

Textile Dyes for Thermal Ink Jet Printing*

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Abstract

Ink jet printing for textiles relies on many of the same technologies as ink jet printing for paper. Commercially available ink jet paper printing technology can be adapted to ink jet printing of textiles if modified textile dyes are used. Textile printing paste used in conventional textile screen printing is incompatible with ink jet delivery technology. Standard ink jet inks do not have the correct chemistry to dye textiles and achieve required color and permanence.

We have developed a prototype textile printer utilizing ink jet printing technology. Implementing the printer required the development of modified textile dyes to achieve compatibility with ink jet technology while retaining required textile dying properties.

This paper reviews the requirements of textile dyes for ink jet printing, presents data on commercially available textile dyes pertinent to ink jet printing, and discusses the results of our printing experiments utilizing modified textile dyes.

Introduction

Market pressures and limitations in screen printing technology are pushing the textile printing industry to adopt modern printing methods. Ink jet printing technology has received significant attention as a possible successor to screen printing due to the ability of ink jet to deliver liquid dye to the substrate. The primary competition to ink jet for on-demand printing of textiles is thermal transfer. Thermal transfer has the significant advantage over ink jet in the area of reduced post processing but also has the undesirable quality of delivering a poor hand to the finished goods. In a market where quality and hand of the finished product is of primary concern dyed goods are clearly superior to transfer printed goods.[i]

To be cost effective and capitalize on the latest print technology advances it is advantageous for the textile printing industry to utilize printing technology developed for the paper printing industry. In order to take advantage of ink jet paper printing technology the colorant must have fluid and chemical properties compatible with the delivery mechanism and the substrate.

Unmodified commercial textile dyes suitable for printing of textiles are incompatible with ink jet printing technology. Properties such as viscosity, surface tension, drying, crusting, particulates, and chemical compatibility are issues. Commercial ink jet inks suitable for ink jet printing are chemically unsuited for printing of textile substrates.

It has been demonstrated that commercial textile dyes can be modified for compatibility with ink jet printing technology [1,2]. This paper describes our efforts to develop a modified textile dye suitable for use with thermal drop on demand ink jet printing technology.

Dye Chemistry

The primary goal when printing textiles is to achieve a permanent, pleasing coloration of the substrate without effecting the hand or physical properties of the substrate. Permanent coloration of the substrate such that the coloration is lightfast, waterfast, and abrasion resistant is a result of chemical compatibility of the dye and the substrate. Substrates with differing chemical properties require colorants with fundamentally different chemical compositions. No single dye will be compatible with and appropriate for every textile. Our investigation has focused on dyes compatible with cellulosic textiles such as cotton, silk, and rayon. Most of the dyes we have investigated are reactive dyes.

The use of reactive dyes with cellulosic substrates requires the use of an activator to help progress the chemical reaction between the dye and the substrate. When screen printing typically an alkaline activator is added to the print paste. Longevity of the printheads is a concern when using ink jet printing technology to place the colorant. Ink jet printheads have a finite lifespan which is relatively short when compared to the number of drops required to print a typical run of textiles. Given the limited lifespan of ink jet printheads it is desirable to use the printhead to only deliver the concentrated colorant to the substrate. Bulk chemicals which must be applied to all locations on the substrate can be applied prior to the printing process using an appropriate less expensive delivery mechanism. In our system we pre-pad the cloth with an alkaline solution using a sprayer.

The disadvantage of dyes is the post processing required to fix the dyes to the substrate. The reactive dyes we have investigated require a post print steaming process. The steaming process swells the fibers and allows the dye to migrate into and bond with the fibers. The additional time, cost of capital equipment, and manipulation required in the steaming process are significant disadvantages compared to thermal transfer where a simpler post print heat pressing process is required.

Drop Generation Technology

Previous papers have described different types of ink jet drop generation technologies and discussed their relative merits [3,4,5,6,7]. Our prototype printer utilizes commercially available drop on demand thermal ink jet printheads. We have found the TIJ printheads to be very forgiving in terms of colorant fluid properties and to be resistant to chemical damage when jetting reactive and acid dyes. We have noticed severe susceptibility to minor crusting which tends to interrupt drop generation

Colorant Fluid Properties

Our experiments indicated the viscosity, surface tension, and particulate distribution to be the most critical factors determining reliable jetting of a fluid. To provide a baseline we measured multiple samples of ink jet inks from Canon and Hewlett Packard ink jet cartridges, the results are listed in Table 1.

Viscosity was measured using an Ostwald capillary viscometer at 23º C. Surface tension was measured using a Surface Tensiomat 21 (Fisher) ring method at 23º C. pH was measured using an ATI Orion pH meter. A sample of each ink was spread evenly onto a filter membrane as a substrate and the color was measured using a UV/VIS spectrophotometer (Perkin-Elmer) at 10º observer.

A variety of commercially available textile dyes were selected for evaluation, the unmodified attributes of the dyes as received from the manufacturer are listed in Table 2.

Table 1 Typical Ink Jet Ink Fluid Properties

Ink Characterizations	Viscosity	Surface Tension	Particle Size Mean	Particle Size Deviation	pH
	cps	dyne/cm	microns	microns	
Deionized Water	0.93	72			5.02
Canon Bubble Jet Black	1.12	45.1	1.92	0.17	9.00
HP ThinkJet Black	1.01	40.0	5.76	0.71	7.60
HP Desk Jet Black	1.48	46.0	2.16	0.21	8.30
HP Desk Jet Cyan	4.51	35.1			7.17
HP Desk Jet Magenta	4.87	33.5			7.16
HP Desk Jet Yellow	5.22	33.6			7.24

Table 2 Unmodified Textile Dye Fluid Properties

Ink Characterizations	Viscosity	Surface Tension	Particle Size Mean	Particle Size Deviation	pH
	cps	dyne/cm	microns	microns	
H Series FR Turquoise	2.07	55.5	2.08	0.15	4.40
H Series FR Yellow	2.10	51.5			4.70
Ciba Geigy FR Magenta	1.29	40.0	2.32	0.21	7.40
BASF FR Black	1.38	35.5	2.09	0.19	4.30
Crompton & Knowles FR Turquoise	1.00	35.0	2.56	0.12	5.50
Crompton & Knowles FR Brilliant Red	1.02	38.5	1.64	0.14	4.60
Keystone Acid Blue	1.84	63.5	2.01	0.24	7.10
Keystone Acid Yellow	1.01	55.2	1.03	0.11	7.30
Keystone Acid Magenta	1.01	70.0	1.87	0.14	6.90
Keystone Acid Tertrazine	1.21	65.0	1.47	0.11	6.70
Keystone Acid Pink	0.99	72.0	1.06	0.12	6.70
Cibacron Fiber Reactive Turquoise	0.93	51.0			6.22
Cibacron Fiber Reactive Yellow	1.25	55.0			7.40
Cibacron Fiber Reactive Red	0.96	41.4	5.00		7.20
Cibacron Fiber Reactive Gray	0.93	44.1	2.00		6.46
Zeneca ProJet Fast Magenta	0.83	71.8	5.00		7.10
Zeneca ProJet Fast Cyan	0.92	70.8	filtered to < 1.0		8.40
Zeneca ProJet Fast Yellow	0.97	68.0	filtered to < 1.0		8.70
Zeneca ProJet Fast Black	0.81	73.3	filtered to < 1.0		8.10
Zeneca ProJet Fast Magenta at 5%	0.91	71.2	filtered to < 1.0		7.10
Zeneca ProJet Fast Cyan at 6%	0.92	72.0	filtered to < 1.0		7.50
Zeneca ProJet Fast Yellow at 4%	0.91	71.8	filtered to < 1.0		6.96
Zeneca ProJet Fast Magenta at 70%	1.02	65.5	filtered to < 1.0		7.65
Zeneca ProJet Fast Cyan at 70%	1.04	71.2	filtered to < 1.0		8.50
Zeneca ProJet Fast Yellow at 70%	1.04	63.0	filtered to < 1.0		8.40

Rapid drying, crusting, and particulate aggretion were the primary sources of printing failure when printing with unmodified dyes. In one experiment a ten cc sample of Hewlett-Packard black ink jet ink was left in an open top container at room temperature. After six months the HP ink was still liquid and had lost approximately fifty percent weight. After one year the ink had finally dried into a soft sticky tar like substance. The unmodified textile dyes all tended to dry rapidly, ten cc dried completely in a few days, leaving a hard crystalline residue. All of the dyes of interest were aqueous based and returned to solutions after drying by addition of water and agitation.

Many of the unmodified textile dyes would jet for a short period as received from the manufacturer. All of the unmodified dyes would eventually stop printing after a short time with crusting of the nozzle orifice being the primary failure mode. Even while jetting continuously crusting would form around the nozzle eventually leading to plugging of the nozzle.

Modification of selected commercial textile dyes using surfactants, humectants, solubilizers, and biocides, such as suggested in [1], resulted in the properties in Table 3.
Each of the dyes listed in Table 3 yielded satisfactory jetting performance. The multiple formulations of each dye were primarily attempts to produce an acceptable color.

Addition of humectants increased the drying times for all of the dyes from days to months but also resulted in dilution of the dye with a loss of color saturation and a slight color shift. The modified dyes eventually exhibited drying and crusting problems similar to the unmodified dyes if left sitting at room temperature in an uncapped printhead. The dye would eventually dry around and inside the nozzle requiring external washing with water to revive the printhead. Contact with the modified dyes did not seem to impact the longevity of the printhead.

Table 3 Modified Textile Dye Fluid Properties

Ink Characterizations	Viscosity	Surface Tension	pH
	cps	dyne/cm	
ProJet Magenta 42	5.79	53.5	8.74
ProJet Magenta 46	3.79	38.5	9.00
ProJet Magenta 50	6.26	45.5	8.80
Cibacron Red 61	5.66	41.0	7.90
ProJet Cyan 43	2.15	58.5	8.80
ProJet Cyan 47	3.96	40.0	8.80
ProJet Cyan 51	4.75	41.5	8.70
Cibacron Turquoise 58	4.49	40.0	7.50
ProJet Yellow 44	6.57	51.0	9.10
ProJet Yellow 52	6.65	47.5	9.00
Cibacron Yellow 59	6.27	42.0	7.70
Cibacron Yellow 60	6.81	42.0	8.10
ProJet Black 45	5.64	53.0	9.04
ProJet Black 49	4.99	47.0	9.00
ProJet Black 53	6.26	43.0	9.00
Cibacron Gray 62	5.92	42.0	7.60
Cibacron Gray 63	5.57	42.0	7.10

Resolution and Print Quality

Addition of surfactants are required to control surface tension and insure proper transport of dyes through the printhead. Surface tension also effects formation of drops and satellites. Surface tension, viscosity, and substrate treatments effect the penetration and wicking of dyes into the substrate.

Unlike paper printing, where minimizing colorant migration into the substrate is desired, textile printing requires significant penetration of the dye into the substrate to insure durable coloration. A dye penetration of fifteen to twenty five percent of the depth of the substrate will usually result in a acceptable image when viewed from the printed side only. Low penetration dyeing results in unsatisfactory performance in terms of durability and colorfastness. Dependent on the weight of the substrate multiple drops per pixel are required to insure saturation and full substrate penetration. Full saturation of the substrate through the use of multiple drops usually results in significant lateral wicking thereby reducing the effective resolution of the image.

Color

When searching for a textile dye color set suitable for use in a four color printer we found the manufacturers of textile dyes to be mostly unaware of the need for process color textile dyes. We were typically unable to receive from the manufacturers a true cyan or magenta. Modifications to the dyes to enhance jetting qualities resulted in further color shifts. Color properties of unmodified and modified dyes are listed in Table 4. Modified dyes are denoted with an asterisk (*).

Table 4 Colorant Color Properties

Ink Characterizations	Dominate wavelength	Purity	Illum C obs 10 x	Illum C obs 10 y	Illum C Obs 10 Y	L*	a*	b*
HP Desk Jet Black	479.00	0.18	0.2881	0.2956	18.82	50.48	0.18	-7.61
HP Desk Jet Cyan	481.00	0.70	0.1581	0.2198	23.31	55.39	-29.46	-42.55
HP Desk Jet Magenta	555.00	0.48	0.3322	0.2061	21.56	53.56	54.96	-29.36
HP Desk Jet Yellow	577.00	0.77	0.4654	0.4589	62.23	83.04	5.97	81.66
H Series FR Turquoise	486.00	0.44	0.1766	0.2631	17.11	48.40	-32.30	-24.87
H Series FR Yellow	576.00	0.82	0.4724	0.4729	63.53	83.72	3.82	92.24
Ciba Geigy FR Magenta	509.00	0.42	0.3987	0.2508	18.49	50.08	50.67	-7.25
BASF FR Black	630.00	0.07						
Crompton & Knowles FR Turquoise	486.00	0.59	0.2221	0.2867	49.72	75.90	-28.96	-21.92
Crompton & Knowles FR Brilliant Red	554.00	0.30	0.3347	0.2362	21.17	53.14	39.80	-19.17
Keystone Acid Blue	481.00	0.45	0.1828	0.2449	27.76	59.67	-27.56	-34.24
Keystone Acid Yellow	577.00	0.60	0.4421	0.4300	68.00	86.00	8.18	64.18
Keystone Acid Magenta	591.00	0.92	0.3006	0.2339	45.77	73.40	37.48	-30.31
Keystone Acid Tertrazine	584.00	0.64	0.4755	0.4177	62.08	82.96	22.94	67.59
Keystone Acid Pink	555.00	0.17	0.3227	0.2745	49.98	76.06	25.85	-12.87

Cibacron FR Turquoise	484.00	0.46	0.2077	0.2739	43.89	72.15	-30.28	-26.87
Cibacron FR Yellow	580.00	0.88	0.4858	0.4702	66.57	85.29	8.85	99.20
Cibacron FR Red	542.00	0.37	0.3545	0.2478	24.83	56.91	43.11	-14.31
Cibacron FR Gray	482.00	0.25	0.2664	0.2917	21.86	53.88	-6.27	-11.16
Zeneca ProJet Fast Magenta	499.00	0.46	0.4483	0.2716	10.24	38.27	45.08	3.63
Zeneca ProJet Fast Cyan	483.00	0.59	0.1839	0.2565	29.36	61.10	-32.14	-31.09
Zeneca ProJet Fast Yellow	577.00	0.66	0.4302	0.4542	78.08	90.82	-4.08	73.13
Zeneca ProJet Fast Black								
Zeneca ProJet Fast Magenta at 5%	560.00	0.33	0.3185	0.2418	36.61	66.98	38.02	-23.06
Zeneca ProJet Fast Cyan at 6%	486.00	0.28	0.2520	0.2967	69.99	86.99	-19.64	-16.71
Zeneca ProJet Fast Yellow at 4%	564.00	0.11	0.3433	0.3670	96.61	98.67	-6.41	23.88
Zeneca ProJet Fast Magenta at 70%	504.00	0.50	0.4300	0.2540	18.96	50.64	58.36	-2.66
Zeneca ProJet FastCyan at 70%	482.00	0.62	0.1757	0.2385	25.40	57.46	-28.02	-35.92
Zeneca ProJet Fast Yellow at 70%	575.00	0.60	0.4228	0.4444	77.67	90.63	-3.40	66.91
* ProJet Magenta 42						55.34	62.83	-8.71
* ProJet Magenta 46						55.43	63.61	-6.74
* ProJet Magenta 50						64.90	51.38	-15.96
* Cibacron Red 61						57.24	55.67	-8.18
* ProJet Cyan 43						65.18	-30.90	-32.52
* ProJet Cyan 47						67.92	-31.45	-35.09
* ProJet Cyan 51						66.51	-31.35	-35.75
* Cibacron Turquoise 58						69.55	-33.05	-29.22
* ProJet Yellow 44						92.90	1.63	66.31
* ProJet Yellow 52						96.15	-3.91	59.87
* Cibacron Yellow 59						93.73	-10.07	80.65
* Cibacron Yellow 60						91.58	-9.64	81.54
* ProJet Black 45						46.11	2.60	-13.80
* ProJet Black 49						39.49	4.35	-12.19
* ProJet Black 53						51.35	3.94	-12.41
* Cibacron Gray 62						57.05	-4.50	-10.78
* Cibacron Gray 63						40.25	-2.76	-8.94

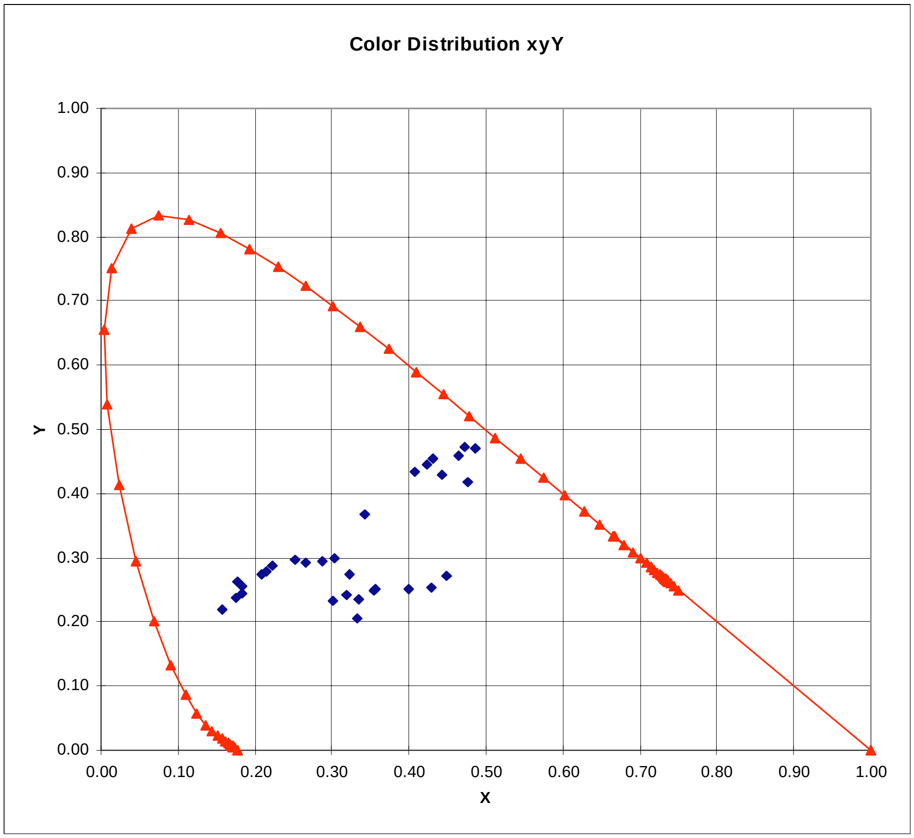

Figure 1 Colorant xyY Distribution

The color of each dye was measured using a UV/VIS spectrophotometer (Perkin-Elmer) at 10º observer. A sample of each dye was spread evenly onto a filter membrane acting as a substrate and measured. The distribution of colors is plotted in Figure 1.

Dye Performance

With proper pre and post treatment ink jet printed textiles can be of similar quality and durability as screen printed goods. Screen printing usually over saturates the cloth resulting in significant washout of excess dye during post treatment. With ink jet printing there is a trade off between image quality and durability. More dye on the substrate will result in a more durable image but will generally result in increased wicking and reduction of image resolution. In most cases when using ink jet printing the minimum amount of dye is applied to achieve the desired durability and very little dye is washed out during post processing.

Pretreating the substrate with an alkali mixture and allowing it to dry before printing results in the best image quality and dye performance. Printing while the pretreatment is still wet results in excessive wicking and image quality degradation. The pretreated cloth must be used within a short window after drying to achieve best results. If the pretreated cloth is allowed to sit for too long the pretreatment looses effectiveness and the percentage of dye bonded with the cloth is significantly reduced.

Post treatment consists of steaming the printed material. The steaming process is a critical step in determining the quality of the final output. A longer steaming time allows more of the dye to bond with the substrate resulting in a more durable image with less wash out and more saturated colors. A longer steaming time has the negative effect of providing a moist environment in which the dye continues to migrate and wick in the substrate resulting in loss of image detail. Our experiments indicate a fifteen to twenty five minute steaming in an unpressurized steamer yields good results.

Conclusions

Drop on demand thermal ink jet printheads can be used to reliably jet textile dyes if the dyes are modified to meet the fluid property requirements of the printheads. Textile dyes can be modified to be compatible with TIJ printing technology and still retain satisfactory dyeing properties. At this time achieving a satisfactory process color set with commercially available textile dyes is difficult. Achieving a dark black seems to be particularly difficult.

Unmodified textile dyes tend to dry quickly leaving a hard crusty residue. This drying and residue are particularly detrimental to printer performance. Modifying the dyes to reduce evaporation is essential.

The limited longevity of thermal ink jet printheads necessitates application of the dye activator in a pretreatment process. The substrate should be allowed to dry before printing. Excessive wicking and image degradation occurs if the substrate is printed wet.

The reactive dyes described in this paper require post process steaming to set the dyes. The steaming process is one of the most critical steps in determining the final quality of the printed good. Too little steaming results in insufficient dye reaction and excessive dye washout. Too much steaming results in dye migration and wicking resulting in poor image quality.

References

1. B. Smith and E. Simonson, Ink Jet Printing for Textiles, Computer Printing Vol. 19 No. 8, August 1987, pp. 23-29.
2. J. Provost, Recent Developments in Ink Jet Printing of Textiles with Reactive Dyes, IS&T Eleventh International Congress on Advances in Non-Impact Printing Technologies, pp. 378-382
3. B. Hunting, R. Puffer, S. Derby, L. Loomie, Issues Impacting the Design and Development of an Ink Jet Printer for Textiles, IS&T Eleventh International Congress on Advances in Non-Impact Printing Technologies, pp. 374-377.
4. W. Tincher, F. Cook, W. Carr, B. Failor, Keynote Paper: Printing on Textile Substrates, IS&T 46th Annual Conference 1993, pp. 368-369.
5. F. L. Cook, Textile Printing Enters The Technological Revolution, Chemical Treatment and Finishing, March, 1995, pp. 73-79.
6. A. Ahmed, Jet Printing for Textiles, JSDC Vol 108, Oct 1992, pp. 422-424.
7. J. Provost, Ink Jet Printing on Textiles, Surface Coatings International, January 1994, pp. 36-41.

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