Blue Light Curable Inkjet Inks for Textile Digital Printing

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TURI TUR Planner Continuing Education Conference, Nov. 9, 2011

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Impact of Digital Printing

- Large format digital textile printing using inkjet drop-on-demand technology
  - Rapid deployment of new designs
  - Very short cycle new product development
  - Low cost short runs, eliminate or reduce inventory
  - Near zero waste
    - water
    - chemicals

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Inks

- Dye-based
  - water-soluble colorants
  - molecular state in water medium
  - relying on chemistry between fibers and the colorant for fixation
- Pigment-based
  - water-insoluble colorants
  - particles in water medium
  - molecular state in a suitable medium

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Pigment Inks

- Suitable for all textile fibers
  - relying on a binder system for fixation
- Curing (polymerization) of binders happens with energy
- Conventional energy - heat
- High energy radiation
  - Electron beam (EB)
    - equipment, protection
  - Ultraviolet light (UV)
    - energy efficiency, ozone, LED, laser
  - Visible light (Vis, VL)
    - LED, energy efficiency, life time

Polymerizable Pigment Inks

- Low viscosity monomers/oligomers used as the base of the ink formulation
  - no water
  - no organic solvents
- Polymerization occurs when the ink is exposed to UV/Blue light
  - free radical polymerization
  - cationic polymerization
  - ease of control, no waste, no washing after inkjet printing

UV versus EB Curing

- UV and EB can fully fix pigment inks at a high speed
- Residual odor from acrylate monomer and photoinitiator remains a problem
  - Free radical polymerization
  - Oxygen inhibition is still a problem
  - Epoxy-based formulations can help
  - Cationic polymerization can be useful
- A survey* conducted in 2008 indicated that capital costs for 45” industrial scale UV cure system ($340,000) is about half equivalent EB system ($640,000)

* Cold Spring Technology, Three River, MA, 2008

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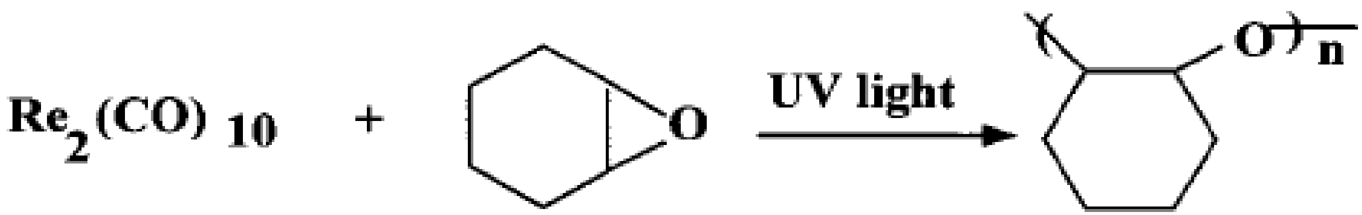
Cationic Polymerization

- "living" polymerization
- Free radical promoted
  - Flexible way to generate cationic species
  - Free radical initiators with wide range of absorption characteristics are available
    - benzophenone and onium salts
    - trioxane and maleic anhydride by benzoyl peroxide
    - dirhenium decacarbonyl



UV Cure Capital and Run Costs*

Capital	**Cost Estimate**	**Comment**
45" Wide **UV** Unit	$250,000	
Nitrogen Supply Unit	$25,000	Lease nitrogen supply unit
Start Up	$15,000	Straight Hourly charge
Installation Engineering	$50,000	Internal plant engineering
Subtotal	$340,000	
Run Cost		
Power Consumption per hour	$8	Up to 4X EB
Nitrogen Supply per hour	$14	$29,120/year 1 shift
Maintenance per year	$50,000	Much higher than EB, regular cleaning of reflectors and bulb replacements

* Cold Spring Technology, Three River, MA, 2008

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EB Cure Capital and Run Costs*

Capital	Cost Estimate	Comment
45" Wide **EB** Unit	$550,000	Approx. 2X UV
Nitrogen Supply Unit	$25,000	Lease nitrogen supply unit
Start Up	$15,000	Straight hourly charge
Installation Engineering	$50,000	Internal plant engineering
Subtotal	$640,000	
Run Cost		
Power Consumption per hour	$2	Much lower than UV due to higher efficiency
Nitrogen Supply per hour	$14	$29,120/year 1 shift
Maintenance per year	$24,000	Filaments/Ti Foils/O rings

* Cold Spring Technology, Three River, MA, 2008

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UV/EB Cost Comparison*

	UV Cure	EB Cure
System Projected Capital Cost		
45" wide inkjet printhead and controller – 6 colors, plus installation	$400,000	$400,000
45" wide cure system	$340,000	$640,000
Total Capital Cost	**$740,000**	**$1,040,000**
Projected Operating Costs		
Annual Energy Costs (1 shift/day)	$16,640	$4,160
Nitrogen Purge Costs	$29,120	$29,120
Annual Maintenance Costs	$50,000	$24,000
Total Annual Operating Costs	**$95,760**	**$57,280**

* Cold Spring Technology, Three River, MA, 2008

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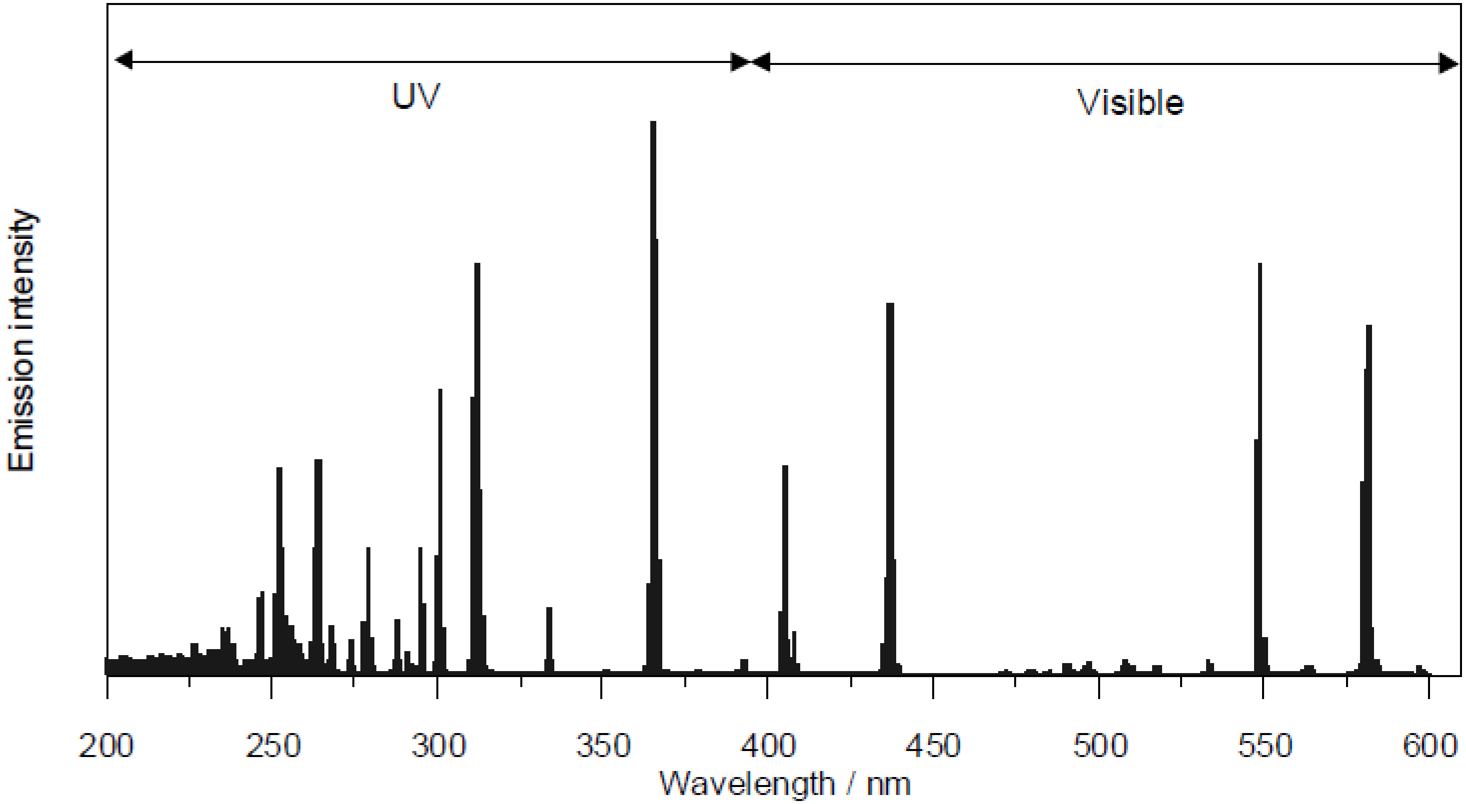
Why Blue Light

- Safer than UV light
  - longer wavelength, 440 – 480 nm
  - less concern of excess exposure for risks of skin cancer and eye damage
- Longer life time
  - UV lamps: 1000 hours
  - LEDs: 50,000 hours
- Environmentally friendlier
  - less ozone generation (no wavelength < 240 nm)
    - OSHA TWA 0.1 ppm at workplace
  - more energy efficient using LED technology

UV Lamp

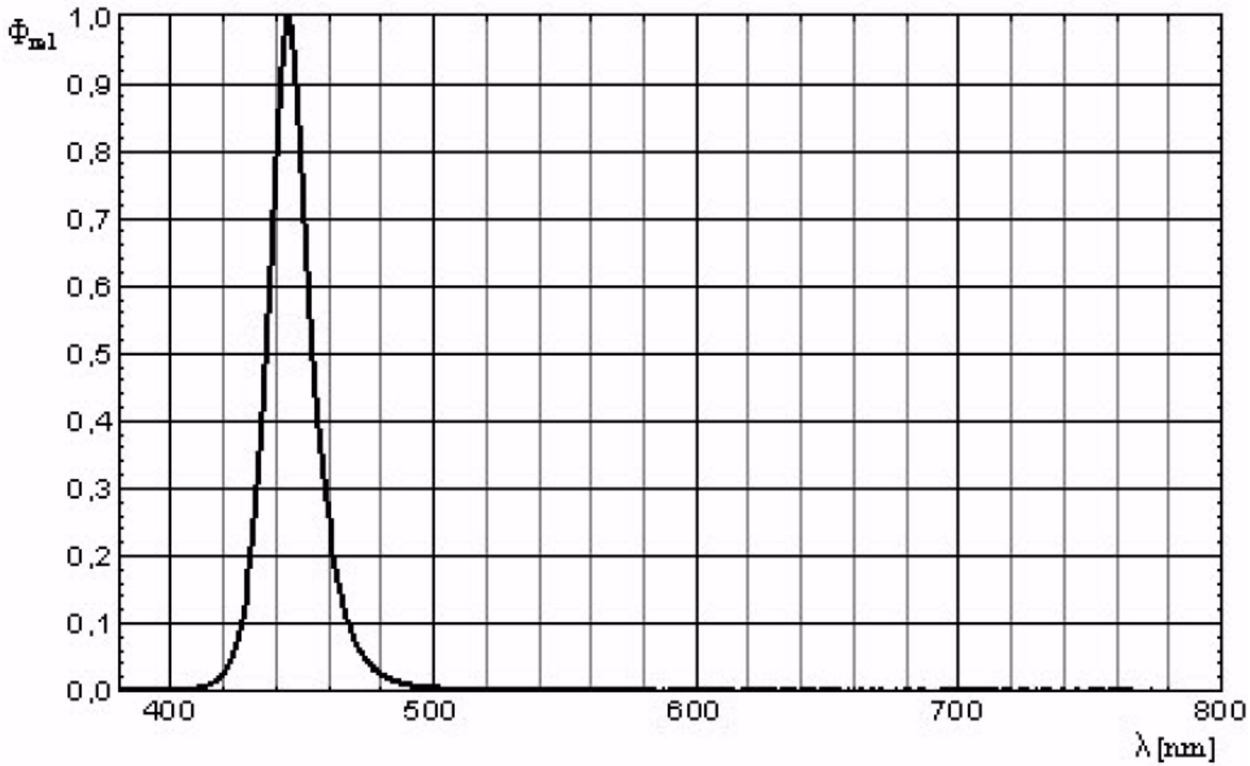
- energy efficient
  - medium pressure mercury arc UV lamp*



* Nigel Caiger and Shaun Herlihy, The Reporter, Vol. 20, No. 4, IS&T, August 2005

Blue LED

- Energy efficient
  - Blue LED*



* Osram OSLON SSL Preliminary Data, March 22, 2011

Energy Efficiency

- UV Lamp (mercury vapor lamp)
  - ballast's factor: 0.92
  - a 6" lamp at 400W/in for the lamp: 2.6 kW
  - 30% UV and 70% IR & convective heat*
  - UV output is 720 W, energy efficiency is ~28%
- Blue LED, Osram Dragon® deep blue
  - 43%[#]

* Sam Guzman, Private email, March 10, 2011
\# http://ledlight.osram-os.com/applications/product-charts/

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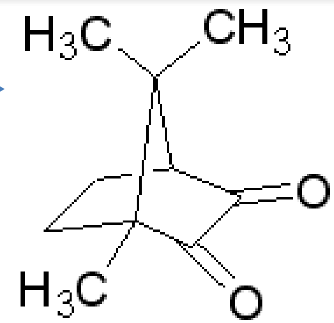
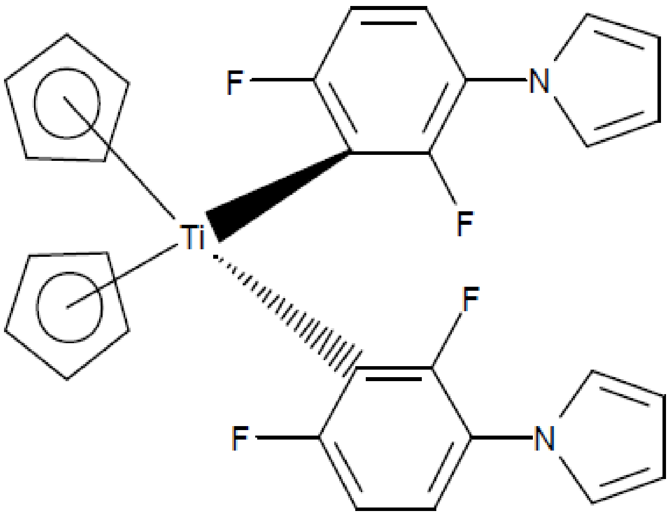
Blue Light Photoinitiators

- Camphorquinone →



- Titanocene and its derivatives →



- Coinitiators: Work as hydrogen donors to form a more effective initiator system
  – 2,2,6,6,-tetramethyl piperidine and 1,2,2,6,6-pentamethylpiperidine effective for triethyleneglycol dimethacrylate*

J. Jakubiak, X. Allonas, J. Fouassier, A. Sionkowska, E. Andrzejewska, L. Linden and J. Rabek, Camphorquinone –amines photoinitating systems for the initiation of free radical polymerization, Polymer, Vol. 44, 2003, 5219–5226

Blue Light Curable Inks

Materials	Weight (gm)
Isobutylvinylether	49.5
Cyclohexene oxide	49.5
Titanocene photoinitiator	0.5
Other additives	0.5

Formulation 1

Materials	Weight (gm)
2-(2-ethoxyethoxy)ethylacrylate	89.5
Polyethyleneglycoldiacrylate	9
Camphorquinone	1
Other addtives	0.5

Formulation 2

Materials	Weight (gm)
Cyclohexene oxide	99
Titanocene photoinitiator	0.5
Other additives	0.5

Formulation 3

Materials	Weight (gm)
2-(2-ethoxyethoxy)ethylacrylate	49.25
Cyclohexene oxide	49.25
Camphorquinone	0.5
Titanocene photoinitiator	0.5
Other additives	0.5

Formulation 4

Formulations 5, 6, 7, and 8 were based on Formulations 1, 2, 3, and 4 respectively with added pigment 2% and dispersant 4%

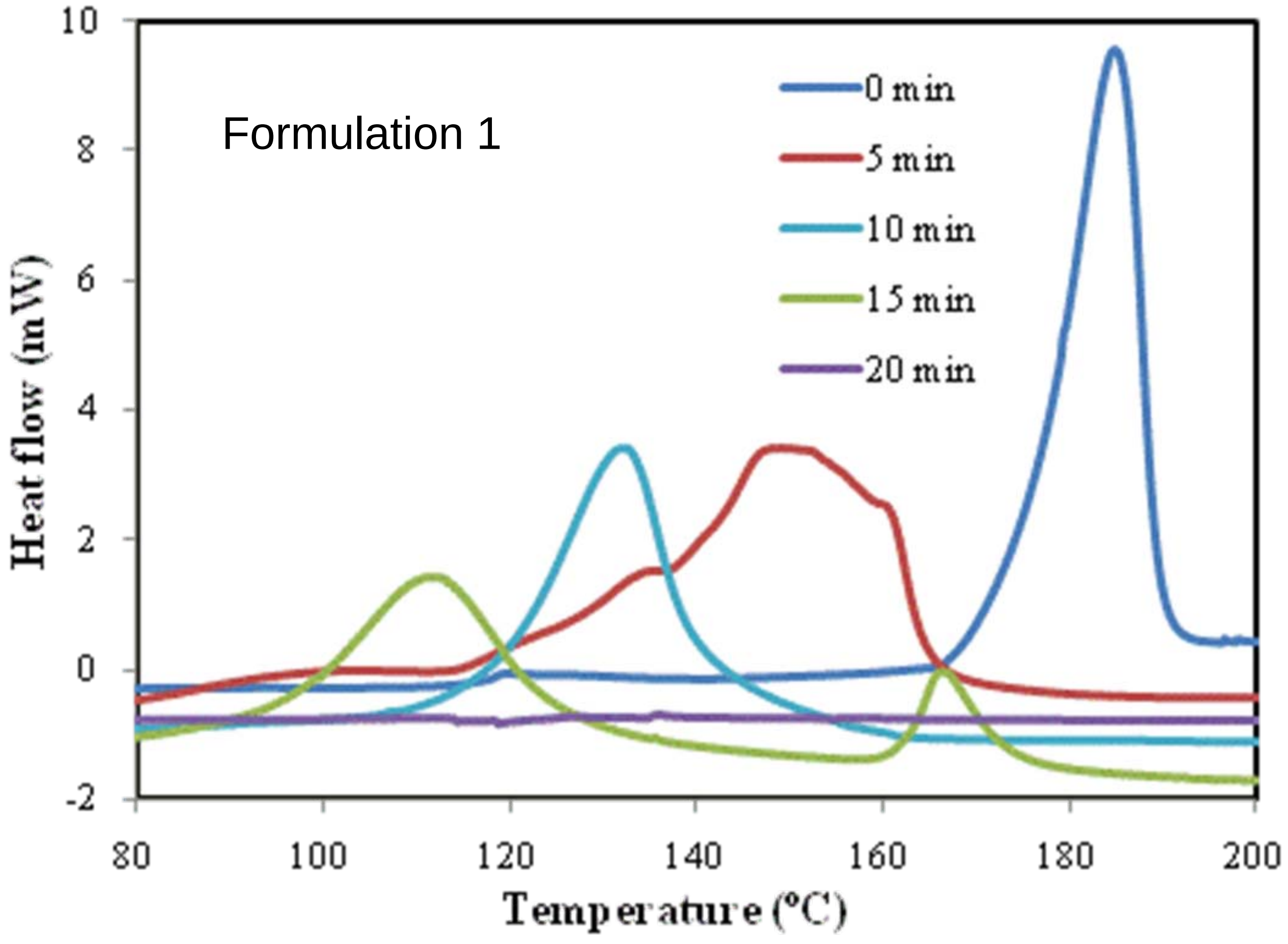
Differential Scanning Calorimetry Analysis

- The degree of cure (the overall conversion of monomor/oligomers to polymers) is directly proportional to the heat of cure which can be obtained experimentally by DSC

$$x\% = \frac{\Delta Hu - \Delta Hrt}{\Delta Hu} \times 100$$

  - ΔH_u is the heat evolved during the process of cross linking of the uncured material which is obtained by integration of the DSC peak.
  - ΔH_{rt} is the heat evolved during the process of cross linking of the material treated with incident blue LED light for different durations and is obtained by integration of the DSC peak.
  - X % is the conversion percentage (degree of cure).

DSC Curve



Formulation 1
0 min
5 min
10 min
15 min
20 min
Heat flow (mW)
Temperature (°C)
10
8
6
4
2
0
-2
80
100
120
140
160
180
200

Degree of Cure

Time	ΔH	Conversion %
0 min	339.1 J/g	-
5 min	312.5 J/g	7.84
10 min	244.9 J/g	27.77
15 min	123.8 J/g	63.49
20 min	112 J/g	66.97

Formulation 1

Time	ΔH	Conversion %
0 min	138.5 J/g	-
5 min	129.6 J/g	6.42
10 min	52.04 J/g	62.42
15 min	33.34 J/g	75.92
20 min	18.64 J/g	86.54

Formulation 2

Time	ΔH	Conversion %
0 min	79.37 J/g	-
1 min	34.58 J/g	56.43
2 min	11.05 J/g	86.07
5 min	1.557 J/g	98.03

Formulation 3

Time	ΔH	Conversion %
0 min	108.2 J/g	-
5 min	75.4 J/g	30.31
10 min	63.6 J/g	41.21
15 min	54.4 J/g	49.72
20 min	48.7 J/g	54.99

Formulation 4

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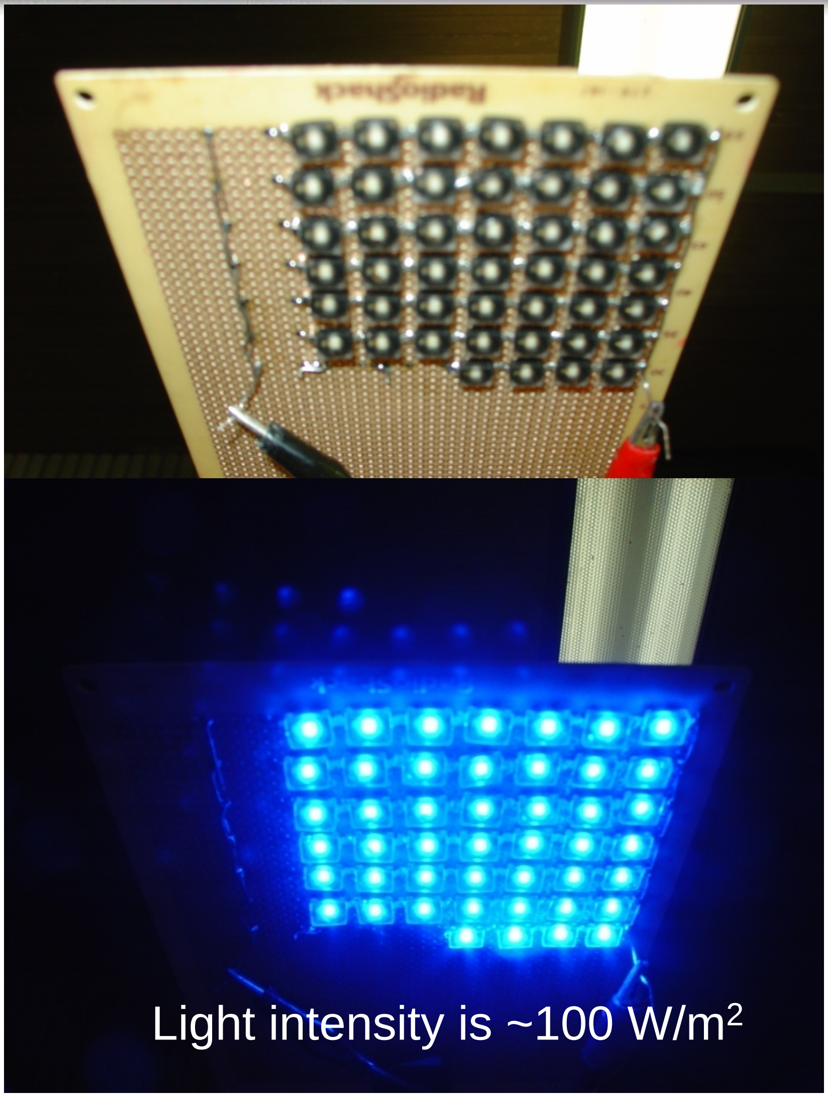
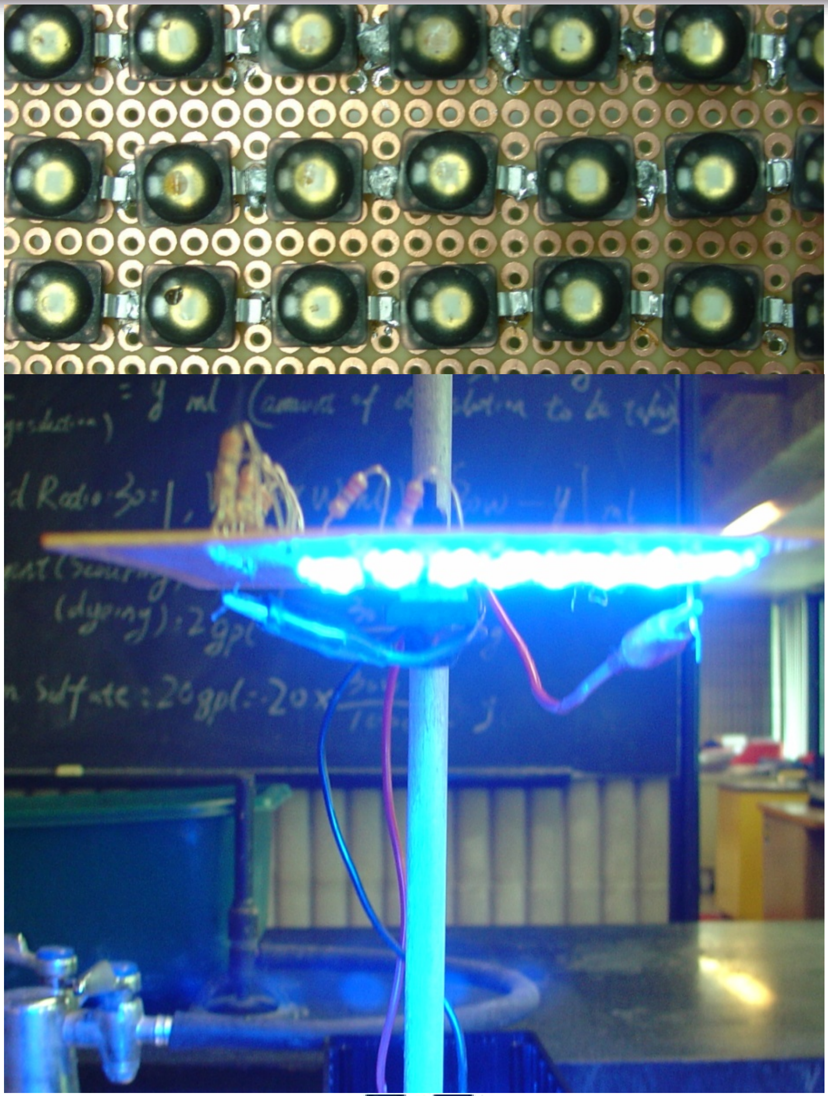
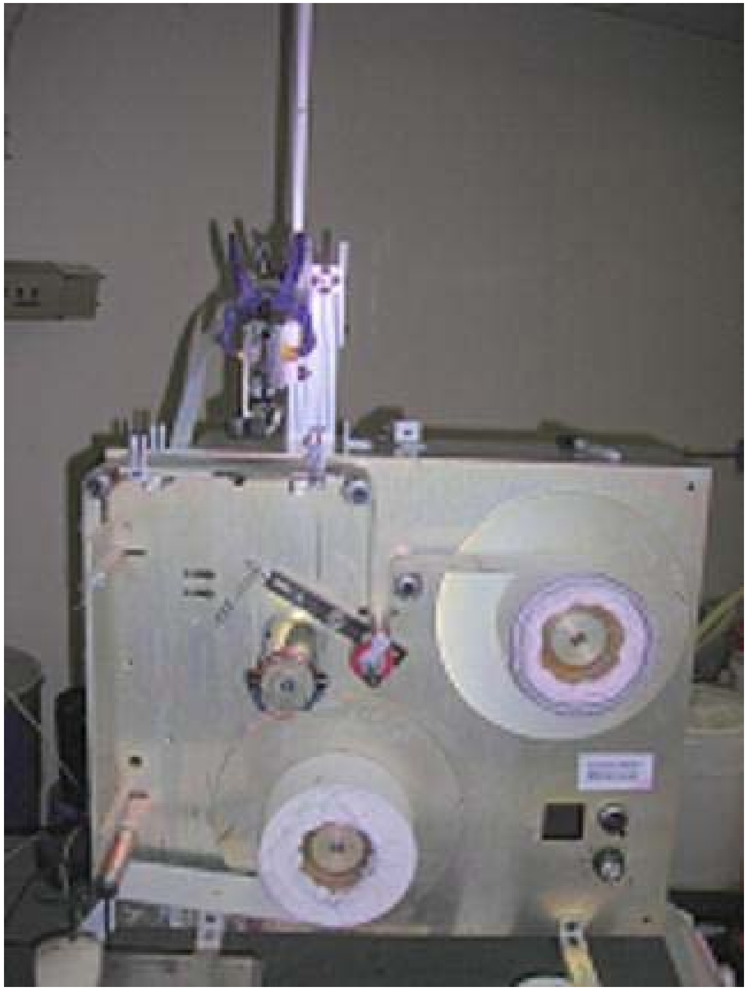
Blue LED Assembly





Lab Inkjet Printing Device

- Seiko Piezoelectric Binary T510B Printhead
- Ink is heated to 50°C to maintain viscosity at up to 15 cP
- capable of printing at 34 m /min



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Inkjet Printed Samples

- The above shows printed strips on 100 % cotton, plain weave, ready for print
- Other fabrics were also used for printing trials

Color Fastness to Laundering

- AATCC Test Method 61

	Gray scale rating
Formulation 5	2-3
Formulation 6	2-3
Formulation 7	3
Formulation 8	2

woven Poly/cotton fabric

	Gray scale rating
Formulation 5	2-3
Formulation 6	3
Formulation 7	3
Formulation 8	2-3

woven cotton fabric

	Gray scale rating
Formulation 5	2-3
Formulation 6	3
Formulation 7	3
Formulation 8	2-3

knitted Poly/cotton fabric

	Gray scale rating
Formulation 5	2-3
Formulation 6	2-3
Formulation 7	3
Formulation 8	2-3

knitted cotton fabric

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Color Fastness to Crocking

- AATCC Test Method 8

	Dry rating	Wet rating
Formulation 5	3	3
Formulation 6	3	3
Formulation 7	3-4	3-4
Formulation 8	3	3

Woven Poly/cotton fabric

	Dry rating	Wet rating
Formulation 5	3	2-3
Formulation 6	3	3
Formulation 7	3-4	3-4
Formulation 8	3	3

Woven cotton fabric

	Dry rating	Wet rating
Formulation 5	3	2-3
Formulation 6	3	3
Formulation 7	3	2-3
Formulation 8	3	3

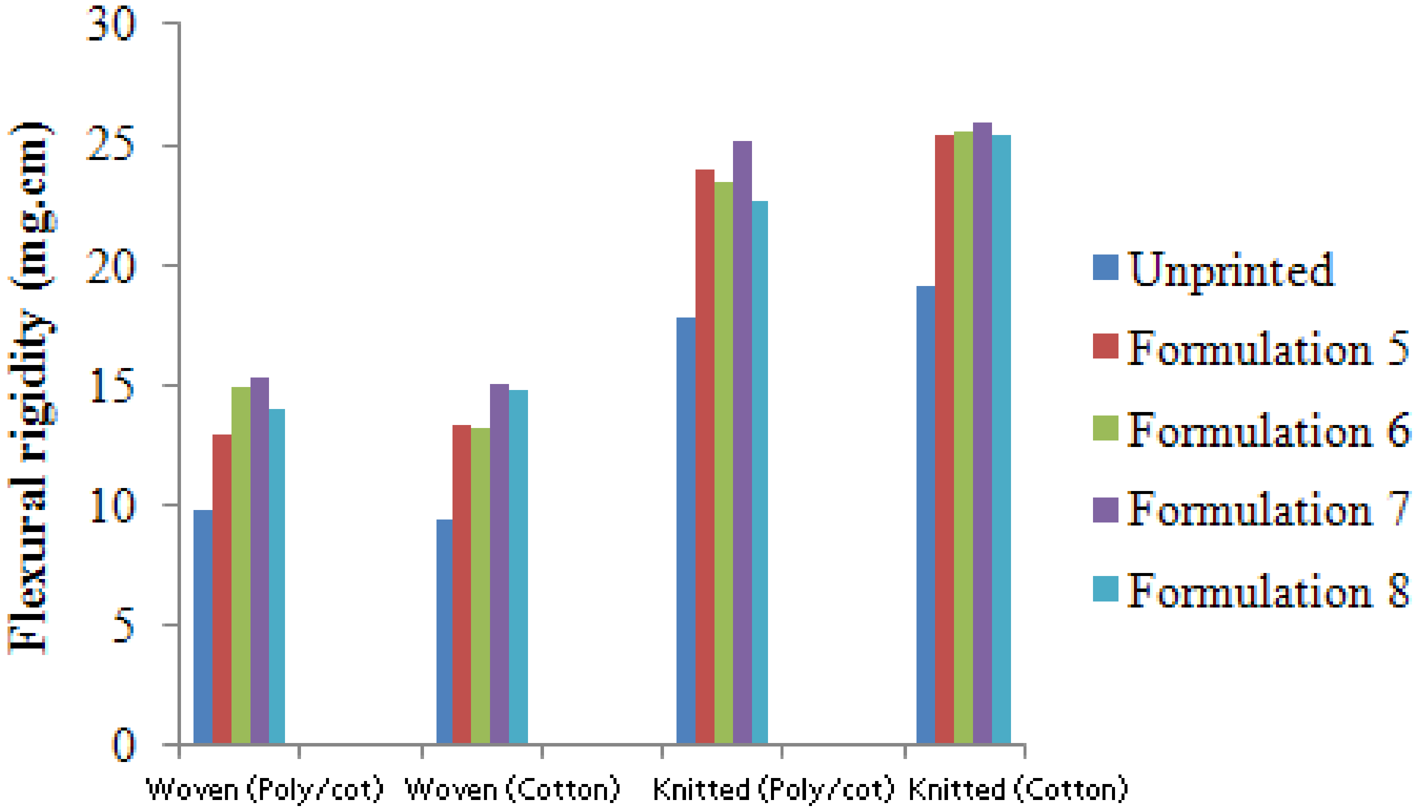
Knitted Poly/cotton fabric

	Dry rating	Wet rating
Formulation 5	3	2-3
Formulation 6	3	3
Formulation 7	3	2-3
Formulation 8	3	3

Knitted cotton fabric

Printed Fabric Stiffness

- ASTM D 1388 – 96 Standard Test Method for Stiffness of Fabrics



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Conclusions

- Blue light curable ink formulation is possible for textile inkjet printing
  - Optimization is being performed
  - Pigment particles size and its distribution are determining factors for the color fastness
- Better results are obtained, being analyzed, and will be reported in the near future

Acknowledgment

- National Textile Center and Massachusetts Technology Collaborative for financial support
- Dr. Rich Himmelwright, Cold Spring Technology Inc.
- Keith McKenzie, Manager of ATMC, UMass Dartmouth
- Graduate students Rohit Kankaliya and Francesco Piscani

Thank you for your attention!

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