Chemistry of Textile Inkjet Inks

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Abstract

A textile inkjet ink formulation essentially depends on the chemistry of substrate. It is important to select the right chemistry of the dyes or pigments and formulate inks that provide good visual and technical properties on the target substrate. However, limitations applied by the working window for available print head technologies, such as the viscosity, compatibility of ink with print head components, temperature restrictions, stability, pH sensitivity, particle size etc, require the inkjet formulator to understand the chemistry of the substrate and colorant, application method, processes involved in the preparation of fabric, post treatment of fabric and application conditions, to be able to formulate ink that provide acceptable visual, optical and technical properties. This paper reviews the current state-of-the-art Ink chemistry required for natural and synthetic fabrics.

Introduction

The concept of printing textiles by inkjet technology is fairly new. Inkjet printing processes have been used in textile industry for some years and have started to claim growing share in textile print production worldwide bringing considerable savings. Conventional printing method does not meet existing and future needs for short run, just in time delivery and quick response to fashion changes.

A numbers of commercial Inks are appearing in the market, many claiming to offer similar technical advantages as other conventional printing technologies. However, the textile industry is a little conservative and appears less keen to adopt inkjet as alternative to traditional printing in its current market, there are serious concerns regarding the cost and throughput for longer production runs. However, inkjet is clearly a winner for it ability to produce high resolution high quality prints with outstanding image definition.

This review is an effort to provide comparative comments and highlight the status of available inkjet Ink chemistries, printing processes and some typical formulation requirements for textiles, which are disclosed in patents over the last 20 years. It is also an aim to underline the challenges and complexities that a textile ink formulator may face.

Issues in Textile Inkjet Printing

Traditionally, textile printing inks are prepared in form of paste that is suitable to use with rotary or silk screens and can be formulated over broad range of viscosities according to the type of screen, image quality and printing speed. Since it is a contact printing method, print paste is forced through to screen meshes to the substrate giving direct control over the ink penetration on the substrate and through-prints can be achieved for fabrics with low densities. It is also a general practice to prepare required quantities of fresh inks just before the production runs or sample strike off so storage stability of a week would be sufficient in most cases. If the colorant or additives are sensitive then it can be prepare and applied immediately.

In Contrast, physical and physical chemical properties of inks for inkjet should be optimised for specified Inkjet Technology and printheads. The rheology of ink is an extremely important parameter in the design of ink because this aids droplet formation through the nozzle in a controlled manner for any given inkjet technology.

There are two main technologies available

- Continues Inkjet (CIJ)
- Drop on demand (DOD)

for both technologies there are different requirements for ink formulations. Continuous inkjet method is more suitable when a low resolution image satisfies the quality requirements. Whereas, DOD is the only inkjet method that is currently able to produce very high resolution images. Valve jet is another non impact method that produces very large drop size and suitable to print substrate where deep ink impregnation is more desirable then print quality. Zimmer has been offering printers based on valve jet technology for printing high pile substrate such as carpets and door mats.

Required Physical characteristics for continuous, DOD and valve jet are given in Table 1. Industrial DOD heads generally require higher viscosity inks, for example 8 to 20 cps. Xaar and spectra printhead are typical example of industrial print heads. Whereas, light duty print heads require low viscosity, for example 3-8 cps. Epson print heads are typical example for such printhead

Table 1: Working window for deferent Inkjet technologies

Ink Properties	CIJ	DOD		Valve Jet
		Piezo	Thermal	
Viscosity /cps	~1.5	5-20	~1.5	<2
Surface Tension dynes/cm	25-40	>32	>35	>24
Max particle size Microns	1	1	0.2	5
Conductivity	Yes	No	No	No

Textile ink formulation is a multidisciplinary technology and it has been realised from very early days that Ink and material chemistry is the key to commercial success of inkjet as alternative to conventional printing. Both dyes and pigment have been used as colorant to create image on variety of woven and non woven substrate. Conventionally reactive dyes, disperse dyes, vat dyes, sulphur dyes and pigment are widely used with variety of substrate. (Table 2). However, only reactive, disperse and pigment inkjet formulations have appeared in patents. We have included typical disclosed formulations (Table 3-6) and processes for each type of chemistry in their respective sections.

Table 2: Common textile substrate and suitable colorant

Ink Chemistry	Cotton	Polyester	Silk	Wool
Reactive	O			
Disperse		O		
Acid			O	O
Vat	O			
Sulphur	O			
Pigment	O	O	O	O

Inkjet textile inks are required to produce print that posses high light fastness, wash fastness and crock fastness. It is important that the print should not undergo any changes during post treatment and must meet the federal health and safety requirements for textile and apparels.

Additionally, inks should exhibit following properties

- Impart sufficient Visual density
- Optimised Viscosity
- Good latency
- Storage stability
- Quick drying on fabric
- Hardware compatibility

Since colouring textile substrate essentially requires compatible chemistry, we have divided inks technologies based on their chemistry and their physical chemical interaction with target substrate and typical formulation chemistries are discussed.

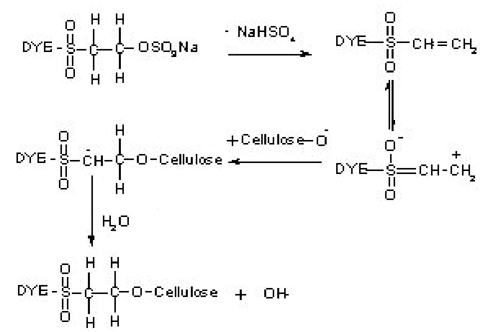
Reactive Inkjet Inks

Various classes of dyes for cellulosic fibres have been developed, but no single type is free from some technical limitations. One of the most successful technological contributions to textile dyes has been the development of reactive dyes. These drive their name from the fact that their fixation on fabric involves the reaction of a functional group of the dyestuff with the fibre, to form a covalent bond between the dye and the fibre. The remarkable growth of reactive dyes since their inception is attributable to their, high brilliancy of shade and all round fastness for general use, together with universal application to pure and regenerated cellulose.

Reactive dyes are applied to cellulosic fibres from aqueous medium in the presence of an alkali to promote the fixation reaction of dye to fibre through covalent bond formation. Bond formation is via the reaction of cellulosate anion with the reactive system of the reactive dye molecule. An alkali is necessary for the formation of the cellulosate nucleophile and also removes any acid liberated during the fixation process. If the medium becomes acidic, the fixation process will cease. A reaction scheme for vinylsulfone based reactive dye with cellulose is given in Figure 1.

The reactive dyes employed for inkjet Inks must be of high purity grade. The chosen dyes should have a high colour strength, posses large extinction coefficients and show adequate solubility to enable water based inks of high concentration to be prepared. It is possible that the ink will fail to deliver good visual strength if it is washed away during post processing. Prints with a low degree of fixation will also result in poor crock fastness and ultimately will be rejected.

Figure 1: β-elimination of β-sulfatoethylsulfate to Vinyl sulfone and reaction with cellulose



Despite the large number of reactive inkjet inks that are commercially available, It is often a challenge to produce print with deep shades. This is commonly realised through multipass printing at high resolutions. Some patents report the use of cationic polymer during the preparation of fabric for printing with anionic dyes(1-3). This increases the dye absorption in the fibre and improves the fixation of dye to fibre. A greater effect can be achieve by selecting dye with high substantivity that has strong chemical affinity towards cellulose, for example by selecting such reactive dyes for inkjet formulation with high tinctorial strength and with narrow half bandwidth wavelength, it is possible to achieve deeper shades and brighter colours with a large colour gamut and prints with good overall technical properties.

The rheology of inkjet fluid determines the quality of drop formation and it is important to use viscosity modifiers that are compatible with the reactive dye chemistry. US Patent 20030177945A1 reports a comprehensive list of such polyhydric alcohol having no primary alcohol groups that can be used as viscosity modifiers (4). International patent WO03/076532 reports the specific use of polypropylene glycol as a viscosity modifier that also improves the jet characteristics (5). Other viscosity modifiers such as alginates have also proved useful (6,7).

Reactive dyes are also susceptible to hydrolysis. If reactive dye based ink formulations containing an alkali, such as sodium bicarbonate, were prepared for inkjet printing then the ink would have an extremely limited shelf life due to the rapid hydrolysis of the dye to a non reactive form. Early patents (4,5,7) report a two phase printing method to address this issue, which require a preparation of fabric, in which the fabric is padded with a solution of alkali and subsequently dried before printing. Alkali may also be applied after printing but this will require a controlled process to avoid any bleeding and loss of image definition. A later patent (8,9) discloses a more appropriate one phase method, which reports the use of a source of alkali that will decompose during heat treatment and releases alkali to provide the correct pH environment required for fixation reaction.

Uses of dyes containing vinylsulfone(8), monochlorotriazines or monofluorotriazines (9,10) groups have been found suitable for inkjet formulations. In general monochlorotriazines reactive dyes are less reactive then di or trichlorotriazines dyes and exhibit good storage stability. However, formulations containing bifunctional reactive dyes are also reported as suitable for Inkjet (11). Reactive part containing cyanmidoethylene group, which is less reactive then dyes containing N-alkyl groups are also reported to have long shelf life (12).

Table 3: Typical Reactive dye based formulation

Reactive Dye	5-15%
Solvent	20-40%
Surfactants	0.1 -1%
Water	40 – 70%
pH regulator	Adjust to 5-8

Acid dyes based inkjet inks

Water based inkjet inks based on acid dyes have strong affinity toward protein fibres and are especially useful in printing synthetic polyamide, silk and wool. Inkjet ink formulations with acid dyes are somewhat more straightforward then any other class of colorant. Acid dyes are substantially water soluble and can be formulated to concentration up to 10% w/w with ease (13), however, this will depend on the selection of dye that has good solubility product. Typically, humectants, co-solvents and other additive are added to the formulation to improve jetting performance. After printing fabric is steamed and subsequently washed to wash-off any unfixed or loosely fixed dye, rendering fabric excellent fastness to wash and rub.

Table 4: Typical Acid dye ink formulation

Acid dye	5-10%
Solvents	10-30%
Additives	1-5%
Surfactants	0.1-1%
Water	60-90%

Textile Pigment Inkjet Ink

Pigment inkjet ink composition for textiles is one of the most challenging areas for an inkjet ink formulator. Pigments do not have any affinity towards substrate and require a binding mechanism to bind the pigment to the substrate in order to achieve required technical properties such as wash fastness and crock fastness. Conventionally, no fabric pretreatment is necessary for patterns with full ground coverage and no further post washing is required, generally after printing subsequent heat treatment is critical for drying and to achieve a high degree of fixation. Pigments can be applied on any fabric and therefore, is suitable for printing fabric blends. However, in addition to meet required fastness properties, there are two major issues that are crucial for success of inkjet jet ink formulation that is suitable for application on textiles. A pigment based inkjet ink should have

- Low viscosity stable pigment dispersion and
- A binder system that is stable and chemistry is suitable for given substrate

Particle sizes in the range of 20 to 200 nm are preferred for inkjet inks for reliable performance through nozzle (14,15), however, particle size as large as 15 micron has been reported as suitable (16) no further detail were given in this account. Ionic and nonionic dispersants both are generally used for stabilizing pigment dispersants but dispersants are tend to increase viscosity due to their high molecular weight. This limits the scope of pigment concentration, in the range of 4-5% w/w, in ink and therefore, deep color densities can only be achieved by multi print passes and by increasing the print resolutions, both resulting into high running cost and low production. Pigments can also be homogenously dispersed in water in emulsion form by modifying pigment particle by encapsulating with polymer (17). Self-dispersing pigment, containing built-in water soluble functionality, gives very low viscosities, were claimed to be suitable for textile (18) but offers inferior fastness to wash and crock, this is due to the fact that pigment particle that is loosely bonded on the binder surface has high affinity towards water and will easily wash away during laundry resulting in a faded image. Since the solubility of dispersant increases logarithmically with temperature, dispersion should remain stable at operating temperature and important for storage stability when it may be exposed to high temperature.

Use of acrylic self cross linking binder has been proven very successful in conventional printing process. Similar binder system are also suitable for inkjet formulations (19,20) but such formulation shows poor latency at higher binder loading limiting the scope of increasing pigment content in formulation (20). Use of cross-linking agent has been reported useful for pigment ink formulations with increase ink stability but mostly suitable to print on cotton and blends where cotton is the predominant part of fabric constitution. Use of cross-likable polyurethane as dispersion aid has also been exploited (21), this may eliminate the addition of binder at later stage, thus allow to formulate low viscosity ink. Drying and curing time required to produce prints with desirable technical properties is also important for a successful formulation, usually 3-5 min would be consider acceptable. it is worth mentioning that most of the pigment formulations will not suitable to use with thermal inkjet printhead technology. There is risk of activating binder that could cure, form film or resulting into increased viscosity, when come in to contact with thermal resistor that generate heat to create bubble for droplet formation.

Table 5: A typical pigment based aqueous formulation

Pigment	3-5%
Binder	5-10%
Solvent	20-40%
Surfactants	0.1 -1%
Water	40 – 60%

Disperse Dye based Inkjet Inks

Disperse dyes are essentially water insoluble dyes and have an affinity for hydrophobic fibres; these are usually applied from fine aqueous dispersions, principally to polyester, but also to cellulose acetate and polyamides. Disperse dyes are capable of providing bright colours good to excellent fastness properties and good printing characteristics. Azo and anthraquinone derivatives are the major types of chemical structure found among disperse dyes and there are many useful disperse dyes based on heterocyclic ring systems.

Since disperse dyes are applied in the form of very fine aqueous dispersion, particle size and dispersion stability are extremely important. Ideally, a commercial disperse dye is required to disperse extremely rapidly when added to water and to give a stable dispersion of very fine and uniform particle size generally suitable for inkjet formulation. Aqueous solubility of the disperse dye can also help the stability of dispersion. Aqueous solubility at 80ºC ranges from 0.2 to 100mg/l.

Currently, disperse dyes are marketed in two major forms, powder and liquid. The powder brands contain a considerable amount of dispersing agent. In the liquid form the dyes are concentrated as free-flowing aqueous dispersion.

Polyester fibre poly (ethylene terephthalate), dominates the world synthetic fibre industry and is major class of fibre for textiles and apparels after cotton worldwide. Polyester does not posses any functional groups that are capable of ion-ion bonding with ionic dyes. However, disperse dyes have affinity towards polyester at high temperatures, capable of adsorbing onto the surface. Therefore, a post heat treatment is necessary to achieve fixation with subsequent washing to wash off any loosely held dye onto the surface and provide good technical properties

Two typical type of inkjet process have been offered, both are suitable for printing on polyester

- Transfer printing
- Direct printing onto fabric

Disperse dyes are widely employed for transfer printing due to their ability to sublime and transfer to the surface that has more affinity for it. In this method of printing an image is printed onto an intermediate transfer sheet, and then image is transferred to another surface by applying heat to the intermediate sheet. An ink that uses such dyes is characterised as heat sensitive, dye diffusion or sublime inks. Not all disperse dyes may be selected for such application, hence, selection of dye for the inkjet formulation for transfer method of printing must be made carefully, such as, their sublimation temperature and application requirements, colour strength, affinity to substrate etc. Intermediate medium is generally used for this method are none porous paper and has limits on what quantity of dye can be deposited on to it. Selection of dye with high colour strength may help to achieve high colour strength desirable for textile application.

Direct printing on substrate is more desirable method for creating image on textile by inkjet. It eliminates the use of intermediate substrate that can be very costly for long production run. For both type of formulation it is important to select the dyes that are suitable for long term storage and resist the agglomeration. Large particle size will apparently result into low colour density. Disperse dyes are also sensitive to pH and may fade if expose to pH above 7. There is also possibility that change in the chemical structure of dye may destabilised the dispersion. Polymers, humectants, solvents, co-solvents and other additives can be added to the formulation according to the Ink requirements for printhead technology, such as viscosity, surface tension and pH.

Table 6: A typical disperse dye based aqueous formulation

Disperse Dye	3-5%
Solvents	20-40%
Surfactants	0.1 -1%
pH regulator	Adjust to 5-7
Water	40 – 60%

Conclusion

Whilst the application of inkjet technology in the textile industry is in its infancy, there are many advantages that can be seen when compared to conventional textile processes. This paper has highlighted a number of areas of textile printing and describes some of the known issues and challenges that face the inkjet formulator today. In particular the use of reactive dyes and pigment with their associated chemistry offers some interesting opportunities if the right formulations can be developed. It is likely, in the short term at least, that hybrid systems may be the most promising candidates which incorporate chemistries, which will be applicable to both man-made and natural fibres, the challenge will be to combine these chemistries into an inkjet printing process.

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Dr. Karim Ali has a B.E Honors degree in Textile Chemistry and a PhD in Color Chemistry from the University of Manchester, UK. Karim joined Xennia in 2006. Prior to this, Karim worked in the area of Textile printing and gained experience in chemical technology of textile. Since working for Xennia, Karim developed a number of novel inkjet inks for Continuous and DOD printhead technologies and is also responsible for developing inkjet inks for textile materials.