for both piezo and thermal print heads. Both chemical and mechanical methods of defoaming and degassing have been used.

The drying rate at a given temperature and humidity determines the idle time and the continuous jetting reliability at that temperature and humidity due to crusting, and these problems magnify when the front face gets dirty due to oozing, misting and filament springback due to poor drop formation. The redispersability of the ink also determines how easily the 'spitting' and 'wiping' of the maintenance cycles can recover the problem.

13.4.4   Shelf lifetime properties and actual jetting reliability tests

Properties 11 to 13 determine the shelf lifetime of the ink. The heat-aging stability test is an accelerated test, which measures basic ink properties at different time intervals at 60ºC heat aging. One week of heat aging is approximately equivalent to three months at room temperature (20–25ºC), and four weeks is approximately equivalent to one year. The test can and should be extended to all other properties at the desired final heat-aging time interval before commercialization. Settling rate at regular or accelerated gravity and phase separation are two other properties which are very important in determining shelf life time, especially for polymeric binder containing pigment ink jet inks.

Properties 14 and 15 put properties 1 through 10 into real jetting tests. Test 14 is about how easily one can get the print going perfectly when a new set of ink cartridges is installed, while test 15 is about how long the reliable jetting can last

once the printing gets going. Tests 14 and 15 can be performed on cheap paper substrates. They do not need the right textile substrate because they only test how well the ink interacts with the printer in terms of jetting reliability. In the next section, we will discuss how well the ink interacts with the intended textile substrate in terms of printing quality.

13.4.5   Ink and media interaction properties and image quality

Properties 16 to 18 are about how the ink interacts with the substrate and the image quality for the textile substrate of interest. Optical density (OD) for black, and color density for cyan, magenta, and yellow, are used to assess the intensity that each process color ink can offer, while the L.a.b. measurements provide the full color space (gamut) which a given set of process color inks can achieve for a given printer, printing mode, software and substrate combination. The color density and gamut information is typically stored in a file called the color profile for the given combination. The color intensity and color gamut along with resolution (how fine a line can be printed), inter-color bleeding (how sharp the interface can be between two colors) and color uniformity determine the image quality and the printability. These properties are obtained through spectra colorimeters and image analysis software. To obtain a high quality image is the first step while making the image durable and permanent is the next key step in digital textile printing.

13.4.6   Durability and permanence of printed images

Durability and permanence of the printed images are the key for a successful set of pigment inks for inkjet textile printing. Unlike the reactive, acid and dispersed dyes, the pigmented inks rely on external polymeric binders to achieve the durability and permanence of the printed images. The polymeric binders provide the permanence properties through mechanical binding of film formation and chemical interaction and cross-linking with the substrate. The mechanical binding works for all fiber types of textile substrates; cotton, polyester, cotton and poly blend, and silk to name a few. But chemical interaction and cross-linking only occur when the polymer and the fiber of the substrate have the right pair of chemical reaction functional groups. Therefore, people claim the binder-containing pigment inks work for all fiber types due to the mechanical binding and work best when there is chemical cross-linking between the polymer and the fiber. The hydroxyl group on the cotton fiber is one of the best examples.

Both mechanical binding and chemical cross-linking require the printed samples to be heated. The heating temperature and time depend on the glass transition temperature (T_g) for the mechanical binding and the chemical reaction rate for the cross-linking, which typically ranges from 100ºC to 200ºC and from 30 seconds to 5 minutes. Two types of heating devices are used for the image

fixation: heat presses and hot air ovens. The heat transfer of hot air ovens is through air flow while the heat press is by contact, so the hot air oven takes longer and/or needs a higher temperature than the heat press to reach the same curing point. In the case of a heat press, not only the time and temperature but also the pressure is very important to determine the cure and the fixation for wash and rub, because higher pressure means better heat transfer. The cure conditions need to be optimized for each ink set and fabric combination to achieve the best possible permanence properties without damaging the fabrics. After proper curing and fixation, water and detergent wash fastness, wet and dry crocks or rubs and dry cleaning fastness tests (19 to 21) can be performed, based on standard test methods from the Technical Manual of the American Association of Textile Chemists and Colorists, in the same way as for conventional screen pigment printing.

13.4.7   Regulatory and safety considerations

Although regulatory and safety considerations are beyond the scope of this chapter, their importance should not be overlooked. Both the wet ink and the dried print samples need to be safe for handling and wearing or use. Before commercialization, the safety and regulation of both the ink and printed samples should be assessed by the right professionals.

13.5   Optional pre- and post-treatments for pigmented digital textile printing

The pre-treatment for pigment printing is optional and the post-treatment is simple: dry heat. For pigment digital textile printing, due to limited formulation space and low viscosity, the pigment, binder and other ingredients loading are limited, so pre-treatment with polymers, cationic materials, catalysts, reactive cross-linking agents, etc., may be needed in some applications to enhance color density, image quality, durability and permanence of the image. Spray or screen print polymer binders over the printed images may be a necessary post-treatment for difficult substrates or applications which require extra durability.

13.6   White ink

White ink is critical in digital textile printing. Without white ink, it is not possible to print pre-assembled dark garments such as T-shirts; in the case of roll-to-roll fabric printing, a large percentage of inks and printing time may be wasted to print the background color with a small percentage of image features. Despite its necessity, the development of white ink for digital textile printing has been slow and difficult. Two general approaches are discharge and hiding. The discharge approach is to destroy the pi conjugation system of the visible light-

absorbing dye molecules so that it will not absorb visible light any more. The hiding approach is to put a light-scattering layer on top of the substrate so that the light will not reach the dark substrate to be absorbed. In the case of discharge, the discharging agent has to match the chemistry of the dye molecules so the selection of dyed fabric or T-shirts is limited and it is rare for the discharging to be complete. In the case of hiding, inorganic or organic pigments can be used to scatter light. The inorganic pigment can be any metal oxides or salts such as titanium dioxide with high refractive index. Organic pigments can be solid bead with relatively high refractive index or with a hollow core. The metal oxides or salts, especially titanium dioxide, may be more effective, but tend to be high density, so settling is a big issue in low viscosity ink jet inks. Organic pigments may not have settling issue or abrasion to wear the print head, but could be less effective. To obtain enough whiteness, pre-treatment may be required or discharge and hiding may be combined. No ideal solution has yet been found.

13.7   Sources of further information and advice

For general background on inkjet, *Inkjet Technology and Product Development Strategies*, written by Stephen F. Pond and published by Torrey Pines Research, is recommended. It covers print head design, ink formulation, media, interactions among these three key components of inkjet and the overall system integration. It also offers some information about the market and the existing and new applications of inkjet technology. For basic knowledge on textile testing, the *Technical Manual of the American Association of Textile Chemists and Colorists* is a standard book. For the most current events and developments, the following websites should be surfed frequently:

- IT Strategies, www.it-strategies.com
- Lyra Research, www.lyra.com
- Web Consulting, www.web-eu.com
- www.tc2.com
- FESPA, Federation of European Screenprinters Associations, www.fespa.com
- ISS Imprinted Sportsware Show, www.issshows.com
- ITME, International Textile Machinery Exhibition

14

Formulation of aqueous inkjet ink

H NOGUCHI and K SHIROTA, Canon Inc., Japan

14.1   Dye–fiber interaction

There are several types of inkjet inks for textile printing, depending on kinds of fabric and dyes. In each combination various dyes and textiles have been developed and improved to satisfy advancing practical requirements. Table 14.1 shows a classification established in the textile industry on the fabric–dye set, from which a primary choice of dye is made.

The principles of dyeing of polymer are exemplified in Fig. 14.1, in which the inter-molecular interaction and chemical bonding between dye molecule and polymer in fiber are shown.

Acid and direct dyes are bound by ionic bond, reactive dyes on the cotton are bound by covalent bond, disperse dyes are bound by Van der Waals forces and hydrogen bonding. The printing processes give favourable chemical and physical conditions for these bindings. Process conditions promote adsorption
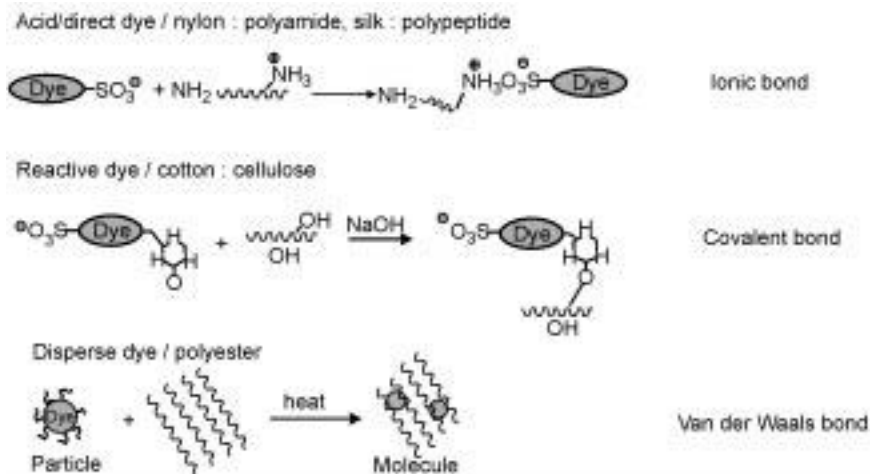
14.1 Inter-molecular interactions and chemical bonds.[1]

Table 14.1 Types of fabric and dye[2]

	Cotton	Rayon	Wool	Silk	Nylon	Acetate	Triacetate	Polyester	Vinylon	Acryl
Direct dye	●	●		■					■	
Bat dye	●	▲		▲	▲				■	
Sulfur dye	■	■							■	
Naphthol dye	■	▲								
Reactive dye for cotton	●	●	▲	■						
Acid dye			●	●	●					♦
Metal chelated acid dye			●	●	●				●	♦
Chrome dye			●	▲						
Reactive dye for wool			●	▲						
Disperse dye					▲	●	●	●		▲
Cationic dye				▲	♦	▲		♦		●

● good; ■ fair; ▲ applicable; ♦ special use.

Table 14.2 Formulation of dye-based aqueous ink

Dye	0.3–10 wt.%
Water-soluble organic solvent 1	5–15
Water-soluble organic solvent 2	5–15
Surfactant	0.1–2.0
Acid or base to adjust pH	
Water	
Additives (see Table 14.5)	

on the fiber surface, diffusion into the fiber, and dissolving in the fiber polymer or formation of chemical bond. In the case of inkjet printing on textiles these post-processes, including instruments for fixing, can be applied. The formulation of the ink composed of materials for water-based systems are shown in Table 14.2.

The main differences between desktop inkjet printers and textile printers are kinds of dye, their concentrations, and physical properties. The reliability and printing characteristics of the formulation are not inherent properties but depend on print head and process architecture. Ink formulation and properties must be tested and tuned on each printing system.

14.2   Organic solvents and surface energy of ink

The surface energy of ink has very important effects on various working properties. Absorption speed influences printing speed, i.e., the scanning speed of the print head and travelling speed on production. The water-soluble organic solvent and surface-active agent determine the absorption speed of inks. Table 14.3 shows the kinds of solvent used in aqueous inks and how organic solvent affects the surface energy of ink.

By choosing water-soluble organic solvent and its concentration it is possible to reduce vaporization of water and to tune properties of ink such as viscosity and surface tension. Table 14.4 shows how surface energy of ink affects various aspects of inkjet printing and has major effects on reliability and print performance.

14.3   Time-dependent phenomena and surface-active components

The most important factor in ink formulation is to optimize the ink properties to the print head. Dynamic behavior of ink is important in creating the objective size of droplets, in stabilizing the speed, and in reducing satellites. Theoretically, drop formation from a liquid stream in air is controlled by two equations:[3]

Table 14.3 Surface energy of solution of soluble organic solvent and water

Chemical name	γ (mN/m)	Chemical name	γ (mN/m)
Ethylene glycol	54.7	Diacetonealcohol	49.6
Diethyleneglycol	53.8	*N,N-bis*-hydroxyethyl urea	56.6
Triethyleneglycol	52.6	Urea	53.4
Polyethyleneglycol 300	52.4	Acetonyl acetone	36.9
Thiodiglycol	47.2	1,2-Cyclohexane diol	35.7
Hexyleneglycol	40.3	1,4-Cyclohexane diol	52.2
N-methyl-2-pyrrolidone	53.1	3-Methyl-1,5-pentane diol	41.3
2-Pyrrolidone	48.5	3-Hexene-2,5-diol	37.9
γ-Buthyrolactone	51.8	Glycerine	57.3
1,3-Dimethyl-2-imidazolidinone	51.3	Glycerin monoallyl ether	46.3
Sulforan	43.1	Glycerin triacetate (triacetine)	38.1
Dimethylsulfoxide	46.8	Water	73.7
Trimethylol propane	49.9	Ethanol	47.8
Trimethylol ethane	53.7	2-Propanol	39.6
Neopentyl glycol	43.6	1-Methoxy-2-propanol	41.4
Ethylene glycol monomethyl ether	57.1	1-Butanol	26.5
Ethylene glycol monoethyl ether	49.0	Furfuryl alcohol	48.8
Ethylene glycol monobutyl ether	30.2	Tetrahydrofurfurylalcohol	53.5
Ethylene glycol monophenyl ether	41.8	1,2-Butane diol	49.9
Diethyleneglycol monoethyl ether	51.9	1,3-Butane diol	48.0
Diethyleneglycol monobutyl ether	34.7	1,4-Butane diol	42.8
Diethyleneglycol dimethyl ether	51.0	2,3-Butane diol	38.4
Diethyleneglycol diethyl ether	42.9	1,5-Pentane diol	38.7
Triethyleneglycol monomethyl ether	52.4	Triethyleneglycol monobutyl ether	33.9
Triethyleneglycol monoethyl ether	44.0	Dipropyleneglycol monomethyl ether	45.4
Tripropyleneglycol monomethyl ether	44.0		

Ratio of mixture is water : solvent $= 90:10$ by weight.

Table 14.4 Effects of surface energy of ink on printing process

System	Wetting to ink container
	Linear flow in capillary
	Frequency response
	Drop and satellite formation
	Foaming and defoaming
	Wetting to nozzle surface
	Start-up property
Ink properties	Surface tension
	Solubility of colorants
	Stability of dispersion
	Weber number and Reynolds number
	Dissolving of impurities from container
Printing and image	Wetting width on printing substrate
	Penetration speed and depth in substrate
	Mottle (tone homogeneity)
	Dot gain
	Color value

Weber Number: $We = \rho U^2 D / \sigma$
Reynolds Number: $Re = UD / \nu$

where ρ = specific gravity (kg/m^3),
   U = flight speed of liquid (m/s),
   D = diameter of flight liquid (m),
   σ = surface tension (N/m),
   ν = dynamic viscosity number (m^2/s).

The inkjet nozzle requires inking properties so that this number is within a certain range to create an objective drop. In this regard it is important to measure dynamic surface tension and viscosity for a few microseconds. Figure 14.2(a), (b) shows dynamic surface tension of solvent and water mixtures.

   We can tune the dynamic and static behavior of formulated ink by selecting an organic solvent. The rheological behavior of ink at the microsecond scale relates to drop formation from the ink stream ejected from nozzles. Dot placement, spreading, and penetration are phenomena of a few milliseconds. Surface energy in this time range has important effects on image formation. Inks placed on the fabrics spread and are absorbed into pores in fibers, and then go inside the fibers. The dynamic surface energy of ink affects both drop formation and image formation. By measuring the static and dynamic surface tension of ink we can tune absorption speed to printing speed. Fabric surfaces vary in nature. Natural fabrics show a hydrophilic nature and synthetic fibers have a hydrophobic nature. Inks for hydrophilic fabrics have a surface-active solvent or surfactant added. The reason is increased wetting speed.

14.4   Additives

Surface-active components in ink influence capillary flow and drop formation, homogeneous coloration, wiping properties, and reduction of foaming by decreasing the interfacial tension of dissolved air. Other factors affecting the choice of the kind and concentration of solvent and surfactants are solubility and stability of ink. In Table 14.5 additives commonly used are listed. They are for finishing a textile product as ingredients in pre-treatment, inkjet inks, and/or post-treatment. The choice of additive also relates to pre-treatment and post-treatment of each production process.

14.5   Reliability

Reliability has various aspects. Start-up is the principal issue in on-demand water-based inkjet systems. By evaporation of water, the concentration of solid components increases near the nozzle surface. This results in an instantaneous barrier for uniform ejection of the ink stream and for drop formation. The barrier reduces transformation efficiency of energy from ejection pressure to ejection
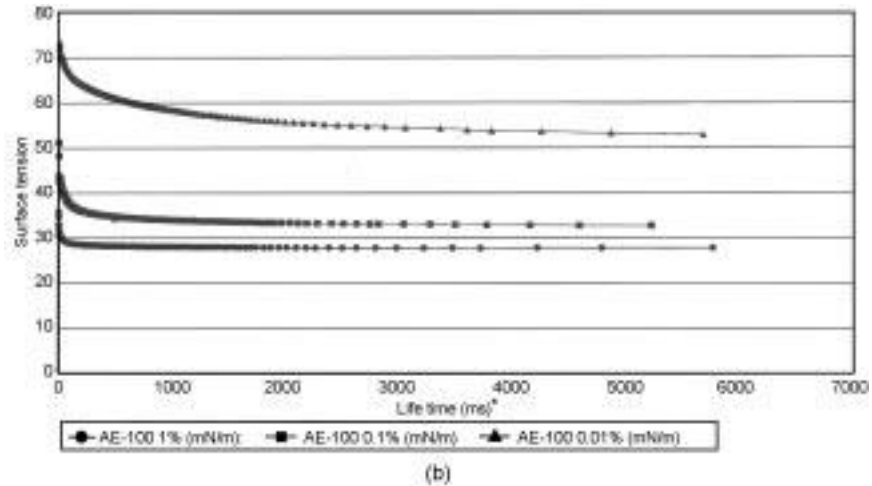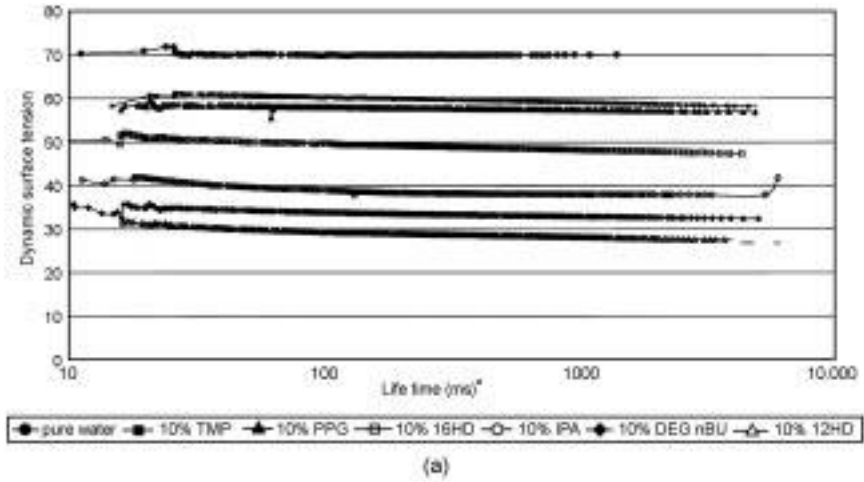
* Life time (ms) = life time of bubble in bubble pressure method for dynamic surface tensiometer.

14.2 Dynamic surface tension of (a) organic solvent in water; (b) surfinol AE-100 in water (acetylene glycol derivative type non-ionic surfactant).

speed and size of droplet. This is called start-up failure. Figure 14.3 shows the evaporation speed of solvents from a mixture.

As shown in Fig. 14.3, evaporation of water is slower by incorporating of water-soluble organic solvents having two or more hydroxyl group or a hydrophilic nature. Start-up failure causes the image edges and ends of the substrate to lose color and sharpness. Cleanliness around the surface of the ejection nozzle also affects steady ejection, so the ink is rendered self-cleaning by redissolving the residual portion of the ink on the nozzle surface. Stability of

Table 14.5 Ink additives

Surfactant	UV absorber
Anti-oxidizing agent	Hygroscopic agent
IR absorber	Fluorescent whitening agent
Anti-flammable agent	Fastness enhancer
Perfumes	Fixing accelerator
Antiseptics	Disinfectant

dye from oxidative, reductive, and hydrolytic breakdown generates unfavorable species on shifting physical properties of ink. Physical shift of ink causes print failure such as clogging, precipitation, pH shift and interaction between print-head materials. Increase of low volatile organic solvents usually give better reliability, although there are some deficiencies in this method. Image bleeding on HT fixing, color stain on washout, mottling after drying, and diffusion transfer on the process after printing may occur, so optimum choice and concentration becomes important.
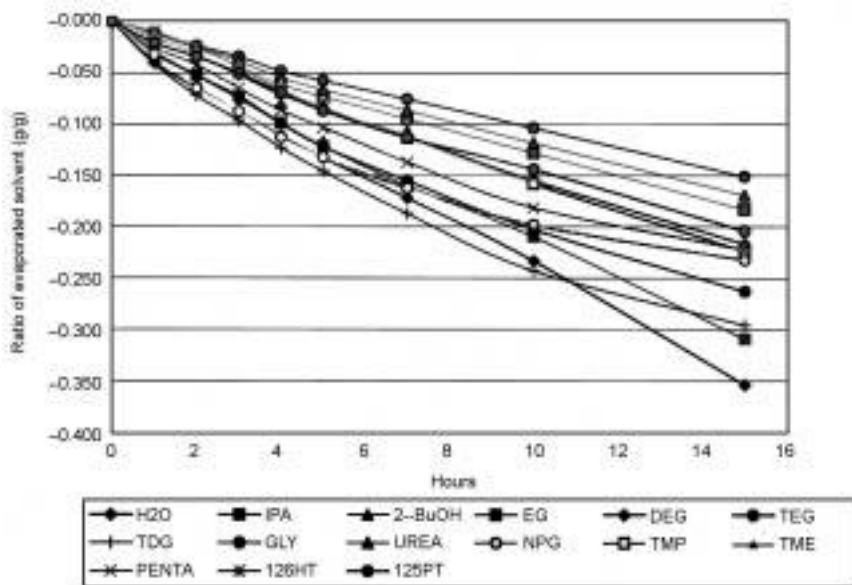
Abbreviations: ETOH: ethanol; IPA: isopropyl alcohol; 2-BuOH: 2-butanol; H_2O: water, EG: ethyleneglycol; DEG: diethylene glycol; TEG: triethylene glycol; TDG: thiodiglycol; GLY: glycerine; NPG: neopentyl glycol; TMP: trimethylol propane; TME: trimethylol ethane; PENTA: pentaerythritol; 126HT: 1,2,6-hexane triol; 125PT: 1,2,5-pentane triol. Condition for measurements: weighting method 25°C, 60% RH, no air flow.

14.3 Evaporation speed of solvents from 1:1 mixture of water and organic solvents.

14.6   Production process of inkjet-printed textiles

Figure 14.4 shows a typical production process of inkjet textile prints. In the process, pre-treatment and post-printing relate strongly to ink properties. Usually pre-treatment material and loading weight by padding or coating on fabrics must be determined carefully.

The pre-treatment materials are hydrophilic, and thus sensitive to moisture content in storage environments. Therefore in storage of treated fabrics, humidity control becomes important. The conditioning of pre-treated fabrics before printing is also important in attaining target image quality. Ink formulation is tuned to adopt these conditioned fabrics on spreading and absorption. If moisture content becomes lower, the saturation and color density curve show reductions. Post-treatment after printing is also related to formulation of ink. If the water-soluble organic solvent is excessively concentrated image bleed will occur during the fixing stage.
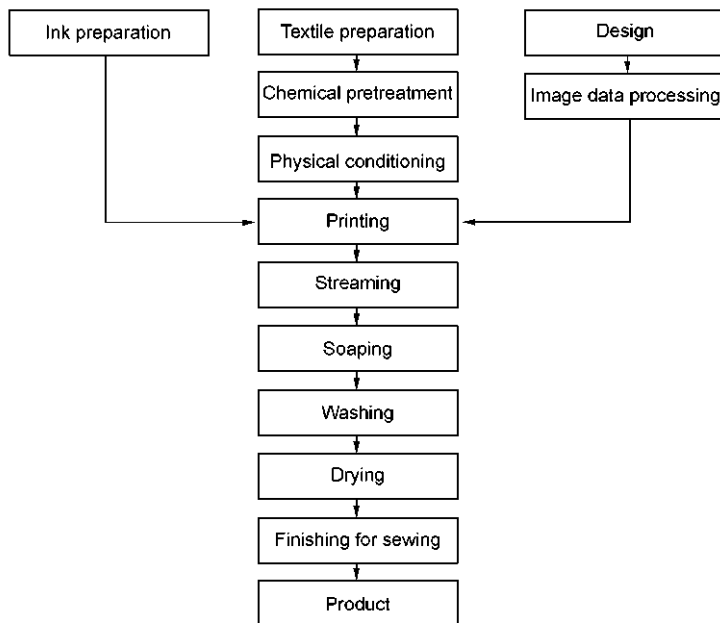
14.4 Production process of printed textiles by inkjet.

14.7   Reactive dye ink

14.7.1 Printing with reactive dye ink

Printing process conditions with reactive dye ink for cotton are exemplified in Table 14.6. The pre-treatment solution commonly contains water-soluble polymer, base (sodium carbonate), and salts (sodium alginate), and urea. All the

Table 14.6 Reactive dye ink process on cotton fabrics

Process	Material	Instrument	Condition
Pre-treatment	Sodium alginate		100–200 g/kg
	Urea		100 g/kg
	Sodium carbonate		30 g/kg
Padding			Pick up ratio 70–80%
Drying		Tenter	100–120°C
Printing	Dye $\sim$ 0.3 mg/cm^2	Inkjet printer	At saturation density*
Steaming		HT steamer	102°C 8min saturated steam
Washing	Wash cool water		
Soaping	1 g/L nonionic surfactant		100°C 3min
Washing	Hot water		60–80°C
Washing	Cool water		

* Dye load weight depends on kind of fabric and condition of treatment.

compounds in the pre-treatment solution should be selected from compounds that do not react with the reactive dye. Amine and hydroxyl group moiety can react with reactive dye. From this point water-soluble organic solvents may possibly react with reactive dyes. This is one of the causes of low yield of printed ink and coloration of wash water along with the printing process. The role of sodium carbonate is as a catalyst to promote hydrolysis by increasing pH. The role of sodium alginate and urea is homogeneous dyeing and keeping moisture in the fabric. There are many alternatives in each component. Ink droplets are laid down evenly by the film-formed hydrophilic nature of pre-treatment materials and the fiber surface. For promoting rapid wetting of ink to the pre-treated surface, inks often contain surface-active compounds.

14.7.2   Reactive dye and reaction mechanism

In Table 14.7 commercial reactive dyes are listed. They are the latest dyes for textile printing, including inkjet printing. Historically, various reactive dyes

Table 14.7 Reactive dye for textile printing

Products by Nippon Kayaku Co.	Products by Ciba Specialty Chemicals, Inc.
KAYACION Yellow P-5G liquid 33	CIBACRON Yellow MI-100
KAYACION Orange P-G liquid 20	CIBACRON Golden Yellow MI-200
KAYACION Red P-BN liquid 33	CIBACRON Orange MI-300
KAYACION Red P-4BN liquid 25	CIBACRON Red MI-400
KAYACION Blue P-3R liquid 40	CIBACRON Red MI-500
KAYACION Turquoise P-3GF liquid 33	CIBACRON Blue MI-600
KAYACION Black P-NBR liquid 40	CIBACRON Turquoise MI-700
	CIBACRON Gray MI-800
	CIBACRON Black MI-900

*Table 14.8* Reactive moieties in reactive dyes

	Type of reactive moiety	Reaction temperature	Dip dyeing	Vat dyeing	Printing
DCT:	dichloro triazine	Low	●	▲	
VS:	vinylsulfone	Medium	●	●	■
MFT:	monofluoro triazone	Medium	●	▲	
DCQ:	dichloroquinoxaline	Medium	●		
CFT:	monochlorofloro triazine	Medium	●		
MCT:	monochloro triazine	High	●	●	●
TCP:	trichloro pyrimizine	High	●		
MNT:	nicotinic acid triazine	High	●		
MCT/MCT:	polyfunctional (uni moiety)	High	●		
VS/VS:	polyfunctional (uni moiety)	Medium	●	●	
MCT/VS:	polyfunctional (same moiety)	Medium to high	●	■	
MFT/VS:	polyfunctional (same moiety)	Medium	●	●	

● good; ■ fair; ▲ applicable.

have been created by attaching reactive moieties to acid and direct dyes. They are summarized in Table 14.8. Of the 12 groups in Table 14.8 the vinylsulfone (VS) type and the monochloro triazine (MCT) type are the majority of the market. Furthermore MCT is the most popular in inkjet inks. Reactive dyes undergo hydrolysis at the initial stage of the reaction, therefore to get long-term stability of formulated ink it is very important to control the pH range and to choose compounds having acidic and basic nature. In the course of development, the kind of acidic or basic compounds or buffer must be determined by careful experiments. The reactive dye generates species such as Na^+Cl^-, SO_4^{2+} by hydrolysis. The washout process is important in removing inorganic and free organic compounds to give the right quality.

## 14.7.3   Stability of reactive dye ink

Figure 14.5 shows possible reactions during storage and in printing and fixing on cellulose. Reactive dyes can react not only with the fiber nucleophile (cellulosate anion) but also with nucleophiles, such as amino moiety and hydroxyl, present in ink or pre-treatment ingredients. From this mechanism there are several unfavorable courses of reaction by reactive dyes. This reaction reduces the efficiency of coloration of a polymer by a dye–fiber reaction (fixation) and results in dye wastage. Therefore some part of the dye is inevitably lost in the post-treatment stages. If the wash-off process is incomplete, the product suffers from reduced wash fastness. A more efficient material and condition for reactive dye has long been sought. The inkjet process has not changed the situation in this regard.
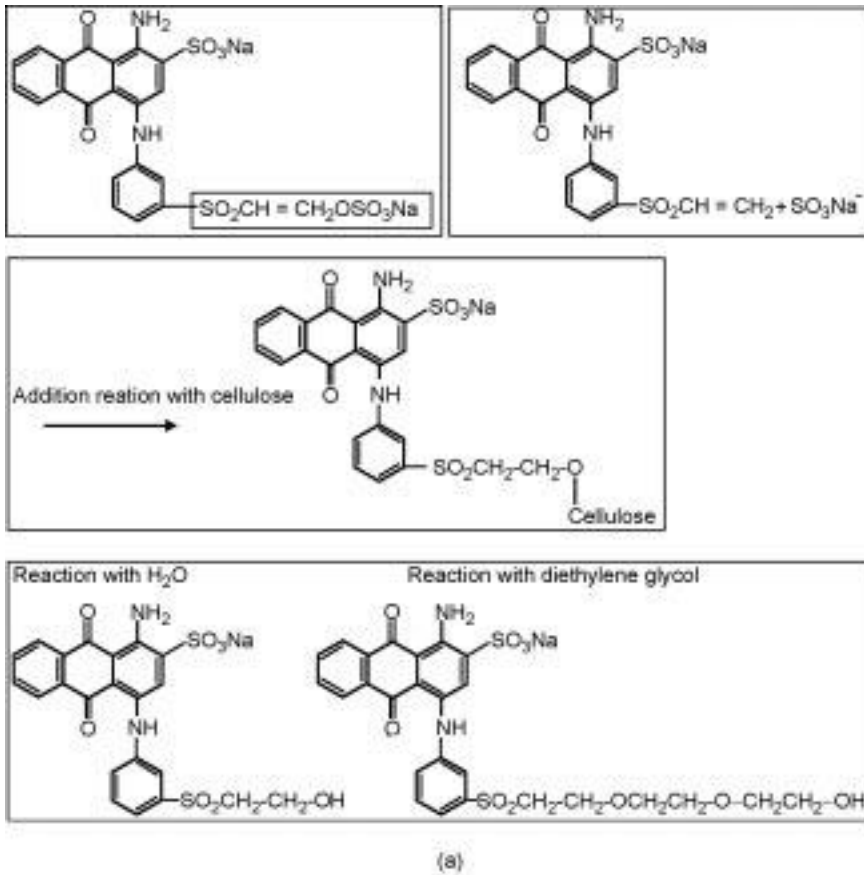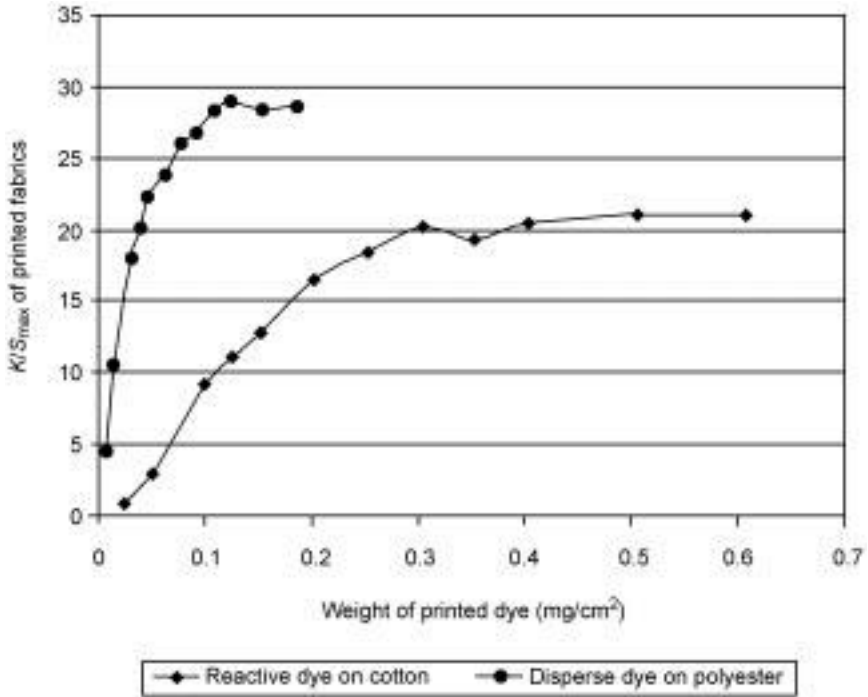
14.5 (a) Reaction of vinylsulfone type reactive dye.

14.7.4   Dye load and coloration

The yield of dye on dyeing is limited by the unreacted part of the dye as explained in Section 14.7.3. For this reason the concentration of reactive dye decline is relatively high compared to desktop printer ink. There is also another reason in the high surface area of fabrics. Figure 14.6 shows the dye load on printing versus $K/S_{\lambda max}$. $K/S_{\lambda max}$ represents the K/S value at the reflection maximum of the final fabric, where K/S is the ratio of absorption coefficient to scattering coefficient defined in Kubelka–Munk theory. In Fig. 14.6 experimental results by disperse dye are also plotted and show the lower dye load weight and higher efficiency on the K/S tone curve. The slower saturation in the tone curve mainly comes from dye loss by hydrolysis. The total amount of ink

Nucleophilic substitution reaction with cellulose

with H₂O

with diethylene glycol
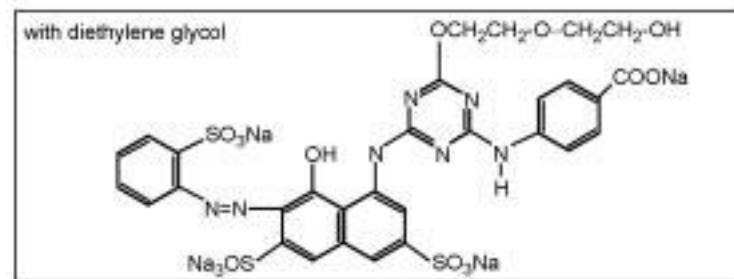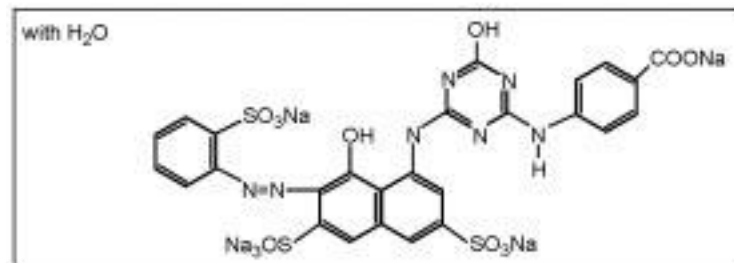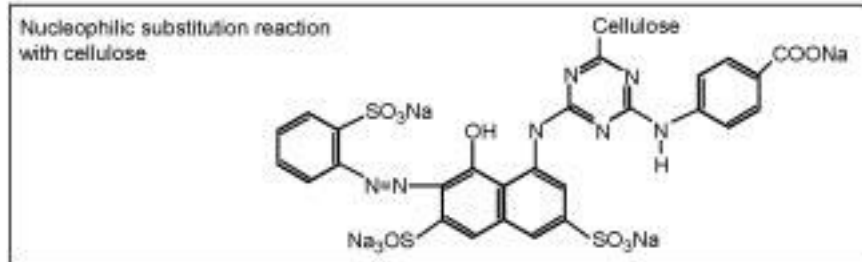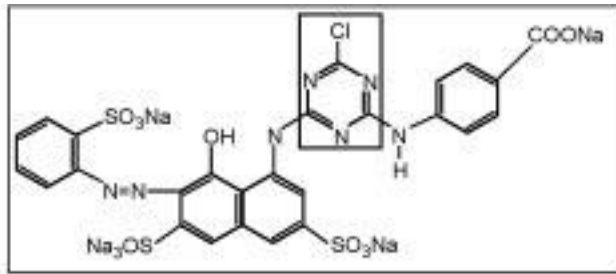
(b)

14.5 (continued) (b) Reaction of monochlorotriazine type reactive dye.

14.6 Dye load on printing versus $K/S\lambda_{max}$ of printed fabrics (K/S values are at reflection maximum of measured textile samples).

on the fabric can be increased by a multi-pass method, but in such a case speed and resolution are sacrificed. For many years, the lower yield in the reactive dye has remained unsolved in textile printing.[4]

14.8   Disperse dye ink

14.8.1 Printing with disperse dye ink

Printing process conditions with disperse dye ink for polyester are exemplified in Table 14.9. The pre-treatment materials give homogeneous wetting to the polyester and ink-receiving layer, giving good image quality and smooth transport to the fiber. Pre-treatment ingredients are selected and formulated from these objectives. Polyester is hydrophobic in nature, so the pre-treatment with hydrophilic polymer has important effects on print quality.

14.8.2   Kind of disperse dye for inkjet

Commercial dyes for coloration of polyester fabrics are exemplified in Table 14.10. For inkjet printing by disperse dye, there are two methods: (i) direct

Table 14.9 Disperse dye ink process on polyester fabrics

Process	Material	Instrument	Condition
Pre-treatment	Sodium alginate		100–200 g/kg
	Citric acid		0–2 g/kg
Padding		Pick up ratio	70–80%
Drying		On tenter	100–120ºC
Printing		InkJet printer	Dye ~0.1 mg/cm^2
Steaming		HT steamer	170–180ºC 8min saturated steam
Wash off	Cool water		
Soaping	1 g/L nonionic surfactant		40ºC
Soaping			60–90ºC
	1–2 g/L hydrosulfite		
	2 g/L causticsoda		
	1 g/L surfactant		
Wash	Hot water		40–60ºC
Wash	Cool water		

printing, and (ii) dye sublimation transfer printing. For sublimation transfer, relatively lower molecular weight and more hydrophobic disperse dyes have been adapted. The structural group of the molecule is the same as that of the D2T2 dye for photo print. The sublimation transfer method is composed of inkjet printing onto a transfer sheet and transfer to fabrics by a heated press. It needs no other post-treatments such as steaming and chemical fixing. Because of its simplicity, the system has been adapted to small production runs in the consumer market. The dispersion technology is the same as for direct printing with disperse dye.

14.8.3   Ink formulation for direct printing

Disperse dyes are prepared as water-borne dispersions by a similar process of pigment dispersion as for inkjet. Inks with disperse dye differ greatly from screen-printing inks in terms of range of particle size, kind of dispersing agent and final viscosity.[5] The role of polymers in the textile paste for the screen ink is moved to the pre-treatment polymer. The dispersed colorants are usually prepared as concentrations (10–20 wt%) of dispersion in water and are highly purified. The range of mean particle size is roughly from 100 to 250 nm (in a distribution from 20 to 400 nm) by eliminating coarse particles including polymer emulsion. The viscosity range of the concentrated dispersion is from 10 to 50 mPa.s. By using low-viscosity, highly particulated dispersions, inks for polyesters are formulated. Table 14.11 shows the preparation processes of disperse dye ink.

The purification processes to get objective levels on storage and ejection stability are important in inkjet disperse inks. For performing the dispersion process the choice of dispersing agent is significant. Table 14.12 lists the system

Table 14.10 Commercial disperse dyes for polyester fabrics

For direct printing		For transfer printing
Products by Nippon Kayaku	Products by Ciba Specialty Chemicals Inc.	Products by Ciba Specialty Chemicals Inc.
KAYALON Polyester Yellow 4GN	TERASIL Yellow DI-100	TERASIL Yellow TI-1000
KAYALON Polyester Orange R-SF 200	TERASIL Red DI-200/01	TERASIL Orange TI-2000
KAYALON Polyester Light Red B-S 200	TERASIL Red DI-300/01	TERASIL Red TI-3100
KAYALON Polyester Pink RCL(N)	TERASIL Blue DI-400	TERASIL Red TI-3200
KAYALON Polyester Blue 2R-SF	TERASIL Blue DI-500	TERASIL Turquoise TI-4000
KAYALON Polyester Turquoise Blue GL-S C200	TERASIL Gray DI-600	TERASIL Blue TI-5500
KAYALON Polyester Black BRN-SF paste 100	TERASIL Black DI-700	TERASIL Black TI-7000
	TERASIL Violet DI-800	

Table 14.11 Preparation process of disperse dye ink

Purification of disperse dye	Elimination of salts and organic impurities
Dispersion	Roll-milling, bead-milling, high-pressure milling
Purification	1 Coarse particle by ultra-centrifugation, ultra-filtration
	2 Inorganic impurities by reverse osmosis
	3 Solublilized part of disperse dye
Addition of additives	
Ink preparation	
Aging	
Purification	By ultra-centrifugation
Bottling	

requirements and physico-chemical properties of the dispersion. The require-
ments from the system and the physico-chemical properties of the ink denote the
design criteria for dispersion. The technical criteria for designing a dispersed
dye are (i) dispersability on ink preparation and (ii) reduction cleaning on wash-
off. These two are frequently incompatible because the former is stabilization
and the latter is easy removal.

Dye concentration in ink is determined by making a standard curve to
correlate *K/S* against the weight of printed ink under system conditions. The
general tendency is exemplified in Fig. 14.6. Part of the dye is not absorbed in
the fiber but is washed out at a reduction cleaning stage under high pH

*Table 14.12* Dispersion design and dispersing agent

Dispersion design		
System requirements	Physico-chemical properties	Dispersing agent
1 Fine particulation	Wetting to active surface of dye particle	1 Poly-sulfonic acid and its derivative
2 Storage stability	Adhesion to dye particle	2 Naphthalene sulfonic acid and its derivative
3 Ejection stability	Low and linear viscosity	3 Lignine sulfonic acid and its derivative
4 Smooth diffusion of particle to fabrics	Low viscosity and good wetting to ink channel	4 Low molecular weight carboxylic acrylate polymer
5 Wash-off property	Good solubility to water	5 Low molecular weight aqueous polyester
6 Stain in white	Good solubility to wash-off cleaning liquid	6 Aqueous polyurethane
7 Keep touch in fabric	Easy removal from fabric	
8 Keep air permeability	Easy removal from fabric	

conditions. The relation depends on all the printing and washing conditions. The concentration of dye in each ink is determined by preparing such a relation as in Fig. 14.6. The yield of dye is better than that of reactive dye ink, because of physical diffusion of disperse dye into synthetic fibers.

14.8.4   Flow rheological property

The preparation of the aqueous dispersion has significant effects on reliability and print performance. How to reduce impurities and how to tune the dye towards the targeted particle size and its distribution are important technical issues, especially in terms of cost. These properties have effects on static storage stability by precipitation, and long-term ejection stability by aggregation, and frequency response through high-speed refilling flow by non-linear viscosity. All these aspects associated with disperse dye, in most cases, present larger difficulties than pigment dispersion in inkjet. The work of Konica-Minolta should be referred to on these points.[6] The series of dispersed dye inks were prepared and examined in terms of storage and ejection performance and non-linear behaviour of viscosity.

   Figure 14.7 shows three types of shear rate versus viscosity curve by disperse dye inks. Ink 1 shows a lowering of viscosity by increasing shear rate. The tendency in Ink 1 is analyzed by imperfect adsorption of dispersant. Unadsorbed dispersant is a cause of agglomeration and larger particles. When ink contains
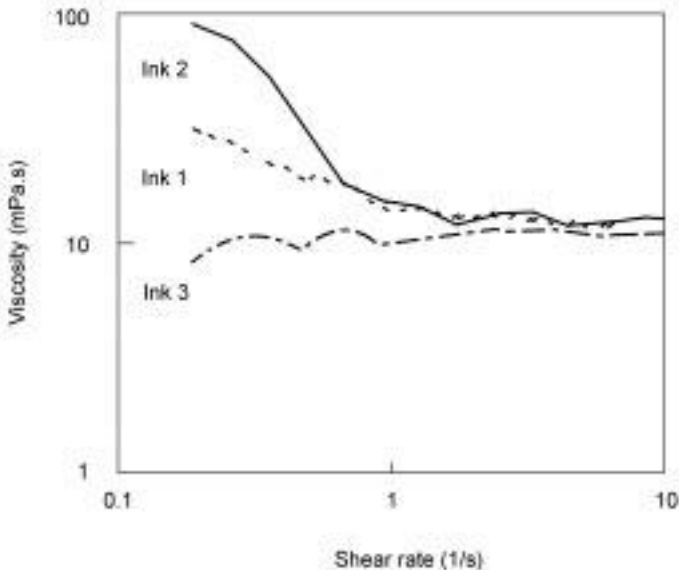
14.7 Viscoelasticity of three disperse dye inks. Instrument: MCR300 Modular Rheometer (Physica Messtechnik GmbH).
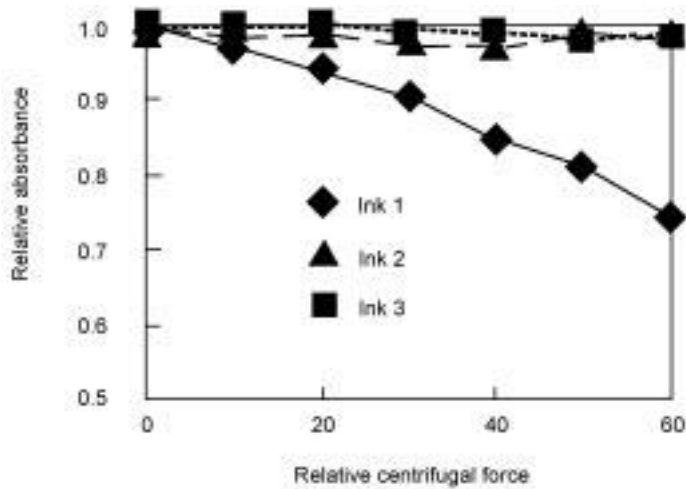
	Dispersant/carrier medium	Auxiliary agent
Ink 1	Optimized for each dye	Not added
Ink 2	Same for all dyes	Not added
Ink 3	Same for all dyes	Added

14.8 Sedimentation properties of three disperse dye inks.

these particles, viscosity behavior tends to curve 1. The curve for Ink 2 shows a large decrease in viscosity by increasing the shear rate. The cause of the large non-linearity in Ink 2 has been explained as structural viscosity by flocculation.

Figure 14.8 shows the results of an experiment relating absorption by sedimentation to centrifugal force applied. From Fig. 14.8 Ink 1 contained larger particles, but Inks 1 and 3 did not contain components of larger particles. This means that the causes of non-linear viscosity of Inks 1 and 2 in Fig. 14.7 are different. The color components in Ink 2 for the black shade were three disperse dyes. Further analysis of the surface energy reveals that if the wetting property of one dye component is weak, the particles tend to aggregate or agglomerate. Ink 3 shows linear viscosity and hence enough jettability and long-term stability. The inks having non-linear viscosity showed a short-term threat of head clogging. These research results in Figs 14.7 and 14.8 suggest that (i) linear viscosity behavior is favorable to inkjet ink, and (ii) wetting of dye and combination of hydrophilic–hydrophobic balance of dispersing agent is important in solving these failures.

14.9   Acid and direct dye ink formulation

Dyeing of nylon/silk/wool using acid or direct dye-based ink is the most popular way in inkjet textile printing. Table 14.13 shows the latest commercial acid and

Table 14.13 Acid and direct dyes for textile printing

Products by Nippon Kayaku	Products by Ciba Specialty Chemicals Inc.
KAYASET Yellow N5G	LANASET Yellow SI-100
KAYASET Red B	LANASET Orange SI-150
KAYASET Red 130	LANASET Red SI-200
KAYASET Blue F-R	LANASET Red SI-330
KAYASET Blue A-2R	LANASET Blue SI-400
KAYASET Black 922(D)	LANASET Turquoise SI-500
	LANASET Gray SI-600
	LANASET Black SI-710

direct dyes for textile printing. On choosing a dye, compared to desktop inkjet printer inks, dyes having lower solubility in water have been adopted for textile printing inks, especially for apparel use. Fiber polymers with repeating moieties, such as amide, peptide and urethane, have a hydrophilic nature and work an ionic attractive force upon acid/direct dyes. Because of these properties, it is not always necessary to apply pre-treatment and fixing agent. Although the wash-fastness of dyed products must satisfy the criteria for quality standards in apparel products, these interactions are sometimes not enough to give high wash-fastness of products. From this tendency the dyes for printing have relatively lower solubility in water. In formulating ink, solubility and long-term stability are key for reliability issues.

Commonly, water-soluble organic solvents having high solubilizing power also exhibit effects on compounds of the ink container and nozzle channel materials in the print head. Careful tests on solubility of dye in certain vehicle solvents under both elevated and lowered temperatures are planned in the manufacturing stage. In the finishing stage fixing agents are applied to increase wash and humidity fastness. The post-treatments give improvements but, in some cases, have disadvantages in other aspects of usability. To overcome these disadvantages, pre-treatment is also another option.

14.10   References

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15

Effect of pretreatment on print quality and its measurement

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15.1 Introduction

A printed textile fabric can be produced by various methods. In the US, rotary screen (69%), flat screen (20%), transfer (10%) and roller (1%) printing are traditionally employed for the manufacture of printed fabrics. Current textile printing speeds are 27 to 55 m (30 to 60 yards) per minute at a 1.5 m (60 inch) printing width. The number of colors in a design can be up to 24. However, typical textile print designs have an eight-color pattern. Also, average lot sizes are 2700 linear meters or longer.[1]

US and EU textile markets are facing challenges from developing economies elsewhere around the globe. The US Textile/Apparel Complex has adopted a demand-activated manufacturing architecture (DAMA) to survive into the twenty-first century. This manufacturing strategy requires 'quick response', time-based competition, small lot sizes (typically 450 m or less), large variety, and linkage into the supply chain.[2]

It has been recognized that the textile printer can achieve these goals by employing digital printing technology. This provides minimized printing lead time, quick sample printing and small lot size. Current digital textile printing, based on inkjet technology, is mainly limited to proofing and sample production. Further developments in ink formulation, jet design, pre/post wet processing requirements and higher throughput will provide the solution for extending digital printing technology beyond the mere preparation of proofing samples. Hopefully, the extension of digital printing into a full production mode will enable the developing textile printing market to thrive in this century.

From the standpoint of traditional textile printing, emerging digital printing is too slow and expensive compared to the mass production characteristics of rotary screen printing. Since the late 1980s customers have demanded short runs, high quality and customization. Digital printing technology supports this customer demand together with digital linkage to the supply chain.[3]

Rotary screen printing is the most popular method (close to 70%) of traditional textile printing. There are many advantages of rotary screen printing:

high-speed production, economical long runs, and a large color gamut from the spot color. Typically rotary screen printers are integrated with dryers and other finishing equipment to provide a continuous printed fabric production – print and dry, or print, steam, wash and dry. The resulting printed cloth has excellent fastness to light, crock (dry and wet), and wash.

Although rotary screen printing offers many benefits, there are also many drawbacks such as low machine efficiency due to pattern changes and correcting printing problems (40% downtime). Also short print runs are not easily accommodated by rotary screen printing. Traditional analog printing involves a lengthy and expensive sampling process in addition to the machine efficiency problem. The design is converted into screen files and screens are engraved. Once the screens are ready, colors are matched and patterns are 'struck-off' on the print machine. With an average strike-off time of 5–6 hours and screen engraving turnaround of two to three days, the total time from design origination to finished product can be several weeks.[4]

Digital textile printing can offer solutions for these run-size and time problems. Digital printing reduces the turnaround time between design origination and finished product. Digital printers do not require a lengthy setup time between patterns and can print continuously. In addition, digital printing also provides the elimination of screen cost in sampling and offers profitable short-run production. Printing without screens eliminates the registration problems and more importantly provides mass customization.[5]

Nevertheless, there are disadvantages associated with digital printing of textiles. It is an emerging new technology and the available inkjet printer models are equipped with inkjet heads typically targeted toward consumer home/office applications. This means that the print heads were designed to be disposable and would not meet the durability demanded in a production environment. Here, there was a lack of proper ink chemistry designed for reliability. Special coatings or lamination were required to achieve proper print quality. Furthermore, original digital printers provide only CMYK process color, which severely limits the volume of color gamut. However, the most advanced wide-format textile digital printers in mid-2004 come equipped with six to eight process color inkjet heads.

Digital textile printing arguably broke the initial technical entry barrier due to recent advances in high speed inkjet printers, specialized inks, and color management software. It can displace screen printing in short, medium and even some high volume production runs on the basis of quality, cost and speed.[6] Due to the low viscosity of inkjet printing inks, textile print media require a pretreatment for improved print quality and post-treatment of the fabric to allow for ink fixation. Print quality, in general, is affected by printing hardware/software (see Parts I and II), substrate (Chapter 12) and ink (Chapters 13 and 14). The present chapter addresses print quality issues related only to substrate and pretreatment: available pretreatments of textile substrates for inkjet printing,

print quality characterization, and pretreatment effects on the print quality of digital textile prints.

15.2   Textile pretreatments for inkjet printing

Traditional screen printing delivers printed fabrics with brilliant colors, sharp and clear patterns, and soft fabric handle. However, it is very difficult to achieve these desirable qualities with inkjet technology. This is due to the different ink delivery methods employed in the traditional method compared to inkjet printing. The viscosity of inkjet inks is very low (up to 5 mPa·s) in order to meet available print head technologies, while traditional printing pastes (inks) have viscosity close to 5000 mPa·s. The printing paste prevents the dissolved dyes from running on the fabrics in the analog printing.[7] There are a wide range of inkjet ink types for substrates constructed from different fiber types. The most common type is water-based inks, which are as low in viscosity as water. Thus, textile fabrics and nonwoven webs require preparatory treatment to achieve acceptable print quality. The type of textile pretreatment depends on fiber contents of fabrics, accordingly on inks based on dyes or pigments, which have substantivity to the fabric's fiber contents.

15.2.1   Matching fiber material and ink chemistry

Woven printing substrates are the most important in textile printing. The volumes of knits and nonwovens used for printing are quickly increasing at the expense of wovens. Printing clothes usually are constructed by weaving or knitting. Woven printing fabrics are produced on a shuttle-less weaving machine by interlacing two sets of yarns, i.e. warp and weft threads, while knitted printing fabrics are formed by intermeshing yarn loops on a circular knitting frame or a warp knitting machine. Typical width of the fabrics is 1.5 m (60 inches). The cotton substrates are the most widely printed (48%), and others consist of cotton/polyester blends (19%), polyester (15%), and viscose (13%). Fabrics made from nylon, acrylics, wool and silk play a minor role in textile printing.[8] Inks for inkjet printing are formulated from the same colorants used in traditional dyeing and printing, but dyes and pigments used in inkjet inks require high purity, submicron particle size, and high tinctorial strength for reliable print head operation and print quality. In addition, the ink's physical and chemical characteristics must be compatible with the fiber chemistry.

Cellulosic fibers are the most frequently used fiber type for print fabrics. Cotton, linen, viscose, and polynosic fibers all consist of cellulosic polymers. Dye classes for inkjet ink formulation suitable for cellulosic fiber printing fabrics are direct dyes, vat dyes and reactive dyes. While direct and vat dyes are relatively large in molecular size and fixed by physical forces, the formation of covalent bonds between reactive dyes and cellulosic fiber makes reactive dyes

the dye of choice. They are of small molecular size and good solubility. Reactive dyes provide a full gamut of colors, are brighter and faster diffusing, and the excess is easily removed in the washing-off process.[9]

Polyester fibers are the most commonly used fibers among synthetic fibers, because of their desirable properties and low cost. Azo, anthraquinone, coumarin, and quinoline disperse dyes are used after reducing the particle size under 1 μm by milling in the presence of a dispersing agent. Proper fixation and post-treatment provide excellent wet-fastness properties.

Polyester/cotton blends have become increasingly popular in recent years. Regenerated cellulose fibers, e.g. viscose, are also mixed with polyester fibers. The popularity of the polyester/cellulose fiber blends stems from the optimum balance of physical properties and wearer comfort. In traditional screen printing, several techniques and dyes and dye combinations were tried with good results, but with difficulties. Ink formulation can be divided into two classes: a single class of colorant and two classes of dye. The former includes pigment, insoluble azo colors, selected vat dyes and selected disperse dyes. Inks formulated from pigments with binder are simple to apply and suitable for fiber blends. Other single dyes show good fastness, but available hues are limited. The latter case uses disperse dye for polyester and reactive dye for cotton in analog printing. However, a pigment and disperse dye combination in polymeric binder will work for inkjet inks.[9]

Polyamide fibers, which include nylon 66, nylon 6 and nylon 11, were the first synthetic fibers produced in commercially significant quantities. Warp knitted nylon fabrics are used for printing. Dyes are selected from the ranges of acid, metal complex acid and direct dyes according to physical and chemical requirements of inks.[9]

Protein fibers are used in higher priced luxury goods due to their desirable appearance and properties far exceeding those of synthetic polymeric fibers. Thus the protein fiber substrates are prime candidates for high value added, short run print production. They are wool, cashmere, and silk. In theory, acid, basic, and direct dyes are suitable for use as protein fiber inks. Ink formulation is limited, however, to acid dyes. Acid dyes are selected because of high colorfulness, acceptable light and wet fastness. For added cost, reactive dyes can be used in inks in higher durability articles made of protein fibers.

In general, all these ink systems require different dye classes for different fiber substrates, and typically require post-steaming, washing and drying to achieve acceptable properties in the printed fabric. There are diverse opinions on post-treatment required in inkjet printing. The different opinions arise primarily due to the varying concepts of where in the textile fabric manufacturing process inkjet printing will actually be performed. Those who believe that inkjet printing will replace current printing technologies in the textile industry feel that post-processing will be readily acceptable. Those who feel that inkjet printing will be practiced by design studios, apparel manufacturers and retail establishments argue for little or no post-processing.[10] Many researchers reported that pre-

treatment and/or ink formulation can eliminate post-treatment requirement in textile inkjet printing. Further information on ink formulation is found in Chapters 13 and 14. Pretreatment of textile substrates in inkjet printing is required to optimize the interaction between the low viscosity ink drops jetted from the print head and capillaries in fibers, yarns and fabric structures. In the next section, we will discuss ink–textile substrate interaction in the context of understanding the needs of pretreatment technology and materials used.

15.2.2   Ink–textile substrate interaction

The choice of textile substrate influences image quality (i.e., inter-color bleed, dot quality, color, visual perception, etc.), ink drying time, and fastness (light, wet, gas, etc.). Fabric substrates are three-dimensional structures, and low viscosity inks can wick into macro-capillaries between yarns and fibers. Inks can also diffuse into the micro-capillaries in fibers. The wicking and diffusion rates are controlled by the surface tension of ink, ink viscosity, yarn and fabric structures, and the polymer morphology of the fiber. Ultimately, dye molecules in the ink droplets must be fixed on or near the surface of the textile fiber substrate for sharp and brilliant color images. The fixing mechanism depends on the dye/fiber combination as discussed in the previous section.

An ink drop jetted onto a fabric substrate wets the surface, then spreads. The wetting and spread are controlled by the surface tension and viscosity of ink, and this initial ink–media interaction ultimately determines the dot gain. The subsequent interactions in the form of wicking (capillary flows of the dye fluid in fibers and yarns) and diffusion determine dot quality, line quality, inter-color bleeding, and mottle. Finally, the solvent (i.e. water) in water-based ink systems is lost by evaporation and absorption.

Dot gain comes from physical dilation and the optical Yule-Nielson effect.[11] The optical dot gain is a measure of the extent to which the area measured by optical density is larger than the real area covered by ink. This is the consequence of the light scattering in the substrate due to light not emerging from the point where it entered, as pointed out by Yule-Nielson. Physical dot gain measures the larger dot size by ink–substrate interaction including spreading. Inkjet printed dot models are shown in Fig. 15.1. Linear dot gains are defined with parameters in Fig. 15.1 as

$$\Delta D_x \ (\%) = 100 \times (D_x - D_0)/D_0,$$
$$\Delta D_y \ (\%) = 100 \times (D_y - D_0)/D_0 \tag{15.1}$$

Dot area gain is calculated from linear dot gains as below:

$$\Delta A \ (\%) = \left[\left(\frac{\bar{D}}{D_0} \right)^2 - 1 \right] \times 100 \tag{15.2}$$
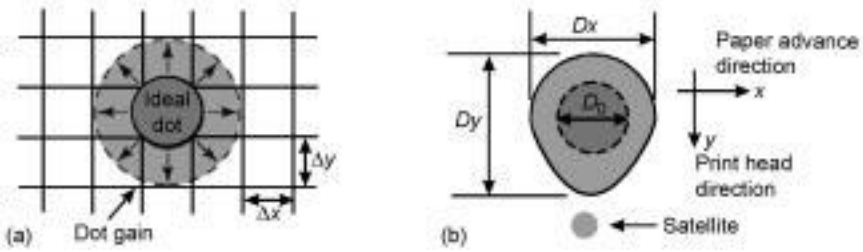
15.1 Dot gain models: (a) ideal model, and (b) dot with a satellite. Δx and Δy are printer resolution, which is inverse of printer addressability.

where $\bar{D} = (D_x + D_y)/2$.

The interaction between ink and textile media also influences the line quality. In addition to line width gain, the fibrous substrate with capillary and micro-pores generates edge raggedness, unsharpness and feathering. According to ISO 13360, edge raggedness is expressed as the standard deviation of differences, d_i, between actual contour and the best-fit straight line as shown in Fig. 15.2.

Inter-color bleeding is most in the invasion of one color into an adjacent area. It stems from the slow rate of ink penetration into the substrate and precipitation of colorant in the second ink caused by additives in the first ink. This can be minimized by pretreatment and ink set selection.

Image noises in the printed area are expressed as graininess for high spatial frequency and mottle. Graininess is a measure of non-uniformity in optical density of spatial scale smaller than $250\ \mu m$, while mottle is that of larger than $250\ \mu m$. Interaction between ink and media generates spatial image noises, i.e. graininess (fine scale) and mottle (coarse scale). Textile substrates have inherently high surface roughness and texture, which causes mottle noises.

The uneven density is caused by ink drops coalescing at the surface and low porosity of the substrates. To reduce this tendency, the textile substrate must be pretreated with high ink absorbing porous particles and/or polymers, which serve as surface finishes on the fabric. These finishes condition the fabric surface to accept printing inks.

We have established the fact that the image quality of digital print depends on substrate surface preparation in the form of chemical and physical pretreatment.
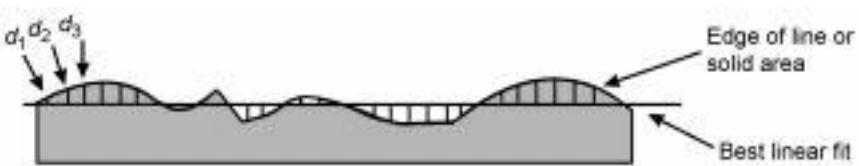
15.2 Edge raggedness, defined as the standard deviation of the differences d_i (ISO/IEC 13660-2002).

The optimal pretreatment process is selected to match the ink system and the fiber content of the substrate.

15.2.3   Pretreatments of textile substrates for inkjet printing

In traditional screen printing, ink pastes contain thickening agent and additives required for fixing chosen colorants. For instance, spot color pastes based on reactive dyes contain alkali (e.g. sodium bicarbonate), urea, and sodium alginate as a thickener. Due to poor resistance to alkali and some additives of inkjet print heads, inkjet inks must be formulated with sub-micrometer size purified dyes and very few additives compatible with print head technologies. Thus all other auxiliaries including thickener are used in pretreatment formulations for target textile substrates. Last decade, we saw rapid development in textile substrate pretreatments for inkjet printing to meet the growing demands of diverse applications.

Textile fabric materials are porous, soft and pliable. In order to achieve well-registered, clear and sharp printing results using water-like printing inks without thickening agents in digital printing, the textile substrates need to be pretreated. The bleeding on untreated fabric in digital printing is another issue that should be taken very seriously. In design studio, retail or end user applications, post-printing washing is not preferred. Thus pretreatments intended for the applications must not only control the wicking and diffusion of ink for higher print quality, but also protect colorant integrity after drying.

Patent literature shows that a large number of patents describing pre-treatments for inkjet printing of cotton fabrics with reactive dye inks were issued in past decades.[12,13] This is understandable from the fact that approximately 50% of worldwide prints are produced with cotton fabrics.

Taniguchi et al.[14] first pretreated polyamide fabrics with bisphenol derivatives, then inkjet printed the pretreated fabrics followed by post-printing washing and clearing off of unfixed dye. The printed fabric showed better color depth, no staining and good wash fastness.

Hees et al.[15] disclosed a pretreatment formula (LupraJet HD) for inkjet printing of polyester and polyester/cotton blends. The disclosed pretreatment works well with inks based on pigments or disperse dyes.

Readers who need further information on pretreatment are referred to Chapter 12. We will discuss the effects of pretreatment on print quality in the next section.

15.3   Effect of pretreatments on print quality

Print quality problems in digital printing of textiles can be categorized into four issues: (1) *appearance-related issues* including line definition, text quality, resolution, image noise, optical density, tone reproduction and (to a lesser

extent) gloss; (2) *color-related issues* including color gamut, color matching and color registration; (3) *permanence issues* including light fastness and water fastness; and (4) *usability issues* including the presence of defects and 'hand'.

Many print quality issues, not surprisingly, are common to both conventional and digital printing techniques. However, inkjet printing introduces a number of peculiarities of its own, for example jaggies (digital artifacts in edges), banding (lines of missing color), and satellites (extra drops of ink). Clearly, for digital printing of textiles to advance, significant improvements in print quality must be achieved.[16]

15.3.1   Print quality measurement

Print quality is defined as how closely the printed dot resembles that intended on an individual and/or collective basis, while image quality is the closeness of the final printed image to that intended.[17] There are many attributes determining perceived image quality: artifactual (unsharpness, graininess, digital artifacts, redeye, etc.), preferential (color balance, contrast, saturation, memory color reproduction, etc.), aesthetic (lighting quality, composition), and personal (preserving a cherished memory, conveying a subject's essence). The last two types of attributes are not quantifiable and not directly related to print quality.[18] Over the past few decades, there has been a virtual explosion in printing and copying technologies, particularly digital printing technologies. These developments have forced many people in the printing/printer business to ask some basic questions about how to specify and assess print quality (PQ) in a consistent way that is not dependent on the specific printing technology they are using. Aside from color measurement equipment (spectrophotometers) and densitometers, there have been relatively few objective means of evaluating PQ of lines, text, print uniformity, registration, etc. In response to this situation, the International Organization for Standardization (ISO) has developed international PQ standards, ISO/IEC 13660 2001(E): Information Technology – Office Equipment – Measurement of image attributes for hard copy output – binary monochrome text and graphic images. Several PQ equipment manufacturers have implemented the ISO standards in their automated PQ equipment.[19] The standards are applicable to digital textile printing, even though their intended area of application is paper media digital printing. Digital print quality attributes derived from ISO 13660 are summarized in Table 15.1.

15.3.2   Pretreatment effects on print quality

Print quality improvements in digitally printed textiles after pretreatments have been reported elsewhere.[7,12–15,20,21] Sapchookul and coworkers[20] evaluated effects of pigment to binder (P/B) ratio on inkjet ink properties (surface tension, viscosity, shear stress and rate) as well as effects of P/B ratio and pigment

Table 15.1 Print quality attributes

Image element	Quality attribute
Dot	• Dot location • Dot gain • Dot shape • Edge raggedness • Satellites
Line	• Line width • Edge sharpness • Edge raggedness • Optical density • Resolution (modulation)
Solid area	• Optical density (tone reproduction) • Color (lightness, chroma, hue, gamut) • Noise (graininess, mottle, background, ghosting)

dispersion techniques on print quality (color gamut and color gamut volume, air permeability, stiffness, and crock fastness). They found that a P/B ratio of 1:2 for all inks gives an optimum color gamut, color gamut volume, and crock fastness.

Fan and coworkers investigated the effect of pretreatments on digital textile prints. They treated woven and knitted cotton fabrics with various pretreatment formulations containing alginate, silicone-based textile softener and nano-silica powder. Digital image analysis and optical microscopy were used to compare various print quality parameters of pretreated fabrics.[21] In the next sections, effects of fabric structures, preparation and pretreatment on print quality (i.e. line width and color gamut) are discussed from results of the author and coworkers' previous research work.[16,21]

15.3.3   A case study of cotton fabric prepared with a special pretreatment

For the case study, we acquired and characterized test fabrics. The fabric structural details are shown in Table 15.2. Test Fabrics, Inc. (Pittston, PA) prepared the cotton fabrics by bleaching and/or mercerization (caustic soda treatment).

Print quality of un-pretreated fabrics

The main objective of the print quality study with un-pretreated fabrics was to explore the relationship between fabric properties and print quality. The results were used as a baseline for a print quality investigation with specially pretreated cotton fabrics. The un-pretreated fabrics listed in Table 15.2 were printed with an Epson Stylus Color 1520 desktop inkjet printer and the OEM ink set supplied

Table 15.2 Description of cotton fabrics studied*

Style	Treatment	Thread count	Yarn size type	Weight (g/m^2)
423 twill	Mercerized	108 × 72	14/1 × 14/1 carded	258
428 sateen	Bleached	96 × 56	20/1 × 14/1 carded	235
437 knit	Bleached	38 × 44	30/1 combed	124
407 poplin	Mercerized	100 × 50	20/1 × 17/1 combed	189
400M print	Mercerized	80 × 76	40/1 × 32/1 carded	107
419 broad	Mercerized	132 × 72	40/1 × 40/1 combed	120

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with the printer. This printer and its ink set are not specifically designed for textile printing.

Line quality analysis

Our results show that different fabric properties affect line quality quite differently. Of the properties studied, one of the most significant is fabric structure. The results of our structure comparisons are shown in Fig. 15.3. As the figure shows, the plain weave fabrics have the highest line width gain, followed by the twill and sateen woven fabrics. The knitted fabric has the lowest gain. However, in the case of the knitted fabric, another important factor may come into play, namely the hydrophobic character of the fabric as demonstrated by wicking tests. The results of these tests are shown in Fig. 15.4. Here, the average line width gain is plotted against the water/alcohol wicking ratio, which is a good indicator of the hydrophilic/hydrophobic nature of the material. From these data, it is clear that the knitted fabric is hydrophobic, whereas the other fabrics are hydrophilic. The correlation suggests that in addition to the effects of structure shown in Fig. 15.3, the hydrophilic/hydrophobic nature of the fabric (or the finish on the fabric) strongly influences the ink–fabric interaction.

Graininess (image noise) analysis

The effect of fabric structure on graininess (image noise) was noticeable, and the fabric variable with the greatest impact on image graininess was found to be yarn size. The results are shown in Fig. 15.5. Yarn type was also considered, but was found to have no significant impact on graininess. Generally, as gray level
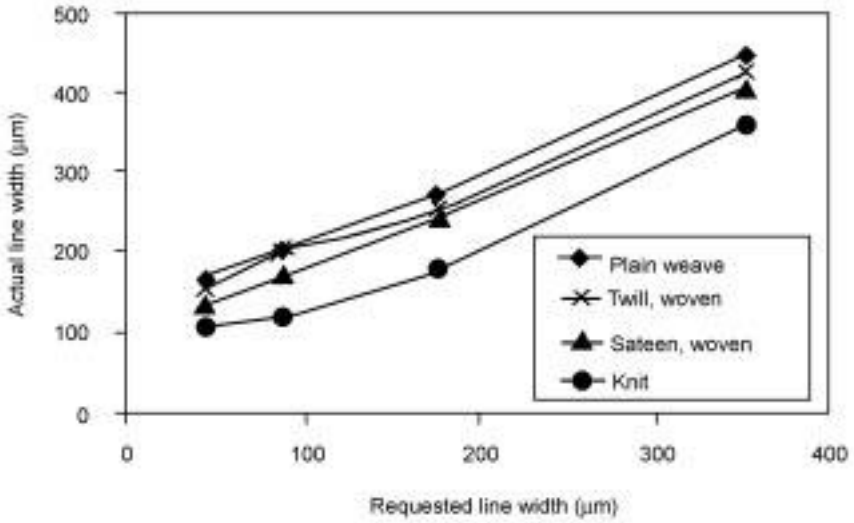
15.3 Effect of fabric structures on line width gain. Samples were prepared with
the fabrics as received. Reprinted with permission of IS&T: The Society for
Imaging Science and Technology, sole copyright owners of *IS&T NIP14
Conference Proceedings*.[16]
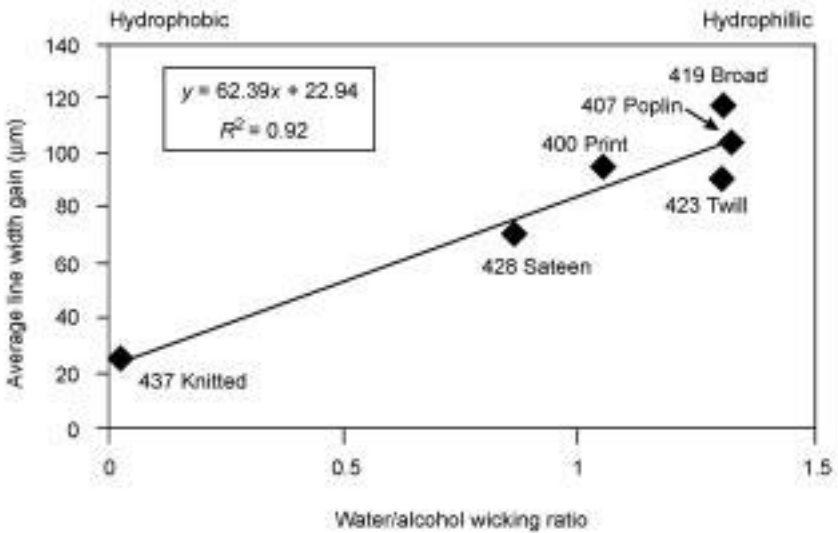
15.4 Correlation between average line width gain and water/alcohol wicking
ratio. Reprinted with permission of IS&T: The Society for Imaging Science and
Technology, sole copyright owners of *IS&T NIP14 Conference Proceedings*.[16]
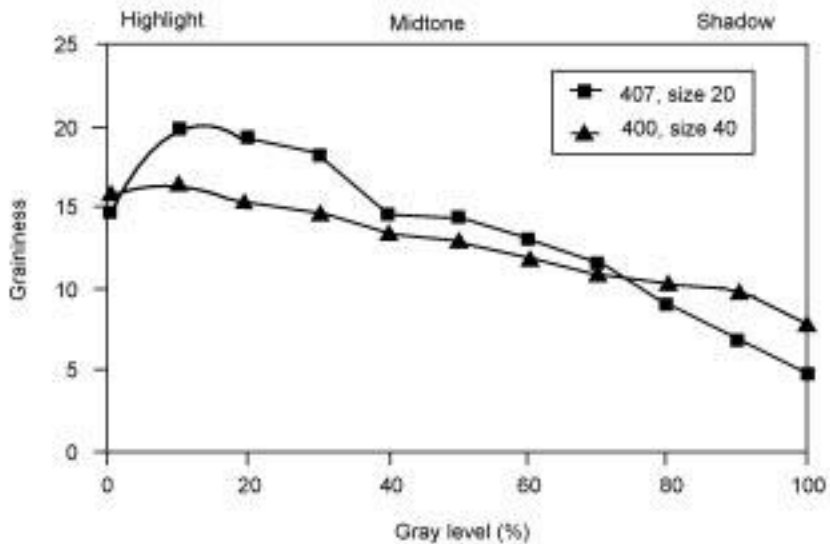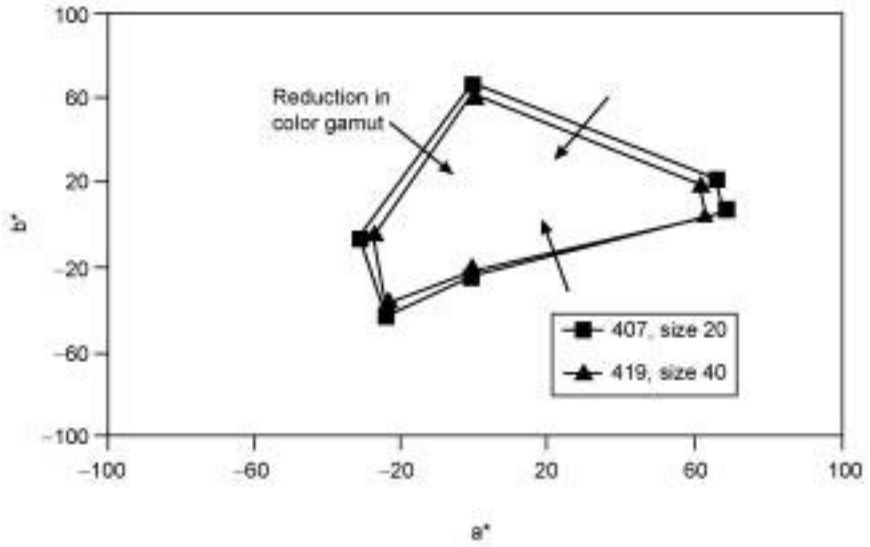
15.5 Effect of fabric structures on graininess. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners of *IS&T NIP14 Conference Proceedings.*[16]

increases from 10% to 100%, graininess decreases. This coincides with the fact that image noise is sensitive to brightness variation. In other words, noise is most noticeable in the highlight and mid-tones regions; it is affected mostly by the size of the yarn and to a lesser degree by the fabric structure.

Color gamut and color accuracy

We were surprised to find that the color appearance of all samples tested was quite similar. Quantitatively, the color gamuts of all the samples were about equal. However, two observations, illustrated in Figs 15.6 and 15.7, are worth mentioning. Figure 15.6 compares the color gamuts of the two fabrics, style 419 and 407. Both of the fabrics consist of mercerized combed yarns, but their sizes are 40 and 20 cotton count, respectively. It appears that the color gamut of print on the fabric (style 407) made of the larger size yarns is larger than that of the finer size yarns. The difference in color coverage area of a*–b* plot (numerical color gamut) is 15.5%. Secondly, although the numerical color gamuts for the plain weave (style 400M) sample and the knitted sample are very close, there is an apparent downshift in the a*–b* plane for the knitted sample, indicating a color shift between the two types of fabric structures (see Fig, 15.7). This apparent shift toward bluer shade stems from the structural difference and/or bleaching treatment of the knit fabric, which gives bluer substrate.

15.6 Effect of yarn size on color gamut. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners of *IS&T NIP14 Conference Proceedings.*[16]
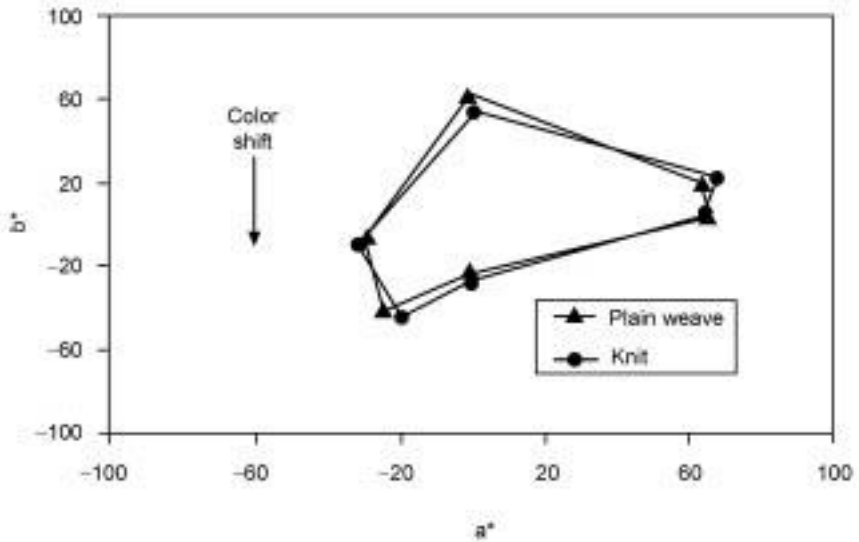
15.7 Effect of fabric structure on color gamut. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners of *IS&T NIP14 Conference Proceedings.*[16]

Print quality of pretreated fabrics

The cotton fabrics described in Table 15.2 were used in this study. All were woven fabrics except style 437 which is a cotton 'T-shirt' knit. The absorbency of cotton fabrics was evaluated according to AATCC Test Method 79: Fabric Absorbency Measurement. As shown in Table 15.3, the absorbency characteristics of these fabrics indicate that surface preparation of the fabrics is different. Notable is the observation that the Knit (437) and the Sateen (428) have a greater affinity for the 2-octanol than they do for water. This shows that these fabrics have hydrophobic surfaces, especially the knit fabric.

The fabric wicking properties were determined by INDA IST 10.0-70 Method 10.3: Fabric Wicking Behavior Measurement. The results are shown in Table 15.4. The data indicate that a slight wicking anisotropy can exist relative to the warp and weft direction in some fabric types. Here a P/F ratio of 1.00 denotes a uniform wicking behavior of the fabric in the warp and the weft directions.

As shown, most of the woven cotton fabrics evaluated wicked fluid at a faster rate in the warp direction than in the weft. The W/O ratio (average value of water and 2-octanol warp and weft wicking rate) is an index of the relative ability of the fabrics to wick hydrophobic versus hydrophilic fluids. With the exception of the Sateen (428) and to a much greater degree the knitted (437) fabric, most of the fabrics studied had a hydrophilic character. This is indicative of the scouring, mercerizing and bleaching treatments given to these fabrics. It is suspected that the knit fabric has some lubricating finish on the yarns as a processing aid.

Pretreatment of cotton fabrics for digital printing

Some preliminary digital printing studies were conducted on all the fabric samples described in Table 15.2. The results indicate that the cotton knit (437) and the plain weave print (400M) fabrics were the fabrics deemed suitable for our further digital printing experiments. Overall, this was expected since twill,

Table 15.3 Water and 2-octanol absorbency*

Fabric	Absorption time (s)	
	Water	2-octanol
423 twill	2.6	2.1
428 sateen	20.4	1.8
437 knit	>1200	1.0
407 poplin	5.8	10.6
400M print	18.6	14.4
419 broad	11.3	16.6

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Table 15.4 Water (W) and 2-octanol (O) wicking rate

Fabric	Fluid	Warp (P) cm	Weft (F) cm	P/F	W/O
423 twill	W	5.87 ± 0.3	5.38 ± 0.2	1.09	1.30
	O	4.70 ± 0.1	3.97 ± 0.1	1.18	
428 sateen	W	3.37 ± 0.1	3.60 ± 0.2	0.94	0.86
	O	4.07 ± 0.1	4.03 ± 0.2	1.01	
437 knit	W	0.20 ± 0.0	0.05 ± 0.0	4.00	0.03
	O	5.80 ± 0.0	5.40 ± 0.1	1.07	
407 poplin	W	5.58 ± 0.1	4.97 ± 0.1	1.12	1.32
	O	4.17 ± 0.1	3.80 ± 0.1	1.10	
400M print	W	4.73 ± 0.2	3.80 ± 0.2	1.24	1.05
	O	4.40 ± 0.2	3.73 ± 0.2	1.18	
419 broad	W	5.75 ± 0.1	4.70 ± 0.2	1.22	1.32
	O	4.32 ± 0.1	3.70 ± 0.1	1.17	

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sateen, poplin and broad fabric styles have inherently coarse surface textures. Furthermore, these fabric styles are less used in textile printing. Moreover, the selection of cotton fabrics, 400M print and 437 knit is based on the absorbency and wicking behavior shown in Tables 15.3 and 15.4. Therefore, fabric 437 cotton knit and the 400M cotton print were the only two fabrics selected for the detailed pretreatment studies herein reported. The selected fabrics were treated with the recipes listed in Table 15.5. The alginate (Prime Alginate T-400) from

Table 15.5 Pretreatment recipes

Treatment	Alginate (g)	Silicone (g)	Silica (g)	Water (ml)
1	4.00	0	0	196
2	2.00	0	0	198
3	0	4.00	0	196
4	0	2.00	0	198
5	0	0	2.00	198
6	0	0	1.00	199
7	4.00	4.00	1.00	191
8	4.00	2.00	2.00	192
9	2.00	3.00	2.00	193
10	4.00	3.00	2.00	191
11	2.00	2.00	1.00	195
12	2.00	2.00	2.00	194

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Multi-Kem Co. and the silicone (Ultratex CSP) from Ciba Specialty Chemicals Co. were used for this study. The nano-silica used was from Nissan Chemical Industries (MEK-ST).

Inkjet printing of pretreated fabrics

The digital textile printing was carried out with an Epson Stylus Color 980 printer. OEM-supplied CMYK inks were used as received. A special pattern was designed to facilitate the evaluation of basic printing parameters after printing. The pattern contains primary colors, red, blue, yellow, green and brown, and lines with different width from 0.5 point to 4.5 points. Epson Photo Paper was used to print the same pattern for print quality reference. The pretreated fabrics were paper-backed for easy transport through the media path of the inkjet printer. After printing, the print qualities were analyzed using an optical micro-scope and a digital image analysis to quantify the print qualities in terms of color-related metrics (L*a*b*) and line quality.

Line quality analysis

Line dilation data for all 13 pretreatment samples were reported.[20] For the plain cotton weave and knit fabrics studied, a pretreatment containing 2% alginate, 1.5% silicone softener and 1% silica shows good balance in colorant retention and line width control. In addition to this pretreatment formula, line qualities of 1% alginate only (traditional printing paste thickener) and photopaper were included in Figs 15.8 and 15.9. Pretreatment containing only alginate has higher line width gains for both woven and knit structures. Nano-silica-containing pretreatment provides line quality close to photopaper quality.

Results show that digital textile printing quality on plain weave and knitted cotton fabrics is influenced by the fabric pretreatments, the most noticeable being the line width. The line quality on these pretreated cotton fabrics was not significantly affected by the fabric structure and the hydrophilicity of the fabric surfaces as long as the pretreatment can give cotton fabrics a balanced hydrophilic/hydrophobic character. We will expand future studies to quantify line quality parameters such as blurriness, raggedness and optical density.

Color depth and color gamut

The visual quality of the textile prints on pretreated fabrics was quite good, considering that neither the printer nor the ink set was optimized for printing on fabrics. The fineness and sharpness of detail, the fineness of line, and the saturation and the quality of the color were all quite acceptable.

Where color is concerned, the CIE L*a*b* color system is used in many applications. L* is the lightness, a* is the red–green aspect and b* is the yellow–
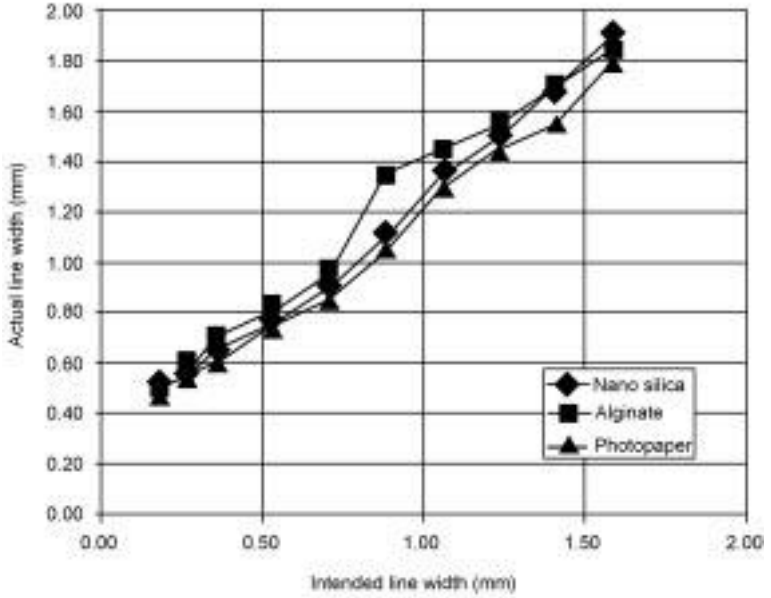
15.8 Effect of pretreatment on line quality (Woven 400M fabric).
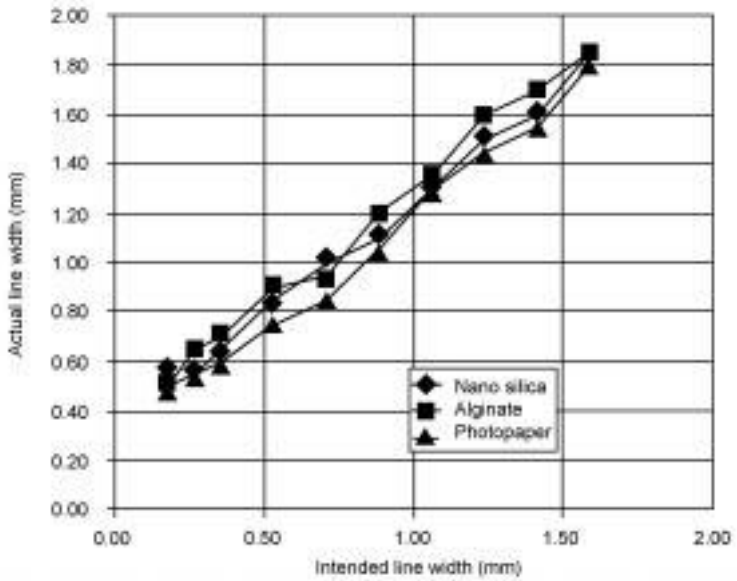

15.9 Effect of pretreatment on line width (Knit 437).

blue aspect of a specific color. The higher the L* value the lighter the color, the higher the a* value the redder the color, and the higher the b* value the more yellow the color. It is observed in Fig. 15.10 that the pretreated woven fabric with 2% alginate, 1.5% silicone and 1% silica (shown as Nano silica) pretreatment shows good results in color depth for all five color shades used. The depths of five colors printed on nano silica treated woven 400M were all very close to that of photopaper. On knit fabric (Fig. 15.11), the combination of 2% alginate, 2% (or 1.5%) silicone and 1% silica gave the better color depth in yellow and red shades, when compared to the photopaper.

From Figs 15.10 and 15.11, we can conclude that the pretreatment recipe containing 2% alginate, 1.5 to 2% silicone and 1% silica was good in achieving dark shades for all five colors (red, yellow, blue, brown and green) on both woven and knit fabrics. That means this combination would render color strength on the pretreated cotton fabrics.

Color gamut plots for selected pretreatments are shown in Figs 15.12 and 15.13. In general, the color appearance of all prepared samples was quite similar. Quantitatively, the color gamuts of all the samples were about equal except for photopaper. This is understandable due to fact that the printer manufacturer optimized ink for its photopaper supplied. However, two observations illustrated in Figs 15.12 and 15.13 are worth mentioning. It appears that the color gamut for the knit fabric (style 437) is as large as that for the photopaper as shown in Table 15.6. Secondly, the numerical color gamuts for the knit samples treated with 1%
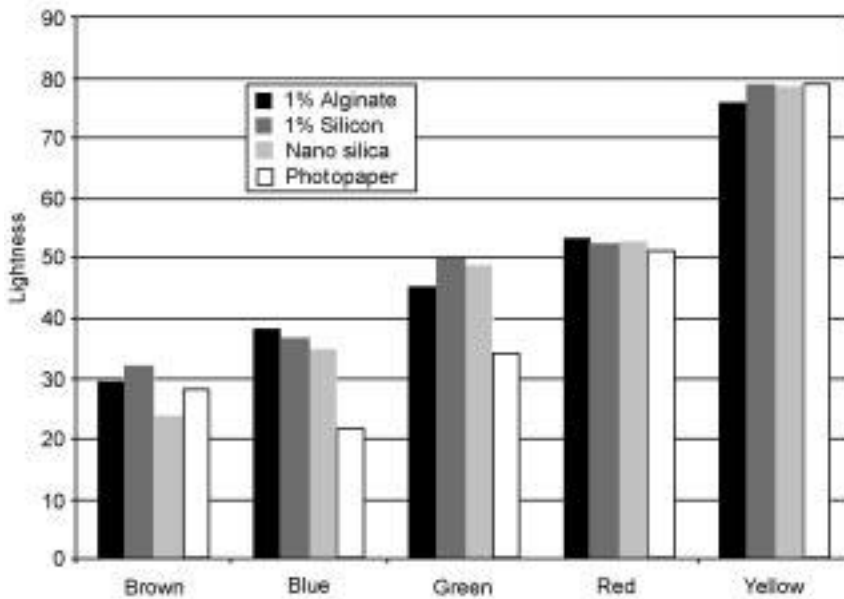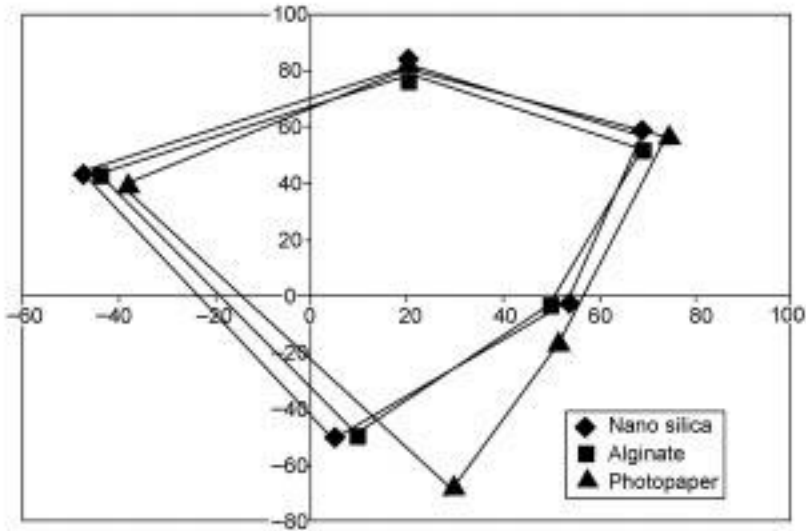

15.10 Effects of pretreatments on the depth of shades (Woven 400M).
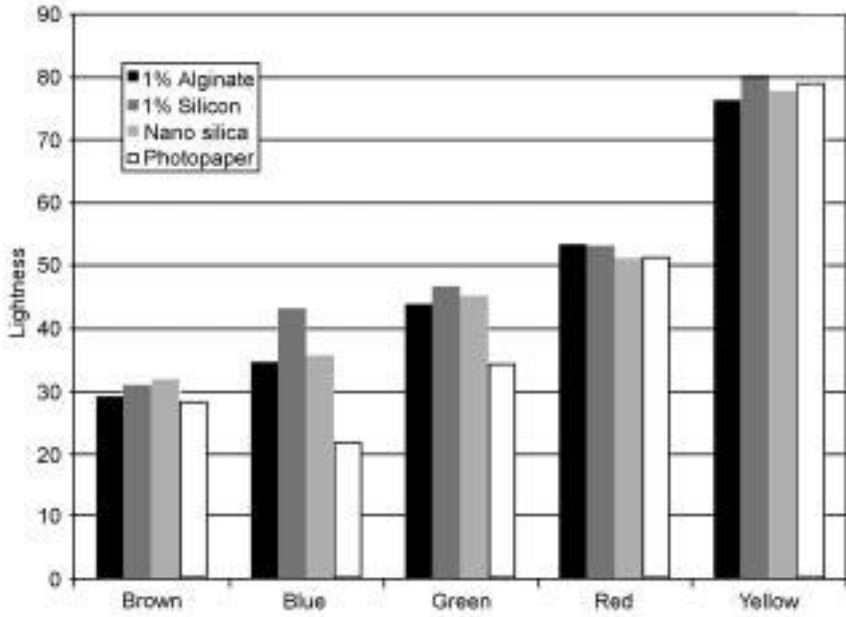
15.11 Effects of pretreatments on the depth of shades (Knit 437).
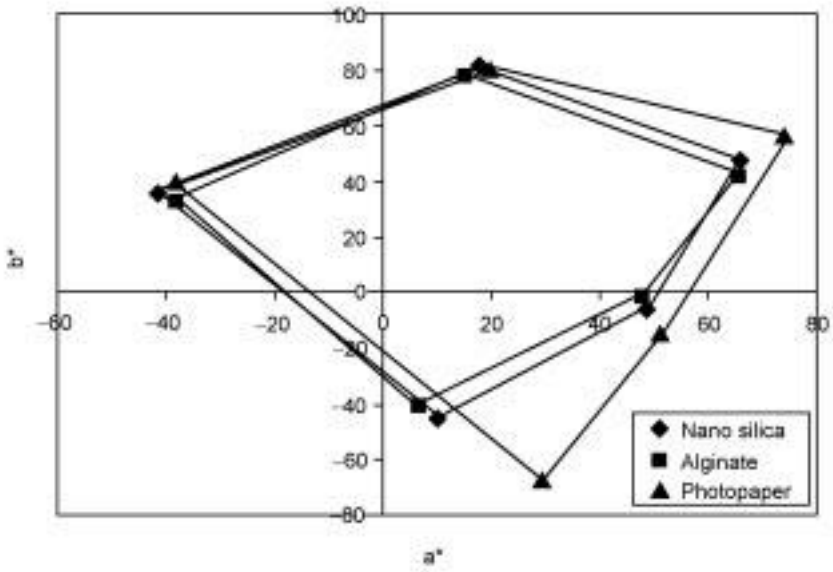
15.12 Effect of pretreatment on color gamut (Woven 400M, mercerized 100% cotton).

15.13 Effect of pretreatment on color gamut (Knit 437, bleached only).

silicon and nano silica are 15.7% larger than those of the woven samples. However, there is an apparent expansion leftward (greener) and downward (bluer) in the a*–b* plane for the knitted sample, indicating a colorfulness differential between the two types of fabric structures.

Figure 15.12 also shows that all pretreated woven fabrics, 400M, were slightly greener (lower a* values) compared to the photopaper except for the green color itself which showed no significant difference between the pretreated fabrics as well as between the pretreated fabrics and the photopaper. This green effect could be from the fabric itself or from the pretreatments resulting from the unnoticeable color. In Fig. 15.13, none of the pretreated knit fabrics showed excessive a* value differences among them, which is similar to the results for their woven counterparts. However, it is believed that the pretreatments may be the cause of the color variation, because the colors on the pretreated knit fabric, 437 knit, also showed a greener tone. Overall, Figs 15.12 and 15.13 show that

Table 15.6 Numerical gamut comparison (Woven 400M versus Knit 437)

Pretreatment	Woven 400M Numerical gamut (arbitrary unit)	Knit 437 Numerical gamut (arbitrary unit)
Photopaper	4537.59	4544.88
Nano silica	3917.83	4534.11
Alginate	3512.62	4155.88

the color gamut was affected only slightly by the pretreatments. The b* values had similar trends among pretreatments except that the photopaper had a little bluer tone.

Based on the experimental results, a pretreatment recipe of 2% alginate, 1.5% silicone softener and 1% silica is recommended for the digital printing of woven and knitted cotton fabrics.

15.4   Concluding remarks and future trends

In this chapter, we reviewed the effects of the pretreatment on print quality of digitally printed textiles. Several digital print quality characteristics were measured on a variety of pretreated cotton fabrics. The main observations in this study can be summarized as follows:

1. The subjective visual quality of inkjet printed cotton fabrics, either as received or pretreated, was as good as that printed on plain paper or photopaper.
2. Several important print quality attributes including line quality, image noise, optical density and color quality were measured. The results clearly show that these objective print quality metrics are needed to evaluate the efficacy of pretreatments, and to investigate the substrate/pretreatment interaction for advancing digital textile printing technology.
3. The effects on print quality of several key fabric properties were studied. These include fabric structure, yarn size, yarn type and pretreatment. The test results suggest that the most significant fabric variables are fabric structure, yarn size and the hydrophilic/hydrophobic nature of the fabric (i.e. absorbency). Fabric absorbency and fabric wicking behavior were measured. The studied knit and sateen fabrics were found to have the most hydrophobic surfaces. Woven fabrics showed some anisotropic wicking behavior.
4. Effects of fabric pretreatments on the quality of digital printing on plain cotton weave and a knit fabric were studied in detail. A special print pattern for quality analysis was designed for use in this study. In the experimental work, a number of recipes derived from the different combinations of alginate, silicone softener and fine silica particles were used as pretreatments for the cotton fabrics. Overall this study showed that digital textile print quality is influenced by fabric pretreatments, the most noticeable being the appearance-related quality, i.e., the line width. The print quality was not significantly affected by fabric structure, and the hydrophilicity of the unpretreated (as received) fabrics. Pretreatments can give cotton fabrics the required characteristics of digital printing substrates, i.e., the balanced hydrophilic/hydrophobic characteristics.
5. It was found that digitally printed cotton fabric with the optimum pretreatment can have as good a quality as that of the digitally printed

photopaper substrate under the conditions pertaining to this case study. This indicates that quality digital printing onto textile fabrics is achievable with proper fabric pretreatment and inkjet technology. Once an optimum solution for fabric pretreatment is developed, digital textile printing can be used not only for preparing prototype samples but also for production quantity and quality printed textile fabrics.

While digital printing technology is a fairly mature technology for the paper printing industry, such developed technology cannot be directly applicable to the textile printing industry. This is because there are significant differences in the physical and chemical nature of various fabric substrates as well as the process variations depending on target markets. Printers currently being used for textiles were originally graphics printers and did not address all of the needs of the industry in terms of width, speed and substrate handling. Several companies have begun addressing these problems, and the future of digital printing of textiles is beginning to take shape. *International Dyer* magazine reported that Reggiani, an Italian textile inkjet printer manufacturer, sells a machine with a printing speed of $120 \, \text{m}^2/\text{hr}$. Other wide format textile inkjet printer manufacturers (DuPont, Mimaki, Mutoh, Cannon, etc.) also market high speed six to seven head machines.[22]

In spite of this advancement, there remain many future challenges and barriers for this exciting new technology to enter the traditional textile screen printing markets. We will briefly discuss these issues by which print quality is determined, and conclude the chapter.

First, printer system design addresses textile-specific problems such as variations from paper printing in colorant volume loading, spot colors versus process colors, substrate texture, dimensional instability and chemistry of substrate. Other crucial system parameters to be optimized for textile printing include ink viscosity, gray levels, drop size, drop frequency, number of print heads, and data communication that will impact on the resulting print speed and print resolution.

Color reproduction and management are the next major challenges for both the paper printing and the textile printing processes to achieve higher color-related print quality. In particular, this challenge is more severe for textile printing if digital printing technology is employed to substitute the table-strike-off process. The use of process color and inks with physical–chemical properties which differ from the analog printing process will add to color matching difficulties.

In a similar fashion to color reproduction, digital prints must emulate the engraving appearance of the analog production prints, if it is adopted for the table-strike-off process. Print quality attributes in terms of dots, lines, large areas including tonal gradations and print growth must have reasonable resemblance between the two processes. In this respect, the printers and the engravers must

work closely together to provide the digital printing system with the necessary knowledge of analog print processes and techniques.

The physical and chemical properties of the ink must be designed to fit the substrate characteristic in order to achieve an acceptable level of various color fastness properties such as crocking, washing, and light fastness. In addition, the proper treatments of the fabric before and after the printing process are essential to ensure good fastness properties.

Commercial-scale digital printing requires sophisticated fabric pretreatment and post-treatment. Proper pretreatment promotes satisfactory appearance and color-related print quality, while proper post-treatment allows fashionable effects and provides additional values such as improved handle, luster, color fastness or soil resist properties to the fabric. On the contrary, inconsistent or poor treatment will result in color and print mark variations. These two value-adding steps also present a problem to users who do not have such facilities. In addition, any inconsistent fabric speed, fabric wrinkling, loose fibers and the touching of the inkjet nozzle due to improper pretreatment will present a great challenge to the print quality result.

Textile printers prefer inks that are compatible with colorants used in the analog printing process to facilitate coordination and to maintain similar color effects. As shown in Section 15.2.1 of this chapter, inks for digital printing are available in reactive dye containing inks for cellulose, acid dye inks for protein fibers, disperse dye inks for polyester, and pigment inks for all types of fibers. However, due to the print head operating restrictions, some inks may not perform satisfactorily in terms of fastness and/or color gamut requirements. Other challenges for the growth of digital textile printing sector are printing speed, print width, ink and other costs.

Indeed, we can end this chapter by quoting Brooks G. Tippett: 'The future of textile printing will be digital, though no one can predict when we will see it unfold.'[4]

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16

Ink jet printing of cationized cotton with reactive inks

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16.1   Introduction

In recent years, ink jet printing has found an increasing application in the printing of textiles. It has demonstrated considerable benefits in terms of strike-off, sampling and more recently in the production of short lots of printed textiles.[1,2] It is also expected that with further advancements in software, printer and ink technologies being made every day, ink jet printing of textiles will become ever more important in the near future.[3]

Reactive dye based inks are used commonly to print cotton and other cellulosic fibers. In ink jet printing, unlike conventional reactive printing, thickener, alkali and urea are applied onto the fabric by a padding process prior to application of color, and this process has a crucial importance on the print quality.[4–8] After ink jet printing, steam fixation, washing and drying processes follow.

In general, the reactive inks used in ink jet printing often have a degree of fixation to cotton of only 70%.[9] In order to achieve the necessary high level of wetfastness, the unfixed dye must be removed effectively. For that reason, time-consuming, energy intensive and expensive washing-off procedures are required similar to the conventional washing-off processes used with fiber reactive dyeing. This washing-off process has a major negative environmental impact owing to the large amount of dye and chemicals removed and the large amounts of water required. Furthermore, unfixed reactive dyes in the wastewater may pose an environmental hazard.[12] This problem can be minimized by increasing the fixation rate of reactive inks as high as possible, and by reducing the amount of chemicals used in the pretreatment process. For this purpose, either reactive dyes[9] or fabric[10,11] can be modified, or fixation-enhancing chemicals can be used.[4]

The chemical modification of cotton prior to dyeing and printing in order to improve its dyeability with anionic dyes such as reactive, direct, acid, sulphur and vat dyes has received considerable attention in recent years. All of these modifications introduced cationic groups in the form of quaternary, tertiary or secondary amino residues. In this way, anionic reactive dyes are attracted by the

cationic charges on the fiber, and as a result a high degree of dye–fiber fixation, a reduced washing off procedure, reduced or no electrolyte use in dyeing, and wetfastness properties equivalent to the untreated cotton can be obtained.[12]

Some recent literature has reported that near 100% dye fixation rates could be obtained in conventional reactive dye printing, as well as with acid and direct dye printing by cationization of cotton with 2,3-epoxypropyltrimethyl-ammonium chloride[12,13] prior to printing.

The actual cationizing agent used in this work was also 2,3-epoxypropyl-trimethylammonium chloride (**I**).[3] This reactive material is conveniently prepared *in situ* by the reaction of 3-chloro-2-hydroxypropyltrimethyl-ammonium chloride (**II**) with alkali according to Fig. 16.1. 3-Chloro-2-hydroxy-propyltrimethylammonium chloride is commercially available as a 69% solution in water and was used as received. 2,3-Epoxypropyltrimethylammonium chloride will react with alcohols under alkaline conditions to form ethers (Fig. 16.2). The reaction product of this epoxy with cotton is a modified fiber with the structure shown in Fig. 16.3.

A by-product of reactions of 2,3-epoxypropyltrimethylammonium chloride in aqueous alkaline solutions is 2,3-dihydroxypropyltrimethylammonium chloride (**III**), a species that cannot react with cotton at the conditions used here (Fig. 16.4). Depending on the specific reaction conditions, 20–50% of the epoxy groups will hydrolyze to form this inactive material.

As a result of reaction with 2,3-epoxypropyltrimethylammonium chloride, cotton will have covalently bound cationic dye sites that are present at any pH value. When dyeing or printing, these cationic dye sites will strongly attract negatively charged anionic reactive dyes to form an ionic bond. Furthermore, due to the enhanced electrostatic attraction, the reactive dye molecules reach the hydroxyl groups in the fiber faster, and the covalent bonding rate is accelerated.[12]
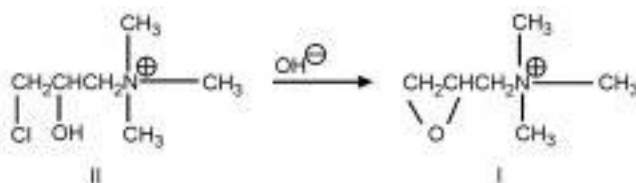
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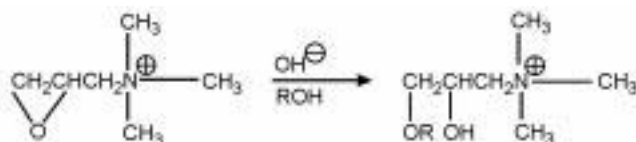
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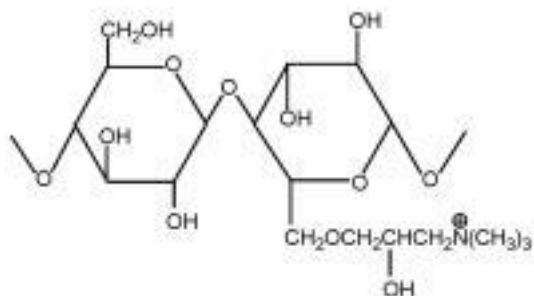
16.3

16.4

This chapter will review two recent studies[14,15] that investigated potential improvements realized by cationizing cotton fabrics prior to ink jet printing with reactive inks.

16.2   Experimental

16.2.1 Materials

A scoured, bleached and mercerized, optical brightener-free woven (twill 3:1) 100% cotton fabric, with a weight of 235 g/m^2, a density of 46 threads/cm in the warp and 20 threads/cm in the weft directions was used throughout both studies. As the cationizing agent, a 69% solution in water of 3-chloro-2-hydroxy-propylt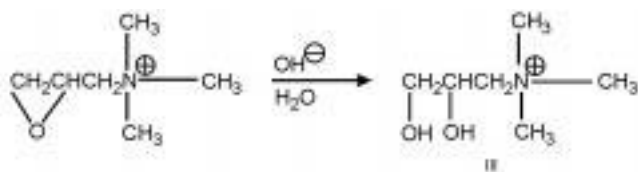rimethylammonium chloride was used. The inks were Cibacron Yellow MI-100, Cibacron Red MI-500 (magenta), Cibacron Turquoise MI-700 (cyan) and Cibacron Black MI-900. A medium viscosity alginate thickener was used in the pretreatment pad bath. A naphthalene sulphonate based anionic scouring agent was used for washing of the prints. Other chemicals in this study were commercial grade sodium hydroxide (50% w/w), soda ash, urea and acetic acid (97%) used as received.

16.2.2   Cationization

The cationization was carried out according to the pad-batch method,[14] on a Mathis HVF padder. The cationic reagent was used at concentrations of 50, 75, 100 and

125 g/l with corresponding sodium hydroxide concentrations of 31.0, 46.5, 62.0 and 77.5 g/l, respectively. Sodium hydroxide concentrations were calculated according to the method optimized by Tabba.[16] The fabrics were padded through the cationization baths at 100% wet pickup, wrapped in plastic, and stored at room temperature for 24 hours. After removal from the plastic, the batched fabrics were rinsed with warm water at 40ºC, neutralized with 2 g/l acetic acid at 40ºC, cold rinsed, and then dried on a conveyor-type drying machine at 100ºC.

16.2.3   Pretreatment process for ink jet printing

Prior to printing, the untreated and the cationized fabric samples were padded on a Mathis HVF padder with soda ash (10, 20, 30, or 40 g/l), urea (100 g/l) and thickener (0, 4, 8, or 12 g/l). The wet pickups were adjusted to 70%, and all fabrics were dried at 100ºC.

16.2.4   Printing processes

The printing processes were performed on a Stork Amber ink jet printer with a pass number of 4 and resolutions of 360 and 720 dpi. All prints were air dried, and steamed on an Arioli sample steamer at 100ºC.

16.2.5   Washing procedures

Throughout the study, the untreated printed samples were washed according to the following five-step washing procedure: (1) 5 min cold rinsing at 20ºC; (2) 5 min warm washing at 40ºC; (3) 10 min hot washing at 95ºC by the addition of 3 g/l scouring agent; (4) 5 min warm washing and neutralization at 40ºC by the addition of 0.5 g/l acetic acid; and (5) 5 min cold rinsing at 20ºC. Cationic cotton samples were washed either according to the same procedure or with the following three-step washing procedure: (1) 5 min warm washing at 30ºC by the addition of 3 g/l scouring agent; (2) 10 min hot washing at 70ºC; and (3) 5 min cold rinsing and neutralization at 20ºC by the addition of 0.5 g/l acetic acid. The liquor ratio was 30:1 for all washing processes. The washed samples were dried on the conveyor dryer at 100ºC.

16.2.6   Testing methods

The color properties of the printed samples were determined using a Datacolor SF300 spectrophotometer with SLI-Form/NG software (SheLyn, Inc.). Relative color strength, staining on white ground and dye penetration were determined using the Kubelka–Munk equations; $(K/S)_f$, $(K/S)_g$ and $(K/S)_r$ respectively.[17] For dye penetration, $(K/S)_r$ values were measured on the reverse side of the fabrics. All K/S values were taken at the λ_{max} of each dyestuff.

Color fastness to washing was tested according to AATCC Test Method 61 (2A) and color fastness to crocking was tested according to AATCC Crockmeter Method 8. Color fastness to light was tested according to AATCC Test Method 16E, 20 AATCC fading units (AFU), and the color change evaluated with the AATCC color change gray scale.[18]

To compare the outline sharpness of the prints, a special print pattern containing lines with different widths was used. The widths of the lines on the fabrics were measured by using an Image Analysis System/Version 3.00 (B.A.R.N. Engineering) to evaluate print quality.[8]

16.3   Results and discussion

16.3.1 Effect of cationic reagent concentration

In order to investigate the effect of the cationic reagent concentration on print properties of cationic cotton, each fabric was printed with the cyan reactive ink at a resolution of 720 dpi. The pretreatment was 40 g/l soda ash, 100 g/l urea, and 8 g/l thickener. Printed samples were steamed for 10 min, and then washed according to the five-step washing procedure. The results are presented in Table 16.1.

Values of $(K/S)_f$ from Table 16.1 clearly demonstrate that cationization enhances the color strength of reactive ink jet prints. The average increase of the color strength was about 34%, suggesting a potential for significant reduction in ink usage. This increase could arise from improved dye substantivity due to the introduction of cationic groups into the cotton, and lower print paste penetration with cationic cotton. As shown from $(K/S)_r$ values, cationization decreases penetration of the prints dramatically, leading to higher surface coloration. The

Table 16.1 Effect of cationic reagent concentration on the K/S and color fastness values of fabric ink jet printed with cyan reactive ink

Cationic reagent conc. (g/l)	K/S values[a]			Washfastness		Crockfastness	
	$(K/S)_f$[b]	$(K/S)_g$[c]	$(K/S)_r$[d]	Color change	Staining of cotton	Dry	Wet
Untreated	18.90	0.34	0.94	5	5	5	3–4
50	25.22	0.54	0.37	5	4–5	4–5	2–3
75	25.37	0.29	0.35	5	5	4–5	2–3
100	25.41	0.24	0.35	5	5	4–5	2–3
125	25.75	0.21	0.36	5	5	4–5	2–3

[a] λ_{max} = 670 nm.
[b] $(K/S)_f$ = color strength on front side of fabric.
[c] $(K/S)_g$ = color strength of staining on white ground.
[d] $(K/S)_r$ = color strength on reverse side of fabric.

lower print penetration may be due to the lower open hole area of the cationic fabric by swelling in sodium hydroxide.[12] Furthermore, the penetration was also restricted by the strong ionic attraction between cationic fiber and anionic reactive ink. Values of $(K/S)_g$ show that the staining on the white grounds is lower for cationic cotton than for untreated cotton, except with the cationic reagent concentration of 50 g/l. It was also recognized that the washing baths with cationic cotton were nearly clear, especially for the higher cationic reagent concentrations. This result can be attributed to the fact that the higher levels of cationization in the printed areas were enough to prevent any dye loss, and thus reduce the staining on the white ground of the fabric. Generally, cationization had no significant effect on the washfastness ratings which are very good for both fabrics (Table 16.1). On the contrary, the crockfastness of cationic cotton was reduced by 0.5–1.0 rating units. This decrease in crockfastness can be attributed to the higher overall dye concentration and higher surface coloration on the cationic cotton.

16.3.2   Effect of cationization on outline sharpness

To determine the effect of the cationization on outline sharpness, each fabric was printed with the cyan ink at a resolution of 720 dpi. The fabric treated with 100 g/l cationic reagent was used as the cationic cotton. The pre-treatment was 40 g/l soda ash, 100 g/l urea, and 8 g/l thickener. Printed samples were steamed for 10 min, and then washed according to the five-step washing procedure. The line widths of the prints were measured by image analysis methods, and the results are shown in Fig. 16.5. This figure shows that the warp direction lines are generally thicker than the weft direction lines on both fabrics. This might be due to the different wicking power of weft and warp yarns. Furthermore, the lines for cationic cotton, especially in the weft direction, are narrower than for untreated cotton. This can be attributed to prevention of spreading of the printed inks by the strong ionic attraction that arises between cationic cotton and the anionic reactive ink. As a result, it is possible to say that cationization enhances the outline sharpness of the prints.

16.3.3   Effect of cationization on steaming time

The possibility of reducing steaming time for ink jet printing via cationization was investigated with a series of experiments. Printings were carried out using the cyan ink on both untreated and cationic cotton treated with 100 g/l cationic reagent. The pretreatment was 40 g/l soda ash, 100 g/l urea, and 8 g/l thickener. Printed samples were steamed at different times, and then washed according to the five-step washing procedure. The results are summarized in Table 16.2.

As can be seen from the $(K/S)_f$ values, color strength of the printed untreated cotton increases by increasing the steaming time up to 8 minutes. On the
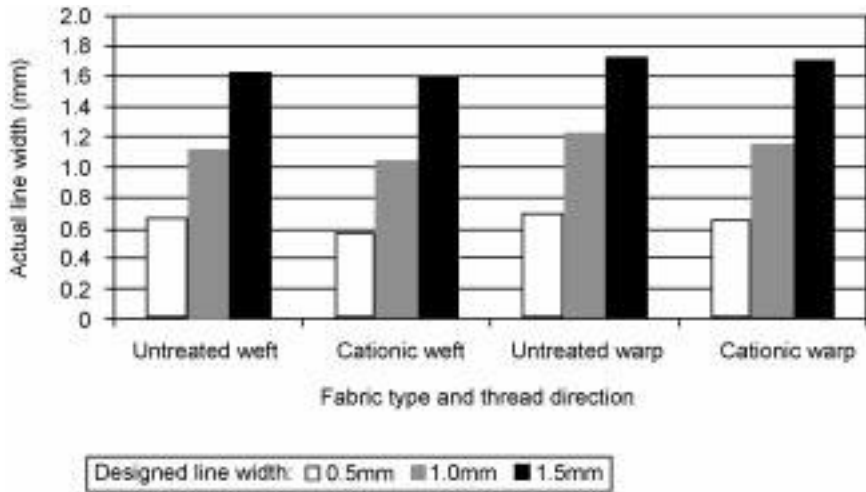
16.5 Effect of cationization on line width.

contrary, there is no significant increase with the cationic fabrics, and the $(K/S)_f$ values are more or less similar for all cationic samples from 2 minutes to 10 minutes. However, the $(K/S)_g$ value and washfastness rating for 2 minutes steaming time on the cationic cotton are slightly worse than for higher steaming times. Taking into account the staining on the white ground and washfastness ratings, it is possible to say that the minimum steaming time must be 4 minutes for cationic cotton and 8 minutes for untreated cotton.

Table 16.2 K/S values and color fastness ratings at different steaming times

Fabric type	Steaming time (min)	$(K/S)_f$[b]	$(K/S)_g$[c]	$(K/S)_r$[d]	Color change	Staining of cotton	Dry	Wet
		K/S values[a]			Washfastness		Crockfastness	
Untreated	2	17.32	0.38	0.38	4	5	5	4
	4	18.83	0.36	0.49	4–5	5	4–5	3–4
	6	20.44	0.40	0.79	4–5	5	5	3–4
	8	20.92	0.38	0.81	5	5	5	3–4
	10	20.70	0.38	0.84	5	5	5	3–4
Cationic (100 g/l)	2	27.21	0.33	0.27	4–5	4–5	4–5	2–3
	4	27.68	0.29	0.31	5	5	4–5	2–3
	6	27.20	0.28	0.32	5	5	4–5	2–3
	8	27.52	0.28	0.34	5	5	4–5	2–3
	10	27.53	0.25	0.37	5	5	4–5	2–3

[a–d] See Table 16.1.

The $(K/S)_r$ values of the reverse side of untreated and cationic fabrics demonstrate that penetration has been increased by increasing the steaming time. Furthermore, the rate of increase on the cationic cotton due to steaming time is lower than for the untreated cotton because of the strong ionic attraction.

The crockfastness results confirm the results obtained in the previous experiment, except for lower steaming times with untreated cotton. The higher crockfastness ratings for two minutes steaming time might be due to lower dye concentration on the untreated fabric.

16.3.4   Effect of cationization on alkali concentration

In order to determine the possibility of reducing the alkali concentration when printing reactive inks on cationic cotton, a series of experiments were carried out at various alkali levels with untreated cotton and cationic cotton treated with 100 g/l cationic reagent. The pretreatments were with 100 g/l urea, 8 g/l thickener and either 0, 10, 20, 30, or 40 g/l soda ash. Printing was done with the cyan ink at 720 dpi. The steaming time was 10 minutes and the printed samples were washed with the five-step washing procedure.

Table 16.3 gives the $(K/S)_f$ values which demonstrate that, as expected, the color strength of the untreated cotton increased with increasing soda ash concentration. In contrast, the $(K/S)_f$ values with cationic cotton showed no significant trend. The color yield with no alkali was quite low with untreated cotton since some alkali is necessary for the reactive ink to covalently bond with the fiber, whereas with cationic cotton, no alkali is necessary for high color yields since the anionic dye molecules can form strong ionic bonds with the cationic fiber. The highest washfastness achieved with untreated cotton was with

Table 16.3 Effect of cationization on alkali concentration for pretreatment process

Fabric type	Soda ash conc. (g/l)	$(K/S)_f$[b]	$(K/S)_g$[c]	$(K/S)_r$[d]	Color change	Staining of cotton	Dry	Wet
		— *K/S* values[a]			Washfastness		Crockfastness	
Untreated	0	1.41	0.52	0.99	2	4–5	5	4–5
	10	19.76	0.46	1.11	4	4–5	5	3–5
	20	20.29	0.39	1.02	4–5	5	5	3–5
	30	20.52	0.43	1.06	5	5	5	3–5
	40	20.57	0.44	0.98	5	5	5	3–5
Cationic	0	27.29	0.66	0.26	4–5	4–5	5	4
	10	26.80	0.34	0.31	5	5	4–5	3
	20	27.26	0.33	0.37	5	5	4–5	3
	30	26.87	0.35	0.41	5	5	4–5	3
	40	26.28	0.35	0.44	5	5	4–5	3

[a–d] See Table 16.1.

30 g/l soda ash. Cationic cotton, on the other hand, had maximum washfastness with only 10 g/l soda ash. White ground staining, $(K/S)_g$, was near optimal also at 30 g/l soda ash for untreated cotton and 10 g/l soda ash for cationic cotton. Crockfastness results, both wet and dry, generally indicated slightly worse performance for printed cationic cotton, probably due to the higher level of surface dye obtained with that system (higher $(K/S)_f$ and lower $(K/S)_r$).

16.3.5   Effect of cationization on thickener concentration

The thickener was applied at various concentrations (0, 4, 8, or 12 g/l) in the pretreatment bath to determine the effect of cationization on the optimal level of thickener. The concentrations of soda ash and urea in the pre-treatment were 40 and 100 g/l respectively. The fabrics, untreated cotton and cotton cationized with 100 g/l reactant, were printed with the cyan ink at 360 and 720 dpi resolutions. The printed samples were steamed for 10 minutes and then washed with the five-step washing procedure. The results are shown in Table 16.4.

As seen in the $(K/S)_f$ values, cationization significantly enhanced the color strength of the printed fabrics regardless of thickener concentration or print

Table 16.4 Effect of thickener concentration on K/S values and color fastness rates of cyan ink jet printed fabrics

Fabric type (print resolution)	Thickener conc. (g/l)	$(K/S)_f$[b]	$(K/S)_g$[c]	$(K/S)_r$[d]	Color change	Staining of cotton	Dry	Wet
		K/S values[a]			Washfastness		Crockfastness	
Untreated (360 dpi)	0	14.56	0.26	0.70	5	5	5	3–5
	4	16.26	0.24	0.61	5	5	5	3–5
	8	17.01	0.26	0.56	5	5	5	3–5
	12	18.67	0.24	0.47	5	5	5	3–5
Cationic (360 dpi)	0	20.15	0.10	0.26	5	5	5	3
	4	22.34	0.14	0.23	5	5	5	3
	8	23.13	0.09	0.23	5	5	5	3
	12	22.95	0.14	0.19	5	5	5	3
Untreated (720 dpi)	0	18.26	0.37	1.36	5	5	5	3–5
	4	18.83	0.37	1.08	5	5	5	3–5
	8	19.21	0.35	0.97	5	5	5	3–5
	12	21.19	0.38	0.88	5	5	5	3–5
Cationic (720 dpi)	0	25.50	0.37	0.47	5	5	4–5	2–5
	4	25.24	0.42	0.38	5	5	4–5	2–5
	8	25.93	0.29	0.37	5	5	4–5	2–5
	12	26.23	0.26	0.36	5	5	4–5	2–5

[a–d] See Table 16.1.

resolution. The cationic fabric forms strong ionic bonds with the anionic ink, leading to high surface coloration without the need for thickener. With the untreated fabric, color strength increased with thickener concentration as expected since the more viscous ink penetrated the fabric less, leaving more color at the surface. Values of $(K/S)_f$ for cationic cotton printed at 360 dpi were comparable to those for untreated cotton printed at 720 dpi. Since four times more ink is theoretically used in 720 dpi prints than in 360 dpi prints, the savings in ink from using cationic cotton can be quite significant.

Values of $(K/S)_g$, a measure of background staining, are extremely low for the cationic fabric printed at 360 dpi resolution. The wash baths were also quite clear for these fabrics. This indicates that the level of cationization was high enough to strongly bond all the ink molecules, preventing any color migration to the white background.

Color values on the reverse face of the fabrics, $(K/S)_r$, are considerably lower for the printed cationic fabrics than for the printed untreated fabrics, providing another indication that ink penetration is significantly decreased due to strong ink–fiber interactions.

16.3.6   Effect of thickener concentration and cationization on outline sharpness

In order to evaluate the effect of the thickener concentration on outline sharpness, the line widths of fabrics printed with cyan ink at 360 dpi were measured by an image analysis method, and the results are shown in Table 16.5. This

Table 16.5 Effect of thickener concentration and cationization on outline sharpness

Designed line width (mm)	Thickener conc. (g/l)	Actual line width in weft direction (mm)	
		Untreated	Cationic
0.5	0	0.744	0.644
	4	0.689	0.553
	8	0.675	0.573
	12	0.679	0.593
1.0	0	1.168	1.127
	4	1.150	1.056
	8	1.127	1.047
	12	1.150	1.047
1.5	0	1.673	1.664
	4	1.660	1.531
	8	1.631	1.595
	12	1.671	1.631

shows that, in general, the lines for cationic cotton are finer than for untreated cotton as seen in Section 16.3.2. The results also show that thickener concentration has a significant effect on the outline sharpness. The line widths on the untreated fabrics reduce by increasing the thickener concentration from 0 to 12 g/l. This result demonstrates that a suitable amount of thickener is required for preventing the entry of ink to the capillaries, since blockage of the capillary spaces reduces the wicking effects.[5] On the cationic fabrics, generally, the best outline sharpness (the finest lines) has been obtained with a thickener concentration of 4 g/l, and the line widths increase above 4 g/l. Higher thickener concentrations than 4 g/l with cationic cotton may cause more surface coloration, and thickness of the lines increases again. Thus, it is possible to say that cationic cotton requires less thickener than untreated cotton because cationization reduces pore size (capillary spaces) of the fabric and a lower thickener concentration may be enough for the blockage of the capillary spaces. In addition, ionic attraction between cationic cotton and ink may have an important effect on preventing the spreading of printed ink.

16.3.7   Printing results with CMYK colors and reduced chemical levels

The previous experiments indicated that ink jet printing with cyan reactive ink on cationic cotton can be carried out with reduced alkali and thickener concentrations and a less lengthy after-wash compared to reactive printing on untreated cotton. To confirm these results with a variety of inks, the following experiment was carried out.

Untreated cotton and cotton cationized with 100 g/l cationic reactant were printed with CMYK (cyan, magenta, yellow, black) reactive inks at 320 dpi resolution. Different pretreatments were used for untreated and cationic cotton fabrics. Untreated fabrics were padded with 8 g/l thickener, 40 g/l soda ash, and 100 g/l urea, while cationic fabrics were padded with 4 g/l thickener, 20 g/l soda ash, and 100 g/l urea. Both fabric types were steamed for 10 minutes after printing. The printed untreated fabrics were washed with the five-step washing procedure, while the printed cationic cotton fabrics were washed with the three-step procedure (see Section 16.2.5). K/S and fastness properties of the fabrics are given in Table 16.6.

The color strength values, $(K/S)_f$, of all inks with cationic cotton are significantly higher than the color values of the inks with untreated cotton. The improvements range from 25% higher for cyan to a remarkable 89% higher for black. The color values of the reverse side of the fabrics, $(K/S)_r$, were also significantly less for all inks on cationic cotton, indicating that the inks penetrated less with cationic cotton. The higher $(K/S)_f$ values could arise from less penetration as well as from increased color utilization, since it was noted that the wash baths for all cationic fabrics were colorless, implying near 100%

Table 16.6 K/S values and fastness properties for fabrics ink jet printed with CMYK colors with reduced chemicals for cationic cotton

Fabric type	Color	K/S values[a]			Washfastness		Crockfastness		Light fastness (20 AFU)
		$(K/S)_f$ [b]	$(K/S)_g$ [c]	$(K/S)_r$ [d]	Color change	Staining of cotton	Dry	Wet	
Untreated	Yellow	13.58	0.03	1.08	5	5	5	4	4
	Magenta	17.97	0.02	0.46	5	5	5	3–5	4
	Cyan	18.51	0.27	0.37	5	5	5	3–5	4–5
	Black	11.16	0.02	0.76	5	5	5	3–5	4
Cationic	Yellow	17.93	0.17	0.24	5	5	5	3–5	3–5
	Magenta	25.90	0.18	0.24	5	5	4–5	2–5	4–5
	Cyan	23.11	0.10	0.17	5	5	5	3	4
	Black	21.12	0.08	0.21	5	5	5	2–5	4–5

[a] Yellow $\lambda_{max} = 430$ nm; magenta $\lambda_{max} = 530$ nm; cyan $\lambda_{max} = 670$ nm; black $\lambda_{max} = 610$ nm.
[b–d] See Table 16.1.

color fixation. However, the staining of the unprinted areas, $(K/S)_g$, was higher on cationic cotton for all inks except cyan. A higher cationization level or use of inks with a greater interaction to cationic cotton could overcome this difficulty.

Washfastness, dry crockfastness, and lightfastness results were essentially comparable for the untreated and cationic fabrics. Wet crockfastness ratings were generally 0.5–1.0 units lower for cationic cotton than for untreated cotton. Since the cationic cotton fabric clearly had more surface color than the untreated cotton, a more reliable evaluation would be to compare the wet crockfastness of untreated and cationic cotton fabrics printed to the same color depth.

16.4   Conclusions

The results demonstrate that cationization of cotton with 2,3-epoxypropyltri-methylammonium chloride can be used to improve reactive ink jet printing properties. As a result of cationization, the color yield of the prints was increased significantly, while the ink penetration was reduced. Hence, cationization permits faster printing, especially with dark-colored designs, since darker shades can also be printed with lower resolution on cationic cotton. Print outline sharpness was also increased. Due to the greater interaction of reactive inks with cationic cotton, ink consumption, steaming times, alkali concentrations, thickener concentrations, and washing procedures could all be reduced from the levels necessary with untreated cotton, leading to a shorter and less costly printing process.

However, cationization had some adverse effects on the wet crockfastness and white ground staining values with some reactive inks. To obtain lower white ground staining and higher wet crockfastness rates, further research investigating different reactive inks which have more substantivity, other anionic dyes such as direct and acid dyes, different thickeners and different print parameters is needed.

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