Coloration Systems for Ink Jet Printing of Textiles

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Abstract

Little detailed information has been published on ink formulations for ink jet printing on textile substrates. Requirements for coloration systems for textile printing will be reviewed and approaches for achieving the desired characteristics will be suggested. Coloration systems based on polymerizable resins with solvent dyes, two phase inks with pigments and inks based on polymerizable dyes will be described. Sample coupons employing these experimental systems were prepared on a TOXOT continuous ink jet printer and properties of these experimental systems on textile substrates will be reported (fastness properties, bending rigidity, etc.)

Introduction

It is generally accepted that ink jet printing will become an important technology in printing of textiles, particularly in a demand activated manufacturing environment.[1,2] Hardware and software systems that have been developed for printing on paper should be readily applicable to textile printing if problems of speed and reliability can be solved.[3]

Ink formulations developed for paper, on the other hand, are not acceptable for textile printing. Washfastness and hand requirements for textiles will require quite different properties in ink formulations from those in current ink systems. The wide variety of fiber and fabric types and the range of desired properties in textiles for different applications will probably require development of a number of different ink systems for each of the types of ink jet printing engines.

Requirements for Ink Systems for Textiles

There is no generally accepted set of criteria for ink systems for ink jet printing of textiles. The requirements for uniform and consistent drop formation place very stringent restrictions on viscosity and surface tension of the fluid. Other requirements of different print engines such as high temperature resistance, conductivity and overall stability are very difficult properties to achieve.

It is probable that inks based on both dyes and pigments will be required. The greatest divergence of opinion occurs in the extent of post print processing that will be acceptable. A number of systems are being developed based on standard dyeing processes currently used in textile coloration. These systems require different dye classes for different fiber types and typically require post steaming, washing and drying to achieve acceptable properties in the printed fabric. Other experts feel strongly that fabric printing must be like paper printing with no post processing required. A number of variations between these two extremes have been proposed. The different opinions arise primarily due to the varying concepts of where in the textile manufacturing chain ink jet printing will actually be performed. Those who believe that ink jet printing will replace current printing technologies in the textile industry feel that post processing will be readily acceptable. Those who feel that ink jet printing will be practiced by design studios, apparel manufacturers and retail establishments argue for little or no post processing.

Finally, the deposited ink must have the necessary fastness properties and must not adversely affect the tactile properties of the printed fabric.

As a basis for the work reported in this paper, the following criteria were selected to guide the development of ink jet systems for textile printing:

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

Polymerizable Ink Systems

One approach to development of low viscosity inks that have the required properties on the printed fabric is to ink jet a mixture of monomers and oligomers that can be post polymerized on the fabric. There are two major problems with this approach. First, the usual mix of mono and multifunctional reactants gives a highly crosslinked system with a dense, rigid polymer backbone (“comb” type polymer) that produces a stiff cured polymer and an unacceptable fabric hand. Second, even with the use of the usual monomers and oligomers, the viscosity of a 100% reactive system is often too high for good jetting.

Both of these problems were solved by adding a substantial quantity of a reactive diluent, vinyl acetate, to the polymerizing system.[5] This diluent gave longer, flexible chain segments between the crosslinks of the polymer and also lowered the viscosity.

In preliminary screening of formulations for printing, films were cast from candidate formulations on glass plates, cured and tested for mechanical properties. The very early portion of the stress-strain curve (<10% extension) is especially important for textile hand properties.

Based on these screening studies a formulation based on an oligomeric polyurethane was selected for further evaluation. The actual formulation of the final polymerizable system on a weight per cent basis was:

Aliphatic urethane diacrylate	24
Tetraethylene glycol diacrylate	8
Vinyl Acetate	48
$LiClO_4$ (conductivity adjustment)	2
UV initiator	3
Acetone	15

Solvent and/or disperse dyes were selected as colorants for the ink jet system. These dye classes are water insoluble and do not dye the fiber but they are soluble in the ink and in the organic polymer layer that forms on the fiber surface during curing. No attempt was made in this work to maximize colorant concentration but levels in excess of 1% by weight were easily incorporated in the ink. Final properties of the formulation are given below:

Viscosity	3.6cp
Surface tension	25 mN/m
Conductivity	800 S/cm
T_g (cured film)	-5 C

The surface tension was somewhat lower than desired but not unexpected for a totally organic system. Subsequent tests indicated that the formulation could be successfully jetted.

The final formulation was tested by printing cotton print cloth (10.5 mg/cm^2) with an TOXOT Jamine™ 1000 S4 continuous ink jet printer. The system was cured for 8 seconds in an Argus™ 7000 series UV curing unit. There was no post processing of the fabrics other than UV curing. The ink deposition after curing was 4.9% on weight of fabric.

Some properties of the fabric printed with the experimental formulation compared to a typical rotary screen printed fabric are shown in Table 1. Although the fabric weights and the pick-ups were not identical, the difference in properties before and after printing at least suggest that the ink jet printed fabric showed comparable properties to the conventionally printed fabric.

Table 1. Properties of Ink Jet Printed Fabrics

Property	Experimental	Rotary Screen
Pick-up	4.9%	5.9%
Bending Rigidity	17% increase	31% increase
Flexural Rigidity	12% increase	81% increase
Dry Crock	5	4.5
Wet Crock	5	3.5

A second approach to control of the structure of the polymer on the fabric has been to use a chain transfer agent to extend chain segments between branch points. The extreme case in this method of control is the thiol-ene UV initiated polymerization. In this polymerization the initiated ene reacts immediately with a thiol which subsequently reacts with another ene. The polymer produced is essentially an alternating copolymer and the properties can be controlled by selection of the appropriate diene and thiol. This system has given some excellent film properties and shows considerable promise as a polymerizable system for ink jet printing of textiles.

Two Phase Ink Systems

Recent developments in emulsion polymerization provide another approach to delivery of low viscosity fluids to textile substrates by ink jet with appropriate properties for binding dyes and pigments to the fiber surface. Instead of polymerization after ink jetting, new small particle polymer latices containing up to 50% solids in water can be deposited on textile substrates by ink jet and thermally cured on the fabric[6]. A number of these latices are now available with particle sizes under 1 micron. Polymer structures in these latices can be varied over wide ranges to give the desired properties on the substrate.

A number of latices containing modified acrylic, acrylonitrile-butadiene copolymer, nitrile-butadiene copolymer and modified butadiene copolymer were obtained and screened using the cured film properties. Based on the screening studies, three latices (one modified butadiene copolymer and 2 modified acrylic polymers) were selected for further study. Inks were prepared by simply adjusting the solids content to obtain the desired viscosity and adding either dyes or pigments to the diluted latex. The formulations were evaluated as described above to ensure that the proper viscosity, surface tension, etc. had been obtained for good drop formation.

Printed specimens were prepared with the TOXOT printer on cotton, cotton/polyester blend, and silk fabrics to determine if a range of substrates could be printed with the same formulation. Samples were prepared with a number of different pigments and with ranges of pigment concentrations, resin to pigment ratios and weight per cent pick-up of ink on the fabrics. Observations of drop formation characteristics and print quality were also made. Results of evaluations of some of these printed samples are shown in Tables 2-4. Table 2 shows the very strong effect on properties of 100% cotton fabrics of three different resin compositions (15% resin and 4% pigment) applied at 5% total weight pick-up. Resin 1 is very similar in composition to resins currently used in rotary screen printing of fabrics. The other two are experimental resins with very fine particle sizes. Note that the properties of the Resin 1 printed samples are similar to values obtained on the rotary screen printed sample shown in Table 1. Both of the fine particle resins give better crockfastness and Resin 2 gives less change in hand. These results suggest that a resin-pigment printing system based on small particle latices can be delivered by an ink jet printer and give very acceptable fabric properties.

Table 2. Effect of Resins on Printed Fabric Properties.

Property	Resin 1	Resin 2	Resin 3
Bending Rig.	+31%	+15%	+36%
Flexural Rig.	+41%	+ 6%	+40%
Dry Crock	4	5	5
Wet Crock	3	4	3.5

Table 3 shows the results of printing of Resin 1 on 100% cotton fabrics at a higher resin solids level (20%) and a higher pigment level (6%) at an overall 5% solids pick-up. These were the highest levels of this resin-pigment system that could be consistently jetted on the TOXOT printer. Results for hand characteristics are similar to those in Table 2 which suggests that the total resin pick-up is the major factor in the increase in fabric stiffness. Some reduction in dry and wet crockfastness has occurred with the increase in pigment to resin ratio. There does not appear to be any consistent effect of the type of pigment on the printed fabric properties.

Table 3. Printed Fabric Properties for Three Pigments.

Properties	Red	Blue	Yellow
Bending Rig.	+36%	+11%	+22%
Flexural Rig.	+18%	+21%	+4%
Dry Crock	4.5	4.5	4.5
Wet Crock	3.5	4	4

Table 4 shows results of printing Resin 2 (15%) with a black pigment (4%) on three different fabrics at a 5% weight pick-up. The very strong influence of fabric type on change in properties of the printed fabric was not expected. Whether this is a function of resin composition, fabric weave structure, or some other phenomena will require further study.

In terms of print quality, it was noted that at very high solids levels, drop formation became erratic and control of drop placement was lost. This limited the solids levels to 20% resin and 6% pigment in the ink. It was noted that the smaller particle size latices gave better drop formation and control at the higher solids levels. Smaller particle size pigments should also improve performance and, perhaps, allow higher pigment loading.

Table 4. Effect of Resin-Pigment Printing on 3 Fabrics.

Properties	Cotton	Cotton/PES	Silk
Bending Rig.	+15%	+226%	+71%
Flexural Rig.	+6%	+241%	+95%
Dry Crock	5	5	5
Wet Crock	4	3.5	4

Operation of the ink jet printer with these two phase systems did present some problems. Nozzle plugging was not a problem but the vacuum used to draw unused drops into the recycle line caused evaporation of the water and plugging of the recycle line. The use of a humectant to reduce the rate of evaporation should help alleviate this problem in continuous ink jet printers.

Based on these preliminary studies, resin-pigment systems using small particle latices are an interesting and promising approach for development of a low-cost ink system for ink jet printing of fabrics.

Polymerizable Dyes for Ink Jet Printing

Dye based systems for ink jet printing of textiles that will not require post processing present a very difficult challenge. Most fabric dyes must diffuse into the fiber structure to achieve sufficient permanence to washing and rubbing. This is usually achieved by steaming or by heating at high temperature. There is usually sufficient dye remaining on the fiber surface to require post washing and drying. Dyes for cotton and other cellulose based fibers present special problems. Most of the dyes capable of being employed in printing of cotton (reactive, vat, sulfur, azoic) require a chemical reaction to “fix” the dye permanently on the fabric. These reactions are never 100% complete and therefore require extensive washing to remove unfixed dye.

It is unlikely that new dyes will be synthesized specifically for ink jet printing of textiles. However, selective modification of existing dyes is a possible approach to development of colorants for this application. The work reported here has been directed toward modification of existing reactive dyes to incorporate reactive groups that are capable of being delivered by ink jet and permanently fixed on the surface of fibers without requiring a post washing and drying step.

Initially studies have been directed toward incorporating a carbon-carbon double bond in the dye structure so that the dye can either be homopolymerized on the fabric or copolymerized with other components by UV or thermal iniatiation. Dyes for ink jet have been prepared by reaction of dyes containing amine groups with acryloyl chloride.[7,8] With dyes containing the amine group in a portion of the molecule that is not involved in color production (Reactive Yellow 3, for example), the double bond can be incorporated with very little effect on the properties of the dye. Confirmation of the structures of the modified dyes was obtained from the usual spectroscopic characterization techniques.

Reactive dyes modified as described above were incorporated in a polymerizable resin system very similar to the one described above. Samples of 100% cotton fabrics were printed on the TOXOT printer with the polymerizable dye and resin system and cured by UV initiation. Properties of the printed fabrics are given in Table 5. The improvement in crockfastness between uncured (3-3.5) and cured samples (5-4.5) strongly suggest that the modified dyes were actually chemically incorporated into the cured resin structure.

Table 5. Fabric Properties Printed with Modified Dyes.

Property	Modified Blue	Modified Yellow
Flexural Rigidity	+42%	+38%
Dry Crock	5	5
Wet Crock	4.5	4.5

Other properties such as lightfastness were also measured to ensure that the modification reaction had not adversely affected the performance of the dyes. Values of 5 and 4.5 after 60 hours of exposure of the printed fabrics in a standard UV exposure unit gave assurance that the dyes had acceptable fastness properties after reaction.

Success with the initial studies on polymerizable dyes has led to additional research on ways to more broadly incorporate carbon-carbon double bonds into reactive dyes. One very attractive approach is to partially react the vinyl sulfone type reactive dyes so that a carbon-carbon double bond replaces the normal reactive group.[9] This reaction can be carried out almost quantitatively and the modified dye can be separated and recovered from the unreacted or hydrolyzed dye by pH control. This reaction allows a wide range of reactive dyes with carbon-carbon double bonds in the dye structure to be prepared. Extensive study of the polymerization reactions of these dyes is currently underway.

Other ways of modifying the reactive class of dyes to produce coloring agents for ink jet printing that will not require wet post processing are possible. This approach appears quite promising for the preparation of low cost colorants for ink jet printing of textiles.

Conclusion

The ink formulations discussed in this paper are by no means commercial systems for ink jet printing of textiles. Significant work remains to optimize and to modify the formulations for commercial exploitation. However, the work to date will, hopefully, provide some new directions and stimulate further research to develop the systems that will be required for successful ink jet printing of textile substrates. Such systems will make an important contribution to the future success of the textile and related industries.

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Biography

Dr. Wayne Tincher received his B.A. degree in Chemistry from David Lipscomb University in 1956 and his PhD degree in physical chemistry from Vanderbilt University in 1960. He was with the Fiber Research Laboratory of the Monsanto Company for 10 years as a Research Chemist and Group Leader. He is currently a Professor in the School of Textile and Fiber Engineering at Georgia Tech. His research interests are in the areas of textile dyeing, printing and finishing processes. Dr. Tincher was awarded the Olney Medal by the American Association of Textile Chemists and Colorists in 1996 for “outstanding achievement in textile and polymer chemistry”.