

---

# Recent Developments in Ink Jet Printing of Textiles with Reactive Dyes

*John Provost*

*ZENECA Colours, Manchester, United Kingdom*

---

## Abstract

With the increased pressure from developing textile markets in the Far East Textile Printers in Europe, Japan and the USA must respond with both increased quality and shorter time of response.

This means supplying new design concepts, sample and production printed fabrics in a wide range of colourways in a timeframe unheard of a few years ago.

One area that has seen development is in the pre-printing area with increasing use of CAD/CAM systems and digital printing systems.

The present paper will review the latest development in the ink jet printing of textiles with fibre reactive dyes and highlight the future direction this technology will take in textile printing.

## Introduction

The textile printing business is a large and complex business with production of prints required on all textile

substrates from cotton to the wide range of synthetic fibres. Each of these fibres has to be printed with a dyestuff class to enable fixation (by various chemical or physical methods) to the textile to impart the 'wash and wear' characteristics demanded by the consumer.

Total production of textile prints approaches 19 billion metres of fabric per year and shows an average growth rate of the order of ~2% per year. However behind the growth figures we are seeing a relative decline in the developed western textile printing markets and a much larger growth in the developing markets in the Far East. For the Developed print markets to survive into the 21st century a strategy has to be developed based on (i) speed of response, (ii) short lot production, (iii) short delivery times, (iv) increased innovation and new fashion ideas, and (v) the formation of 'partnerships' with the major retail groups (the printers' customer).

To achieve this strategy the printer must take an integrated approach to the whole textile print process<sup>1</sup>.

The printer has to examine:

- \* the pre-printing stage (CAD/CAM)
- \* the quicker production of sample prints (using digital printing technologies)
- \* selection of the right dye range to ensure minimum transfer from sample to bulk production and consequent less down-time on the bulk printing machine.

---

Originally published in *Proc. of IS&T's Eleventh International Congress on Advances in Non-Impact Printing Technologies*, October 29-November 3, 1995, Hilton Head, South Carolina.

The first two steps, the use of CAD systems and the quick production of sample prints are the 'key' elements of this strategy. It is in this area that we are seeing rapid developments in the use of jet printing techniques using the digital output from CAD systems. The major reason for the concentration of research programmes on jet printing is the realisation that the same dyes could be used in this technology as those used in current conventional screen or roller textile printing. It should therefore be possible to develop new systems initially for 'sample' printing that would eliminate the need for preparing separations and engraving. As the technology matures we could see jet printing replacing established technologies initially in coupon printing (~100 metre samples) and ultimately full scale production.

### Pre-Print Stage in Textile Printing

If we examine the production time scale of a textile print from design conception to bulk print we can see the considerable advantages to be gained from design selection and sampling using ink jet print technology. To obtain a "feel" for the production time scale of a textile print let us examine the situation for a totally manual approach to the production of a textile print. Figure 1 gives an overview of the stages carried out in the production of a textile print.

An original design was manually traced, films produced and individual screens or rollers engraved for each colour (i.e. if a textile design has 24 colours then 24 screens have to be produced unlike the CMYK system used in the graphic arts industry). A sample print ('proof' print) is then produced in a number of colourways on the textile substrate supplied by the customer prior to submitting to the customer for approval. After approval the production printing takes place.

The time scales indicated in Figure 1 are still typical of those currently achievable by the textile printer, i.e. from the initial submission of a design to production can take up to 3 months. From the 1983 ITMA in Milan relatively low cost and increasingly powerful PC based CAD systems have been available. There has been equally dramatic increase in the associated technology of Visual Display Units (VDU's), graphic controllers, scanners and, importantly, high volume data storage systems (rewritable optical discs).

With the right investment the printer can scan designs into a CAD system where he can reduce the number of colours, manipulate designs, put into repeat, colour and produce separations. The digital information produced can then subsequently be used to produce screens directly, via the latest laser engraving technology, or by conventional means using computer produced films. Figure 2 summarises the situation for many of the systems currently available.

However, the 'rate determining step' and major bottleneck is the production of the many colourways at the sample print stage. Any technology that can reduce the time taken for colourway/sample selection will greatly decrease the time taken to produce prints. This has consequently led to research activity in the field of textiles over the last 20 years in 'non-impact' printing, particularly in the use of jet printing. The whole area of developments in ink jet printing on textiles has recently been reviewed<sup>2</sup>.

In textile production jet printing machines are available for carpet printing based on valve control technology (with direct or indirect deflector types). The two commercially available systems are: the Millitron system<sup>3</sup> which uses an array of jet with continuous streams of dye liquor which can be deflected by a controlled air jet and the 'Chromojet' system<sup>4</sup>. Both these

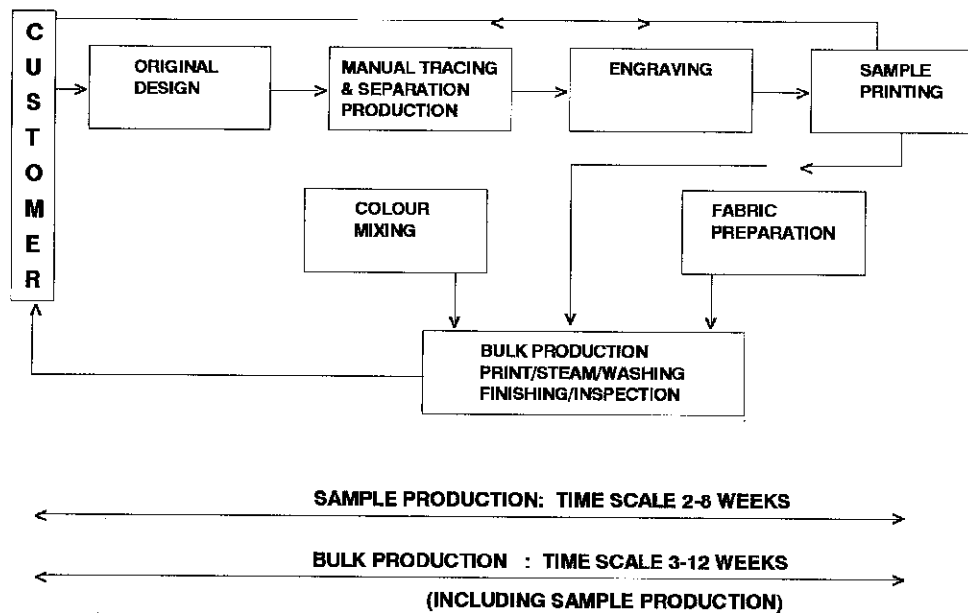


Figure 1. Textile Printing by Conventional Manual Methods

systems offer only coarse resolution which has not proved acceptable to the textile printer.

For 'proofing' purposes STORK of Holland introduced the 'Trucolor' TCP system at the 1991 ITMA exhibition in Hannover<sup>5</sup>. This was the first commercially available system which used fibre reactive dyes—specially developed PROCION reactive dyes from ZENECA Colours and specific pre-treatment technology. The STORK system is based on the Hertz binary continuous jet system<sup>6</sup>. A full description of the principles can be found in the paper by Hertz and Samuelson<sup>7</sup>.

Further developments on this system based on collaborative research between a number of European partners under a EUREKA Project<sup>8</sup> and a Brite-Eurem Project<sup>9</sup>. (Partners include STORK, ZENECA, F. Schoeller in the EUREKA project with the addition of KBC in the Brite-Eurem Project) will be displayed at the 1995 ITMA in Milan.

Other textile projects in jet printing include:

- Continuous Multi-Level Deflected Technology
  - C.S.I.R.O.
  - TOXOT (Image)
- Continuous Binary Systems
  - Burlington Project<sup>10</sup>
  - STORK<sup>5</sup>
- Bubble Jet Technology ("Drop on Demand" System)—Japanese Developments
  - Canon - Kanebo—"Wonderprint" Systems<sup>11,12</sup>
  - Seiren - "Viscotex" System
  - Wakayama Senko—"Joy Print"

Other Japanese companies are also developing systems based on bubble jet technology.

The majority of these systems are developing ink formulations based on dye systems rather than pigments aiming to obtain fixation with the textile substrate.

Cellulosics printing (cotton, viscose rayon) and blends

with cellulose accounts for nearly 70% of all textile printing consequently considerable research has been aimed at developing stable ink formulations based on reactive dyes.

## Reactive Dyes on Textiles

Reactive dyes were first introduced by ICI (now known as ZENECA) in 1956<sup>13</sup> and as the name suggests they are coloured compounds which have suitable groups capable of forming a covalent link between the dye and the textile. In textile printing two essential types have developed; (i) monohalogenotriazine types which react by a nucleophilic substitution mechanism and (ii) groups which react by the addition of the nucleophilic group of the substrate to a C=C double bond on the reactive group (the most common of this class are sulphuric acid esters of  $\beta$ -hydroxyethylsulphones which form vinyl sulphone groups under alkaline conditions).

Due to the differing reactivities of the two types and the need for long term print formulation stability the first type—the monohalogenotriazine types are the most popular in textile printing, accounting for approximately 85% of conventional textile printing on cellulosic fabrics.

The reactive scheme for a typical monochloro-triazinyl dye is shown in Figure 3. The reaction takes place under alkaline conditions and heat (normally steam fixation at 102°C for 10 minutes) together with other additives such as urea.

The reactivity of these dyes towards hydroxyl groups obviously gives extra problems in the production of a stable ink formulations.

In conventional textile printing the reactive dye is applied to the textile with alkali and all the necessary additional chemicals in the form of a print paste. The print is then normally steamed to fix the dye to the

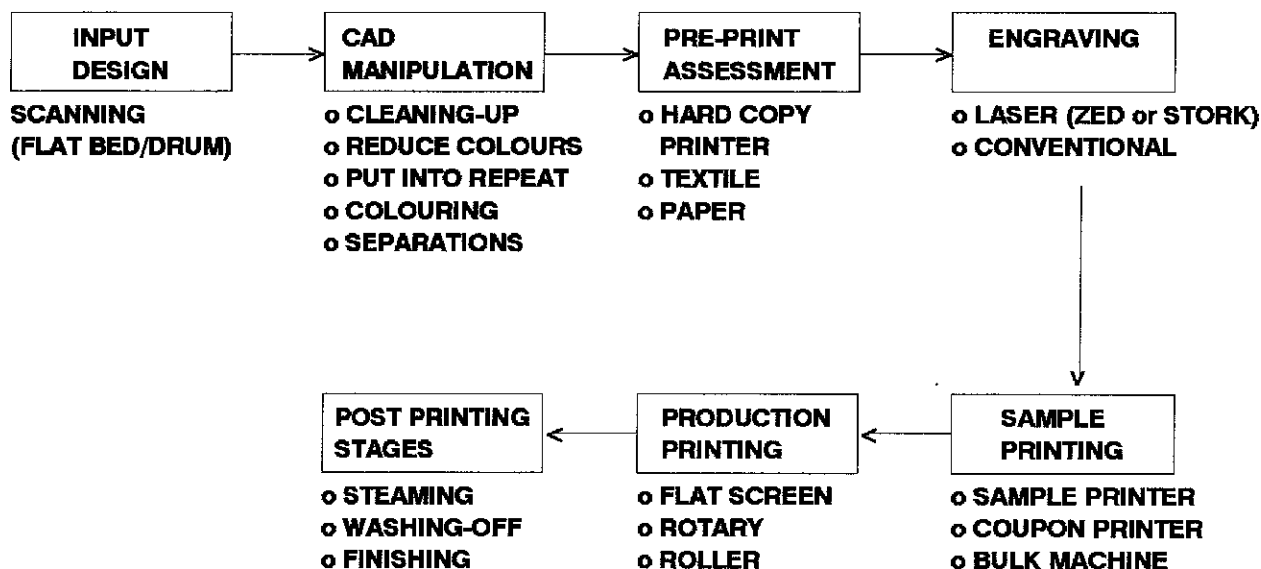


Figure 2. Integration of CAD Systems into Print Production

hydroxyl groups within the cellulose and subsequently washed to remove any unreacted colour, chemicals and the thickener. A much more complex process than conventional ink jet printing on paper. This requirement for extra chemicals to fix the reactive dye, the reactivity of the dye itself under alkaline conditions and the relative small amount of ink formulation applied has led to the modification of conventional print technology and the introduction of chemical pre-treatments<sup>2,5</sup>.

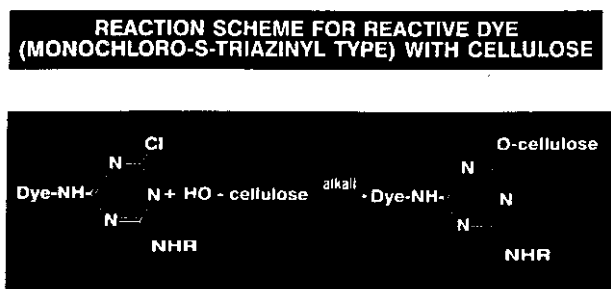


Figure 3. Reactive Scheme for Reactive Dye (Monochloro-s-triazinyl type) with Cellulose

### Textile Substrate Pre-Treatment

As discussed earlier STORK introduced the first commercially available textile system using reactive dyes in 1991. The reactive dyes used and the pre-treatment technology were developed by ZENECA Colours<sup>14</sup>. The reactive dyes are based on PROCION P dyes and contain a monochlorotriazine reactive group.

With this system (and the majority of other systems based on bubble-jet technology) the chemicals required for fixation of the dyes have to be applied by a padding application prior to jet printing. However, the resultant colour yield with this process is still not comparable to that achieved by conventional printing processes due to the small amount of ink formulation applied by jet printing. With the STORK TruColor TCP 2500 at maximum intensity approximately 20 gm of each ink formulation is applied per square metre (independent of the substrate weight/sq metre). In conventional printing the amount of print formulation applied can be adjusted to a particular substrate/sq metre and in many cases can be up to 200 gm/sq metre. Therefore extra chemicals are required to enhance the colour development of the reactive dye. A typical process route for mercerised cotton is illustrated in Figure 4.

The ZETEX Enhancer SJP<sup>15</sup> is a hydrophilic quarternary ammonium based chemical developed specifically for jet printing. Similarly for other textile substrates (silk, wool, viscose, etc) other process routes have also been developed<sup>14</sup>. Polyester substrates (which can not be coloured by reactive dyes) require either disperse dye formulations or specific pre-treatments to allow the reactive dyes to develop a comparable colour yield (but no fixation) to disperse dye colours.

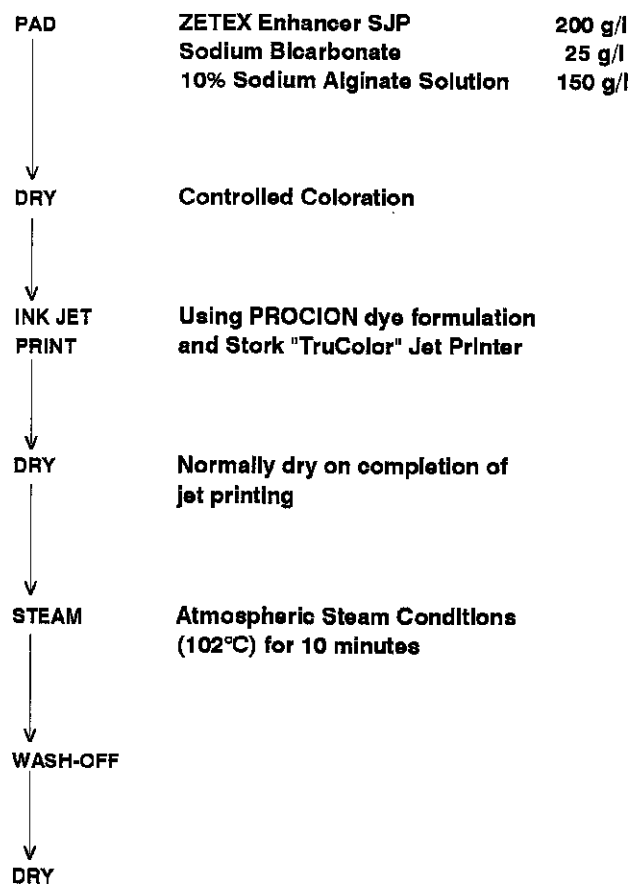


Figure 4. Process Route for Jet Printing of 100% Mercerised

### Application Areas of Current Jet Printers

The major application areas of jet printing have been in the pre-printing (proofing and sample print areas) and for colour communication. Essentially they fall into 3 main areas:

- at the colouring and design stage. Samples on fabric can be obtained quickly in a choice of colourways without having to make films, screens or print paste so customers can make the "Go/NoGo" decision for a particular design in a particular colour combination.
  - at the engraver, to check the designs he has made. The designs can be completely checked before the screens are engraved.
- and thirdly
- Jet printers can be used as a method of producing small-scale production prints of exclusive designs (for example for ties, scarves and pocket handkerchiefs) within a very short time compared to any procedure involving an engraving stage.

Similarly one-off sample prints for use in garments for selection purposes by a retailer, photographing for mail-order catalogues or publicity material in advance of bulk production can be produced.

Since the introduction of this approach customers can submit a new design (or could equally submit digital

information produced from his own CAD system) to the textile printer. The textile printer could then scan the design into a CAD system, subsequently working through the necessary cleaning-up, repeat setting, separation and colouring stages that many of the new systems are capable of carrying out. The 'key' element of the procedure is that the textile printer can use the CAD generate digital information to drive the jet printer and produce a sample print. The subsequent jet printed sample follows the normal post printing operations of steaming and washing-off. This enables the production of realistic small samples in a short time without the requirement of engraving screens or producing conventional sample prints.

Only when firm decisions have been made would screens be engraved and a conventional sample printed for final approval prior to bulk production.

In addition production of colour atlases that can be ink jet printed onto cloth opens up new possibilities in the specification and communication of colours. Easy translation of jet sample prints into bulk production recipes could also be made easier by the use of colour atlases. These recipes can be transmitted electronically to automatic dispensing colour systems for production of colours for production printing. This then gives the capability of 'integrating' the total textile print production process.

### Recent Developments

As discussed in the Introduction conventional textile printing uses a separate screen for each of the colours required. The conventional textile printer has therefore the complete range of colours to choose from when producing a design. For example, if a customer requires a bright orange colour he can choose a bright orange reactive dye to satisfy the customer. With Jet Printing

technology ('continuous' and 'drop-on-demand') colours are normally produced using 4 colours only (Cyan, Magenta, Yellow and Black), therefore to produce a bright orange the Yellow and Cyan are used. A comparison of the colour space produced using the four PROCION reactive dyes used in the STORK 'TruColor' jet printer and that available to the conventional printer using all available reactive dye is shown in Figure 5 (in CIE Lab space). Approximately 70% of the full gamut can be produced using the CMYK 'set' of PROCION dyes. However, the full colour space and the requirement to achieve full half tones (i.e. to simulate the production of conventional prints) are two requirements requested by printers. The production of such half tones can be achieved using continuous jet printers such as those based on the Hertz technology but the production of the full colour gamut requires a more radical development. At the October 1995 ITMA STORK introduced a new jet printer based on the Hertz technology capable of jet printing 8 colours (the PROCION dye CMYK colours with the addition of 4 new PROCION reactive dyes; Golden Yellow, Orange, Red and Blue). This has extended the gamut to that approaching the full reactive dye gamut available to the conventional textile printer. The availability of such a system will now enable the pre-printing stage to produce all the colours that can be subsequently printed by conventional printing. The further acceptance of jet printing by the textile printer will almost certainly lead to further developments in 'coupon' (larger scale sample) and ultimately bulk production.

### References

1. J. R. Provost, 'Dynamic Response in Textile Printing', *Textile Chemist & Colorist*, June 1995, Vol 27, No. 6, p11.

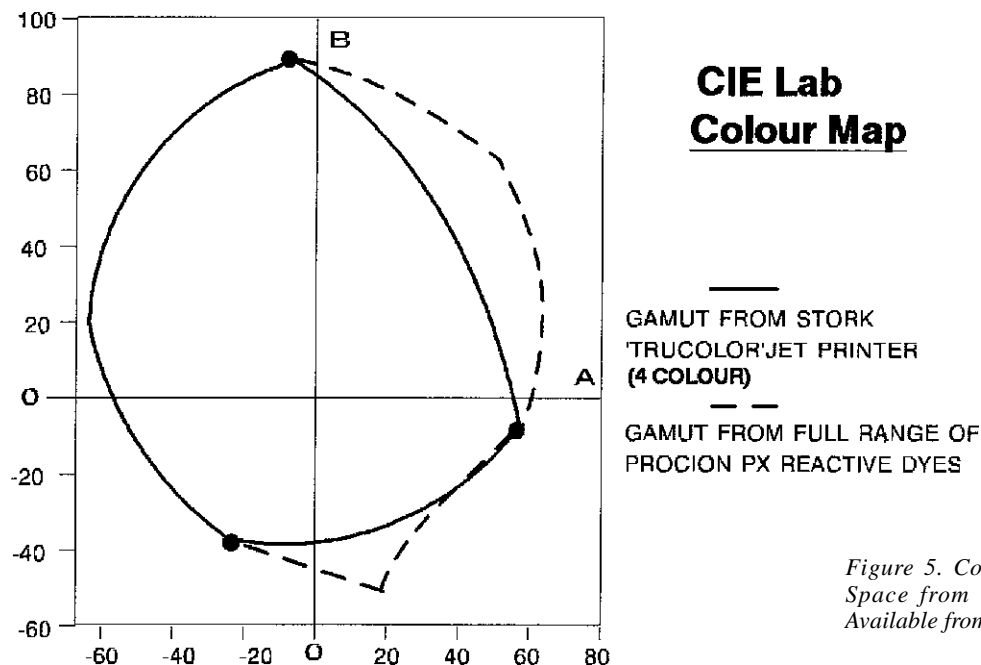


Figure 5. Comparison of Reactive Colour Space from CMYK Print and Full Gamut Available from Conventional Textile Printing

2. T. L. Dawson, 'Jet Printing', *Rev. Progress in Coloration*, **22** (1992) 22.
3. K. Dunkerley, 'Developments in Carpet Printing', *Rev. Progress in Coloration*, **11** (1981) 74.
4. T. L. Dawson, B. Roberts, 'Dyeing and Printing Method for the Coloration of Carpet Yarn and Carpet Piece by Jet Impregnation', *JSDC* **93** (1977) 439.
5. S. O. Aston, J. R. Provost, H. Masselink, 'Jet Printing with Reactive Dyes', *JSDC* **109** (1993) 147.
6. C. H. Hertz, 'Ink Jet Printing', *Advances in Electronics and Electron Physics* vol **65** (1985) 91 (Academic Press).
7. C. H. Hertz, B. A. Samuelson, 'Ink Jet Printing of High Quality Images', *J. Imaging Tech* **15** (1989) 141.
8. Eureka Project, EU796.
9. Brite-Euram Project, BRE2-CT93-0544.
10. Graham, L., 'Ink Jet Systems for Dyeing and Printing of Textiles', *Textile Chemist & Colorist* **21** (1989) No. 6, p27.
11. Anon., 'Kanebo and Canon Jointly Develop Bubble Jet Printing System', *Japan Textile News*, March 1993, p90.
12. Kanebo/Toshin, U.S. Patent, 5 345 863 (17th September 1994).
13. A. Johnson (Ed.), 'The Theory of Coloration of Textiles' (2nd Edition), *Society of Dyers and Colourists* 1989, p428-486.
14. J. R. Provost, 'Ink Jet Printing on Textiles', *Surface Coating International (JOCCA)* **77** (1994) 36.
15. ZENECA, European Patent Application 534,660 A1 (14th September 1992).