Digital Inkjet Dyeing and Printing of Textiles with Vat Dyes

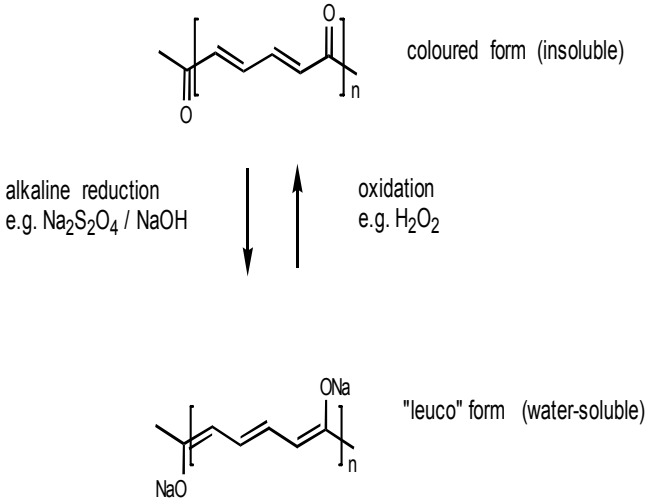
Robert M Christie, Shah M Reduwan Billah, Roger H Wardman; School of Textiles & Design, Heriot-Watt University,Galashiels,TD1 3HF, Scotland, UK.

Abstract

The well-established commercial inkjet ink formulations for cellulosic textile fibres commonly make use of reactive dyes. Cellulosic fibres are also dyed and screen printed commercially with vat dyes, especially for high performance and technical applications. However, inkjet printing with vat dyes remains problematic. Within the EC Framework 6 integrated project DIGITEX, Digital Fast Patterned Microdisposal of Fluids for Multifunctional Protective Textiles, we have developed an inkjet system for digital dyeing and printing of cotton using solubilised vat dyes. Aqueous-based inkjet inks using solubilised vat dyes have been developed with appropriate physical and rheological characteristics providing good jettability during printing on to cellulosic fibres. Dye purification and judicious additive selection to minimise premature formation of the vat dye and consequent reduced ink storage stability were essential to produce high quality inkjet inks. With these formulations, and with appropriate optimised fabric post-treatment, inkjet vat dyeings and prints on cotton may be produced with a high standard of technical performance.

1. Introduction

Digital inkjet printing technology is becoming increasingly important industrially for textile coloration, attracting growing interest from print technologists and designers, especially in view of its potential to provide high production flexibility and responsiveness [1]. Inkjet technology also has distinct attractions from an environmental perspective, compared with traditional dyeing and printing techniques. Inkjet printing ink formulation technology is now well-established commercially and uses the dye classes that are appropriate to the fibre type. For example, acid dyes would normally be used for application to protein fibres and disperse dyes for polyester. Inkjet printing of cellulosic fibres, including cotton, viscose and lyocell, most commonly uses specifically selected reactive dyes [2-4]. However, cellulosic textile fibres are also commonly dyed or screen printed industrially with vat dyes, especially for high added-value applications, since they can offer superior performance in terms of lightfastness and more aggressive laundering procedures compared with reactive dyes and, in application, they can consume less water for washing and clearing. Vat dyes thus retain considerable commercial importance for the production of high quality dyed and printed cellulosic textiles, for example as used in curtains, bedding and upholstery [5]. There is thus considerable interest in the development of a methodology to deliver vat dyes on to textiles using digital inkjet technology. However, inkjet printing with vat dyes remains problematic, because of the insoluble, pigmentary nature of vat dyes and also because of the aggressive chemical processing required in their application. A generalised scheme for the well-established chemistry involved in vat dyeing and printing is illustrated in Scheme 1. The insoluble coloured (pigmentary) form of the dye is subjected to a reduction process, generally using sodium dithionite under alkaline conditions. This process provides the water-soluble *leuco* form of the dye which is substantive towards and capable of penetration into the cellulosic fibres. An oxidation process, commonly utilising hydrogen peroxide, is then used to regenerate the insoluble pigmentary form within the fibre. In this form, it becomes mechanically trapped as individual crystallites and as a consequence provides an excellent set of fastness properties.



Scheme 1. The chemistry of vat dyeing and printing

One potential approach to inkjet delivery of vat dyes which might be followed is to print the dyes as if finely-dispersed pigments, followed by the required reduction/oxidation fixation process, carried out either using fabric pre-treatment or post-treatment. Alternatively, a process may be envisaged whereby the water-soluble leuco form of the vat dye is delivered by means of inkjet. However, such a process would expose the printhead to the aggressive alkaline reduction medium used, and would also present significant difficulties with ink stability because of the ease of air oxidation of the leuco dye solutions. Within the EC Framework 6 integrated project DIGITEX, Digital Fast Patterned Microdisposal of Fluids for Multifunctional Protective Textiles, we have developed an inkjet system for digital dyeing and printing of cellulosic fibres using solubilised vat dyes as reported in this paper. Another partner within DIGITEX has been developing an inkjet process based on delivering a stabilised aqueous dispersion of the pigmentary form of the vat dye.

2. Experimental

2.1 Materials

CI Solubilised Vat Yellow 4, Green 1, Blue 5, Red 1, Brown 5 and Black 16 were obtained from Karan Dyestuffs Ltd, India. The dyes were purified by a multiple recrystallisation procedure with filtration of residual solids at appropriate stages.

2.2 Equipment

A Xenjet 4000 inkjet dispenser system was used with a Xaar Omnidot 760 piezoelectric drop-on-demand printhead, integrated with a syringe vacuum system connected to a Xaar ink supply controller, XUSB drive electronic box and print table. Viscosity and surface tension were adjusted during the ink formulation according to the printhead requirements. Viscosity was measured using a Brookfield DV-II Viscometer and surface tension using a Kruss tensiometer, model K6.

3. Results & Discussion

Solubilised vat dyes are sodium salts of sulphate esters derived from leuco vat dyes as illustrated in the general structure given in Figure 1. These dyes are applied to cellulosic fibres from aqueous solution, facilitated by their water solubility, and are subsequently converted on the fibre to the vat dyes by acid hydrolysis, which cleaves the sulphonate ester group to generate the leuco dye, followed by oxidation. The only previous reports of inkjet printing using this class of dyes are focussed on paper applications [6,7]. In this paper, we now report the development of a process for inkjet delivery of solubilised vat dyes on to cotton fabrics.

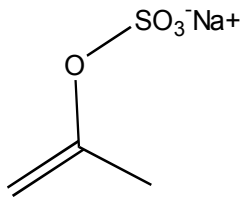


Figure 1: Generalised structural features of a solubilised vat dye

A number of particular issues required special attention for ink formulation using these dyes. For inkjet printing, the dyes are required to be of high purity, especially in terms of minimising inorganic salt content and avoiding particulates. The commercial dyes as received required the development of a large scale purification process involving multiple recrystallisations with filtration of residual solids at appropriate stages. During the purification process, it was necessary in some cases also to incorporate an anti-oxidant and to exclude light to avoid premature vat dye formation, which can be photoinitiated in the presence of air. Ink formulation was also complicated by the premature hydrolysis/oxidation phenomenon which can result in formation of a precipitate of the vat dye during storage. Some of the traditional formulation ingredients commonly used in textile inkjet ink formulation to ensure appropriate physical characteristics for jetting (for example humectants, co-solvents, viscosity modifiers) were found to promote this decomposition, and it was thus necessary to experiment extensively with alternatives in order to produce a suitable ink. A key feature of the optimised ink formulation process was the development of an appropriate anti-oxidant system which provided adequate ink storage stability and shelf-life, but which did not significantly inhibit the final oxidation stage after application to the fabric.

Ultimately an optimised aqueous-based ink formulation, with a dye content of 5-10%, was developed providing good jettability, storage stability for several months and adequate colour strength development on the fabric. Following printing, it was found to be advantageous to subject the print to a thermal treatment at 120-150^{o}C in order to ensure fixation of the dye to the cellulosic fabric and also to initiate the hydrolysis/oxidation stage. Solubilised vat dyes are commonly converted to the vat dye form on the fibre by treatment with sodium nitrite and sulphuric acid. This method was found to be suitable for injket printed systems and more efficient than using methods based on hydrogen peroxide. However, we have also found the UV-initiated photooxidation may be used to effect the final conversion, offering particular advantages for inkjet printing. Prints with appropriate washfastness and lightfastness characteristics were obtained, as detailed in Tables 1 and 2. In some cases, it was necessary to make repeat passes of the print in order to achieve reasonable depth of colour.

Table 1. Washfastness for CI Solubilised Vat Blue 5 inkjet ink printed on cotton

Number of passes	Colour change	Staining of adjacent fabrics of the multifiber					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
1	5	5	5	5	5	5	5
2	5	5	5	5	5	5	5
3	4/5	5	4/5	5	5	5	5

Table 2. Lightfastness (Xenotest) (all printed with two passes) of inkjet printed vat dyes on cotton

Dye	Blue wool scale rating
C.I. Solubilised Vat Blue 5	6-7
C.I. Solubilised Vat Red 1	7-8
C.I. Solubilised Vat Green 1	7
C.I. Solubilised Vat Yellow 4	6-7

4. Conclusions

Aqueous-based inkjet inks may be prepared from solubilised vat dyes. Using these inks, formulated to provide the appropriate physical and rheological characteristics for good jettability, vat dye prints on cotton may be obtained showing good technical performance, following an optimised fabric post-treatment process. Dye purification and judicious additive selection to minimise premature formation of the vat dye and consequent

reduced ink storage stability were essential to produce high quality inkjet inks.

5. References

1. H. Ujiie, Digital printing of textiles (Woodhead Publishing, Cambridge, UK, 2006).
2. S. O. Aston, J. R. Provost, H. Masselink, "Jet printing with reactive dyes", JSDC, 109, 147 (1993).
3. M. Kanik, P. J. Hauser, "Printing of cationised cotton with reactive dyes", Coloration Technology, 118, 300 (2002).
4. A.W Kaimouz, R.H. Wardman, R.M. Christie, "The inkjet printing process for lyocell and cotton fibres, part 1: The significance of pretreatment chemicals and their relationship with colour strength, absorbed dye fixation and ink penetration", Dyes and Pigments, 84, 79 (2010).
5. U. Baumgarte, "Vat dyes and their application", Rev. Prog. Coloration, 5, 17 (1974).
6. S. Koike, Y. Tomida, Canon, Japan, US Patent 5053078 (1991).
7. S. Koike, Y. Tomida, Canon, Japan, US Patent 5257038 (1991).

Author Biography

Robert Christie is Professor of Colour Chemistry & Technology at Heriot-Watt University, UK. His career has also included periods in the colour manufacturing industry with Ciba and Dominion Colour Corporation. His research interests are in organic pigments, fluorescent dyes, hair dyes, chromic textiles, inkjet printing on textiles, environmental issues and the textile design/technology interface. He has published 5 textbooks in colour chemistry, over 100 journal articles and patents and has presented at more than 40 international conferences.