Integration of Fabric Formation and Coloration Processes

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PROJECT GOAL: The goal of this project is to study the integration of the fabric formation and coloration processes, with a view to establish a viable approach to combining the two. Such a development would dramatically reduce overall fabric handling, and in turn, improve the productivity of fabric formation and textile wet processing. This anticipated reduction in handling should enhance agile manufacturing capabilities and provide the domestic textile market with an advantage in the industry.

ABSTRACT:
With rapid progressions in the textile industry, it has become increasingly evident that there is a need for development of a textile printing system which will have the capacity to keep pace with current and future mass customization manufacturing requirements in the printing segment of the textile industry. Digital inkjet printing has the potential to provide such characteristics, in a continuous system combining digital inkjet printing with the fabric formation process. Analyzing various fiber types requires that a specific correlating link be developed to correspond with a given substrate and its respective dye class. Research conducted at Philadelphia University and North Carolina State University has focused intently on discovering a link for cotton substrates and reactive dye coloration. For future exploration of polyester, research into the design, synthesis and use of special cyclodextrins, (which have the dual capacity to function as suitable hosts for certain colorants, and act as sizing agents), will be the key component for successful integration for the given substrate.

BACKGROUND:
The Future of Textile Production
Currently, digital inkjet printing is being selectively utilized throughout the textile industry, primarily for producing samples as a component in the design process and for small-scale production prints of exclusive design [1]. However, due to its inherently slow application speed, the digital printing process has yet to be adopted and successfully used as a component for full-scale production. Roller screen printing, which is traditionally used in production, although successful, is a time intensive and relatively inflexible process, causing it to be deficient in the high demand requirements of contemporary quick response textile manufacturing. As stated in a prior NTC-sponsored research project, entitled "Quick Response Printing," it is clearly evident that "textile printing systems are needed that will meet the requirements of time-driven, demand activated manufacturing for applying complex patterns to textile substrates [1]." An additional NTC-sponsored research project, "Textile Ink Jet Performance and Print Quality Fundamentals," built a strong foundation that "digital ink jet printing is a critical technology for mass-customization manufacturing of textile product [2]." Furthermore, researchers involved in the aforementioned project established that current textile ink jet systems require specially prepared substrates; yet there is limited available literature available on such required preparation.

Prior research in this area outside the NTC has focused on screenless printing and quicker turn-around in fabric printing [3,4]. However, none of this research involved an attempt to combine the fabric formation process with dyeing or printing. Rather, much of the research was focused on adapting technologies, such as photographic, xerographic, ink-jet, and laser printing into the textile market [5,6]. Therefore, if the fabric production and digital printing processes, which are somewhat compatible in production speeds, could be combined, the resultant integration would include numerous positive outcomes for the textile industry, including dramatically reduced overall fabric handling, which in turn, will enhance agile manufacturing capabilities and provide the ability to produce quick style changes and on demand production.

APPROACH:

In attempting to integrate the fabric production and digital inkjet printing processes, several factors must initially be taken into consideration, particularly the presence of sizing agents and a need for dye fixation. In the construction of a woven textile fabric a polymeric coating must be employed on the warp yarns for additional strength and resistance to abrasion during the weaving process [7]. Specifically known as warp sizes, starch, polyvinyl alcohol, and carboxymethyl cellulose are most commonly used when working with a cotton warp. A typical sizing mixture consists of a combination of starch, partially hydrolyzed polyvinyl alcohol, and a small amount of a lubricating agent, such as fat, to ensure a more secure weaving process [7]. More importantly, however, both synthetic and natural sizes must be removed following the weaving process (*via* desizing) to provide access of colorants to the fiber surface in the subsequent dyeing or printing stage. Therefore, to successfully integrate the two processes into a continuous system, a link must be developed to join fabric production and digital printing. However, due to the wide range of dyes being utilized in production today, different links must be investigated to connect varying substrates with their respective dye classes.

Cotton

Cotton is the most widely used of the natural cellulosic fibers and is well known to most consumers, making it a critical area of investigation for integration. Cellulose is a polysaccharide made up of cellobiose units, which combine to form a cellulose molecule, as depicted in Figure 1.
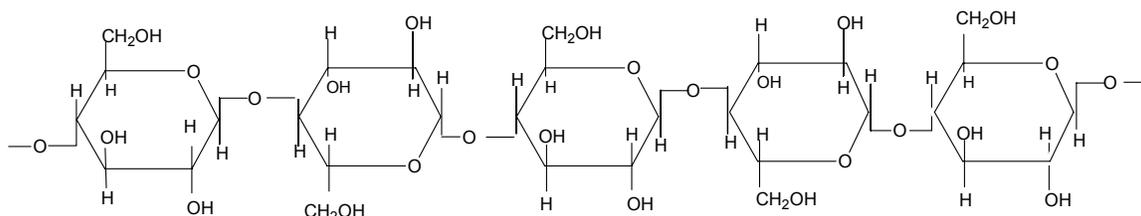

Figure 1. Schematic Diagram of a Cellulose Molecule [8].

In the simplified diagram of cotton, Figure 2, the hydroxyl (OH) groups are clearly indicated. These hydroxyl groups are critical for several reasons, but most importantly directly pertaining to integration, cellulose fibers absorb water-soluble dyes and finishes, which aids in chemical processing.
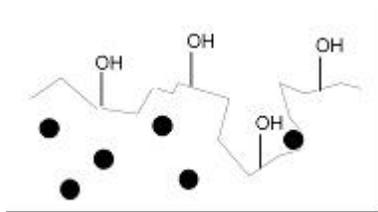
Figure 2. Surface Diagram of Cotton [9].

Reactive dyes are water-soluble anionic dyes, which react with the hydroxyl groups of cellulose to become covalently bonded to the cellulosic fiber [7]. The chemical reaction between a reactive dye containing a chlorinated reactive group (RG) and a cellulosic fiber takes place in the presence of a base, as illustrated in Figure 3 [7]. In this investigation, sodium carbonate (Na_2CO_3) is the base being utilized. Urea ($(NH_2)_2-C=O$) is used in the fixation step to absorb moisture.

$$\text{DYE-RG-Cl} \quad + \quad \text{H-O-CELLULOSE} \quad \xrightarrow[\text{- HCl}]{\text{Base}} \quad \text{DYE-RG-O-CELLULOSE} \quad + \quad \text{SALT}$$
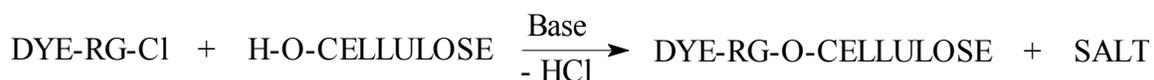
Figure 3. Diagram illustrating the bonding of a reactive dye to a cellulosic fiber.

The resultant covalent bond provides good washfastness properties, and is much stronger than the weak hydrogen bonds formed between direct dyes and cellulose, making reactive dyes the preferred choice when working with cotton. Furthermore, since a base, in this case Na_2CO_3, is required for the dye to bond with the cotton substrate, and is typically applied to the fabric as a pretreatment solution prior to digital printing, the link to integrating the fabric formation and coloration processes is based upon the Na_2CO_3/urea solution.

Since it has been established that the covalent bonding of reactive dye with cotton occurs when the substrate is pretreated with Na_2CO_3 and urea, the physical property which must be explored for integration is an ability to protect the cotton yarns from abrasion and breakage during the weaving process, *i.e.*, investigate whether the Na_2CO_3/urea combination will additionally function as a warp size. To determine such properties, three groups of 100% cotton, 20/2 N_{ec} yarns were treated with solutions of compounds listed in Chart 1. Two of the groups of yarn were padded with their respective solutions, using a Werner Mathis AG lab-scale padding unit, such that solution uptake was 80% of the weight of the dry yarns. The control yarn samples were not treated with any solution, and cornstarch was used to mimic the traditional starch sizing currently used in woven production on the second group of yarns. In addition to the sodium carbonate and urea used in Solution C, thickener and silica were added to the solution for increased viscosity. Following application, the samples were dried in a Tsuji Senki Kogyo tenter oven at 130ºC for two minutes. After all of the yarns were conditioned under standard temperature and relative humidity for 24 hours, half of the yarns were tested for single end strength using a Testmetric SDL constant rate of extension tensile testing machine, in accordance with ASTM Test Method #2256. Using a CSI Flex Tester, the remaining yarns were then subjected to an abrading force of one pound for ten cycles, proportional to that which would be incurred on an active loom. These yarns were tested for single end yarn tenacity, as previously noted, following abrasion to determine a change in tenacity similar to that which occurs during

the course of weaving. The average change in tenacity and standard deviation values for samples A, B, and C are shown in Table 1.

Chart 1: Average Change in Single End Yarn Tenacity
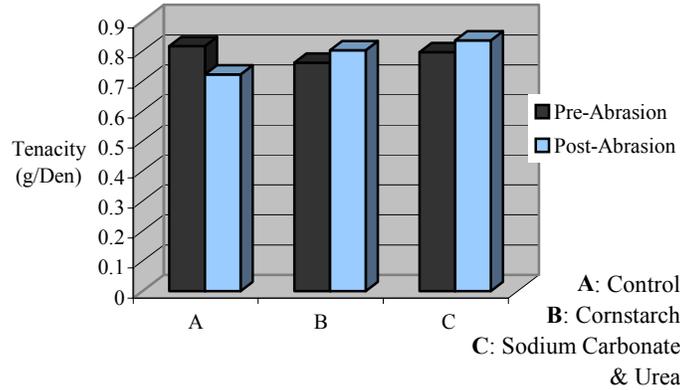**(as a result of simulated weaving)**

Table 1. Tenacity (g/Den) Data for Cotton Substrate

Sample	Average Single End Tenacity	Standard Deviation
A: Control		
Pre-Abrasion	0.82 g/Den	0.07 g/Den
Post-Abrasion	0.72 g/Den	0.09 g/Den
B: Cornstarch		
Pre-Abrasion	0.76 g/Den	0.18 g/Den
Post-Abrasion	0.80 g/Den	0.09 g/Den
C: Sodium carbonate + Urea		
Pre-Abrasion	0.80 g/Den	0.14 g/Den
Post-Abrasion	0.84 g/Den	0.07 g/Den

The results are promising for future integration. The control samples were clearly abraded during simulated weaving, reducing the average single end tenacity. The two remaining samples however, demonstrated an increase in tenacity following abrasion, within a minimal range. Although it is not feasible to conclude that the yarns actually increased in strength after abrasion, the results suggested an increase in strength for samples given the cornstarch and Na_2CO_3/urea treatments. Since this increase in strength may be due to the small sample pool tested, further testing will take place to augment the present results. In addition, the high standard deviation values for the yarn samples tested prior to abrasion may be a reason for the observed changes in strength following abrasion. It is clear at this point that the Na_2CO_3/urea formulation was effective for imparting resistance to abrasion, which is a key component for integration.

After performing textile material tests to determine yarn strength before and after weaving, the next stage in route to integration is digital inkjet printing. In the initial experiments, 100% cotton plain weave fabric was produced on a 400-end Sumagh sample loom, using 20/2 N_{ec} yarn. From the resultant fabric, untreated, cornstarch treated, and Na_2CO_3/urea treated samples were obtained.   The Mutoh Full Color Inkjet Printer shown in Figure 5 was used to apply 100% pure

color stripes of cyan (Cibacron Turquoise MI-700), magenta (Red MI-500), yellow (Yellow MI-100), and black (Black MI-900) reactive dyes to the fabrics. The printing process used an Epson DX-3 head, operating at 720 dpi, and a two-pass, uni-directional color application.
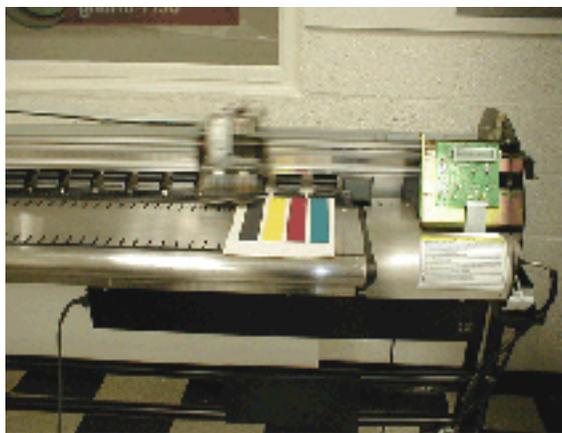

Figure 5. Mutoh Full Color Inkjet Printer.

The resultant samples were steamed at 103ºC for 8 minutes and soaped at the boil using Synthrapol detergent. These procedures were employed to establish the dye-fiber bond and to remove any unfixed dye and dyeing assistants from the fabric [7]. The untreated control fabric and cornstarch treated fabric failed to retain any of the reactive dye applied during digital printing. This indicates that a covalent bond between cellulose and the reactive dye did not occur. While these two fabric samples were not useful for colorfastness assessment, the Na_2CO_3/urea treated samples were conditioned at standard temperature and humidity levels and tested for colorfastness to light (AATCC Test Method #16), laundering (AATCC Test Method #61), and crocking (AATCC Test Method #116), where the rating scale used was 1 (poor) to 5 (excellent). Results are shown in Tables 2-4.

It is evident that the printed samples treated with Na_2CO_3/urea exhibited very good colorfastness and that dye-fiber fixation has occurred. In view of these promising results, efforts to integrate the fabric formation and coloration processes on cotton will include expanded testing for fiber strength and comprehensive testing for edge acuity, which assesses print line and area quality.

Table 2. Results from AATCC Test Method #16

Sample		Colorfastness to Light	
		20 hours	40 hours
A: Control		N/A	
B: Cornstarch		N/A	
C: Sodium Carbonate/Urea Formula with Thickener and Silica	**Cyan**	5	5
	Magenta	4-5	4
	Yellow	5	4-5
	Black	4-5	4

Table 3. Results from AATCC Test Method #61

Sample		Colorfastness to Laundering (Color change)
A: Control		N/A
B: Cornstarch		N/A
C: Sodium Carbonate/Urea Formula with Thickener and Silica	**Cyan**	5
	Magenta	5
	Yellow	5
	Black	5

Table 4. Results from AATCC Test Method #116

Sample		Colorfastness to Crocking	
		Wet	Dry
A: Control		N/A	
B: Cornstarch		N/A	
C: Sodium Carbonate/Urea Formula with Thickener and Silica	**Cyan**	4	5
	Magenta	3	5
	Yellow	4	5
	Black	4	5

Polyester

In addition to investigating the integration of fabric formation and coloration processes for cotton, polyester, a popular fiber used in both the apparel and home furnishings industries, has been considered as a substrate [10]. Polyester, a hydrophobic fiber, is typically dyed with disperse dyes [7]. Furthermore, it is known that the treatment of starch with a bacterial enzyme produces certain oligosaccharides known as cyclodextrins (see Figure 6).
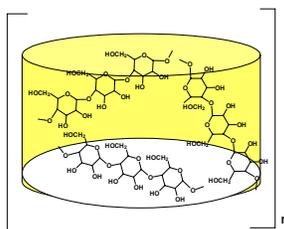

Figure 6. Representation of the cyclodextrin structure.

Modeling Studies Involving Cyclodextrins (CDs) and Textile Dyes
As outlined in the Year 2 research proposal, one of our approaches to combining the fabric formation and dyeing steps calls for the simultaneous use of CD compounds as warp sizes and hosts for dye molecules that can be released onto the fabric surface following the weaving process. With this concept in mind, our studies in this area during Year 2 have focused on the use of molecular modeling methods [11] as a tool for selecting optimum CD and dye sizes for this project.

Cyclodextrins are toroidally shaped molecules that show very interesting complexation behavior. The presence of a hydrophilic exterior coupled with a hydrophobic interior allows them to be soluble in aqueous solution on one hand and hosts for hydrophobic molecules on the other hand. Typically, the designations α, β, and γ are used to refer to CDs with 6, 7, and 8 glucopyranose units, with internal diameters of 5.3, 6.5, and 8.3 Å, respectively (see Figure 7).
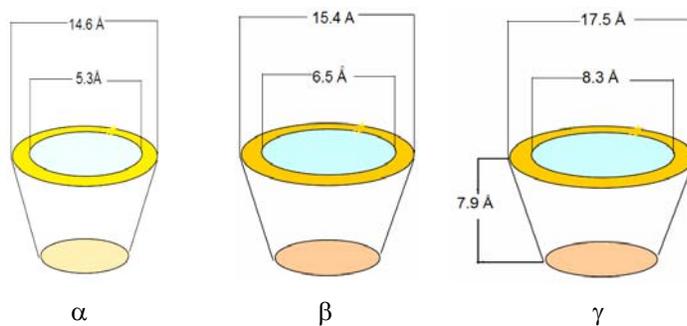

Figure 7. α, β, and γ CD with their interior and exterior dimensions.

1. Modeling complexation between β-CD and guest dyes using molecular mechanics
Equilibrium geometries for the host CD and dye **5** of our Year 2 research proposal were determined separately using MM2 forcefields and a conjugate gradient minimizer. The molecular axis of the dye was determined to be 22.8 Å, which means that three β-CD molecules are required to completely entrap the dye molecule, since the vertical axis of β-CD is 7.9 Å. Following the geometry optimization process, the dye structure was placed inside the cavity of three β-CD units, and the augmented MM2 forcefield method was employed to locate the equilibrium geometry of β-CD with the dye **5** inside. It was found that the β-CD cavity could entrap two parallel dye molecules without experiencing any noticeable steric interactions. See Figures 8 and 9.
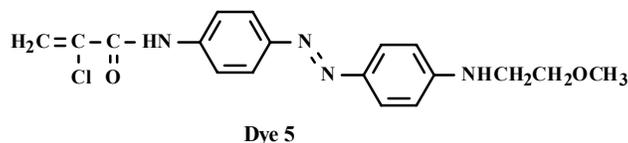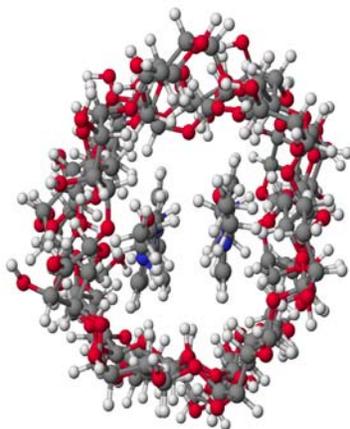

Dye 5

Figure 8. Equilibrium geometry of β-CD with two dye **5** molecules inside, calculated using MM2 forcefields.
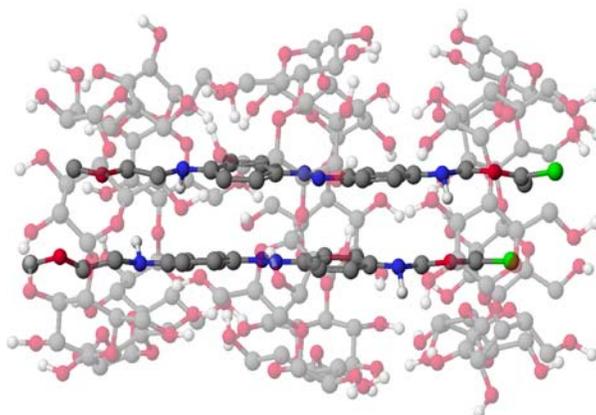

Figure 9. View from a different angle, showing dye **5** molecules (solid) in the cavity of three vertical β-cyclodextrin units (shaded).

2. Modeling complexation between γ-CD and guest dyes using molecular mechanics

We also calculated equilibrium geometries involving *γ-CD as* the host and dyes **4** and **5** of our Year 2 research proposal. In this case, we found that the CD molecule can hold 3 dye molecules, as illustrated in Figure 10. Using calculations involving MM2 forcefields and a conjugate gradient minimizer, the molecular axis of dye **4** was determined to be 16.8 Å, which is slightly longer than two *γ-CD* units. The structure of monoazo dye **4** is as follows:
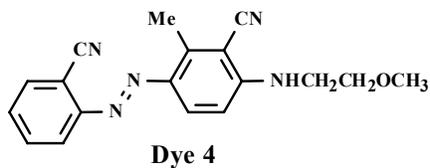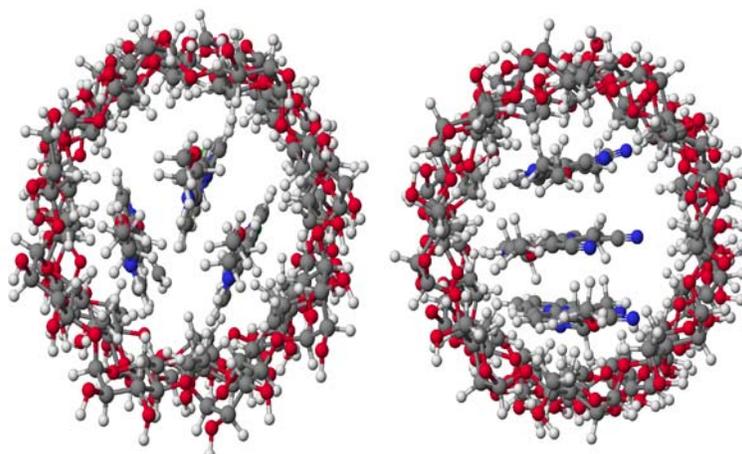

Dye 4

Figure 10. Equilibrium geometries of γ-CD with three dye **4** molecules inside (right) and three dye **5** molecules inside (left), calculated using MM2 forcefields.

FUTURE WORK:

Continued Cyclodextrin Exploration

In view of the larger interior diameter of γ-CD compared to β-CD, which allows γ-CD to accommodate up to three molecules of dyes **4** and **5**, future modeling studies and bench experiments will utilize the larger CD unit. In addition, CD crystal structure data from the Cambridge databases will be used in modeling studies, as a mechanism for accelerating our studies. A "C" compiler will be purchased to facilitate online access to the databases.

We also plan to carry out the synthesis of monoazo dyes such as dye **5**, in order to produce pure samples for CD-dye adduct formation at the bench. Figure 11 provides an outline of the synthetic route we have in mind. Steps 1 and 2 are well-established diazotization and coupling reactions, both of which employ acidic media. The third step takes advantage of the selectivity of Na_2S reduction of a nitro group in the presence of an azo bond (cf. **B → C**). The final step is actually a two-step, one pot process in which the aminoazo dye **C** condenses with α,β-dichloropropionyl chloride followed by elimination of HCl. This final step can also be carried out using α,β-dibromopropionyl chloride, with concomitant elimination of HBr [12]. We plan to compare the efficiencies of the two reactions.
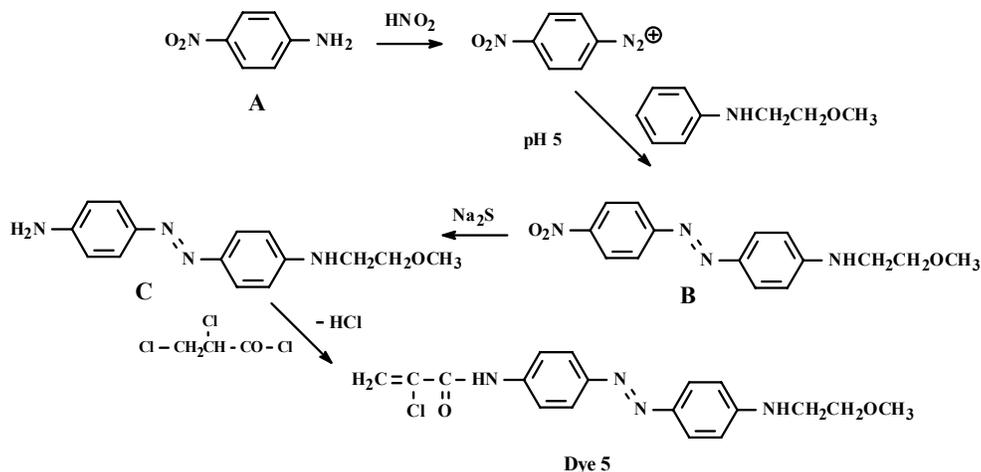

Figure 11. Currently used four-step sequence for the synthesis of dye **5**.

Simulated Production
Once a link has been successfully discovered that will transcend separate fabric formation and coloration processes, for both 100% cotton and 100% polyester substrates, a small production facility will be assembled using a sample loom and a desktop digital inkjet printer. The simulated production will provide manufacturing productivity data that will be compared to real-time manufacturing speeds currently in use. A decrease in manufacturing time would dramatically increase productivity and reduce handling costs associated with the individual fabric formation and coloration processes.

CONTACTS WITH INDUSTRY:
Contact has been made with several companies regarding this project. Wacker Biochemical was contacted as a source for preliminary cyclodextrin exploration, and has provided both samples and information pertaining to this project. Huntingdon Yarns of Philadelphia supplied the cotton yarn used in our experiments. Additionally, interaction with the following companies has occurred, Ciba Specialty Chemicals Corporation USA, Mutoh America, Inc., Wasatch Computer Technology, MacDermid Colorspan, DuPont Digital Printing Group and Rohm and Haas. Falcon, ENCAD, and Colorspan have also provided four digital printers, which are being used in this research and these companies continue to interact with the project.

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