National Textile Center
FY 2003 (Year 12) Project Proposal

Project No. C03-PH01

Competency: Chemistry

Universal Set of Dyes for Digital Inkjet Textile Printing

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Objective:
The primary focus of this project is to develop a universal set of dyes for inkjet digital printers that enables printing on *chemically diverse textile materials*. An important outgrowth of this project will be the creation of an integrated laboratory within the Center for Excellence of Digital Inkjet Printing for Textiles at Philadelphia University that is devoted to fundamental research aimed at improving the performance and environmental compatibility of the chemicals used in inkjet printing for the US textile industry.

Relevance to NTC Mission:
A universal set of dyes that can function effectively on multiple substrates will reduce the costs associated with digital inkjet printing technology for textile applications. Currently, less than 5% of the world's textile printing production is located in the US [1], but digital printing has opened the door for on-demand and decentralized manufacturing, which has the potential to bring a greater percentage of printing production back into the US economy. The successful completion of this project will lead to a reduction in the price-to-performance ratio of this technology.

State of the Art:
The performance demands of digital inkjet printing for textile applications are extreme, e.g., there are more than a half dozen common types of synthetic and natural fibers, each of which has its own pretreatment requirements and ink compatibility characteristics, see Table 1. Furthermore, whether the printing technology employed requires spot or process color, the need to frequently change colorways and/or fabrics creates costly machine downtime and added chemical waste that may require expensive remediation. The availability of a set of dyes for digital inkjet printing

Existing Technology		
Fabric Type	Pre-treatment Requirements	Dye Type
Cellulosics, Silk, Wool • *reactive hydroxyl or amine*	Control of: • drop absorption • wicking • pH for fixation	**Reactive Dyes** • *colored anions* • *potential for covalent bond*
Polyester and other Synthetics • *hydrophobic* • *solid solution with dye*		**Disperse Dyes** • *hydrophobic, non-ionic* • *transfer by sublimation*
Silk, Nylon, Wool • *cationic dyesite* • *electrostatic interaction*		**Acid Dyes** • *colored anions*
Proposed Technology		
Cellulosic, Synthetic, Protein	**Chemical Switch**	**Universal Dyes** • *chemoselective affinity*

Table 1.

that can function on multiple textile substrates will: (a) decrease the need for companies to maintain a complex inventory of colorants, (b) reduce machine down time, and (c) minimize the amount of dyes contained in printing effluents. Although there has been significant activity over the past decade in both European and American patents involving inks and their formulation, the general approach has been to retrofit existing chromophores and auxiliaries for textile applications rather than rethinking the overall "chemistry" of this rapidly evolving digital technology.

Approach:
A multi-disciplinary approach will be used to develop new dyes that exhibit chemoselective affinity for a variety of diverse textile substrates. This is a formidable task, but there are several factors coming together at this point in time that make it possible to achieve the objectives of this project.

- Chemical sensor technology is progressing rapidly in a variety of fields. For example, in medicinal chemistry molecules containing boronic acid functional groups are used to bind with compounds that contain diol moieties (e.g., carbohydrates) with a high degree of specificity in neutral aqueous systems [2]. Such tight binding allows boronic acids to be used as the recognition entity in the construction of sensors for new classes of compounds and as affinity ligands to distinguish different functional groups. Of particular interest is the recognition of glucose because chemical-based glucose sensing presents a promising strategy for the development of an implantable system for continuous monitoring of sugar levels in diabetic patients. Cellulosic materials contain a linked array of hydroxyl groups and should be amenable to recognition using this property of aromatic boronic acids. Preliminary studies at Philadelphia University indicate that an aqueous solution of phenyl boronic acid shows significant affinity towards cotton fabric. In fact, a method to evaluate the stability of boronic acid-diol complexes using an anthraquinone dye, Alizarin Red S, has been recently described [2]. New molecular frameworks containing anthraquinone chromophores in combination with chemical sensors that complement binding sites on multiple fabrics will be developed. These sensors will essentially serve as bidentate chelating ligands having chemoselective affinity, and their selectivity can be improved by cooperative binding of substrates via two or more groups. In addition to introducing chemical sensor technology to the printing industry, other approaches, including immobilization, derivatization, and paper-to-fabric transfer reactions with a variety of groups present as a linker system will also be pursued. The chemistry of the pretreatment process, if it is still required, will be designed to complement that of the newly developed inks.
- Developments in combinatorial chemistry [3] have made it possible to rapidly synthesize a large number of related compounds in parallel. As new molecular frameworks are designed, their structures will require modification to optimize their performance and combinatorial chemistry is the ideal tool to accomplish this. The usefulness of this technique in the synthesis of aminoazobenzene dyes was demonstrated in an earlier NTC project (C00-P01: K.Bhat, PI). A Quest automated synthesizer coupled with a state of the art CombiFlash™ chromatographic purification system, purchased with funds from the project, now enables the synthesis and purification of 15-20 new, unique compounds per day. All new synthetic dyes will be screened for mutagenic activity using the well-known Ames' test. The chemistries for combinatorial synthesis will involve Friedel-Crafts acylation reactions followed by acid-catalyzed cyclization of acyclic precursors and/or diazotization of a 2-aminoanthraquinone derivative and subsequent coupling with a substituted phenyl boronic acid. An alternative approach will utilize a Diels-Alder reaction between the required diene and napthaquinone followed by aromatization of the Diels-Alder product. A wide range of boronic acids is commercially available (e.g., Combi-Block, Inc.) for use as combinatorial building blocks. Many of these acids already contain at least one additional functional group that can serve as an auxochrome and help generate large numbers of new compounds either via solid support or solution phase synthesis.
- Chemoinformatics and molecular modeling have matured over the past decade into valuable research tools for designing novel chemicals and correlating molecular structure with a wide variety of physical, chemical, and toxicological properties. In conjunction with molecular modeling, a comprehensive structure-property database will be established that incorporates the performance results of the new "library" generated by combinatorial syntheses. This database will be augmented with information from the vast experimental literature on classical anthraquinone dyes. Quantitative structure-activity and structure-property relationships (QSAR/QPARs) will be developed from the database to guide additional synthetic work required to optimize the technical performance of the colorants and, simultaneously, to reduce their genotoxicity; both multilinear regression (CODESSA™) and artificial neural networks (Neuroshell Predictor) will be employed for this purpose [4, 5]. The software QikProp from Schrondinger, Inc. will be employed to predict biological behavior of the newly created structures. Since the new

auxochromes generated in the course of this project will alter various physical properties of the molecule, time-dependent density functional theory will be used to predict shifts in the absorption, λ_{max} and the molar extinction coefficient, ε.

- In 2001 the Center for Excellence of Digital Inkjet Printing for Textiles was established at Philadelphia University. The Center provides a choice of several state of the art printers for comparing existing ink formulations with those developed in this project. Preparation of inks with the proper rheology and fixation properties is extremely critical. A fine balance must be maintained between developing inks that optimize drop formation and those that create sharp, dense and permanent images. A typical ink formulation consists of: demineralized water, hygroscopic thickener, dye, surfactant, biocide, buffer, and sometimes an antioxidant. Currently, the optimum combination must be determined empirically. The ink will be tested for the following reliability parameters: jetability (all nozzles firing at the start), jet sustainability (continuous jetting and consistent gradients over time), Decap (all nozzles firing after resting), and consistency (flow rate and shelf-life over time). In addition, the Grundy Laboratory at Philadelphia University is available to perform standardized tests of the printed samples, e.g. evaluations for colorfastness: AATCC Test Method 61-1996 No.2A (washfastness), AATCC Test Method 16-1998 option E (lightfastness) and AATCC Test Method 116-1996 (crocking).

In summary, during the course of this project a multifaceted laboratory will be created to perform fundamental research designed to improve the technical performance and safety of the chemicals available for digital printing. This laboratory will integrate existing resources at Philadelphia University to facilitate:

- the design and synthesis of new dyes that have multiple functionality;
- the development of ink formulations and pretreatment procedures that complement these new dyes and optimize their performance on commercially-available (piezo electric) inkjet printing systems;
- the performance evaluation of all new inks with respect to jettability, jet sustainability, flow rate, decap, colorfastness, genotoxicity, etc.;
- the use of chemoinformatics and molecular modeling to develop QSAR/QSPRs that correlate molecular function with molecular structure.

This Year's Goal:

- To establish the specific building blocks and chemistry needed for the combinatorial synthesis.
- To create a "library" of new dyes carrying diversity elements at multiple sites on an anthraquinone framework.
- To initiate molecular modeling on a wide array of anthraquinone derivatives and textile substrates, and to establish a dynamic structure-property database for QSAR/QPAR development.
- To establish a standard operating procedure (SOP) for the overall process.

Outreach to Industry:

This project will be conducted in conjunction with the Center for Excellence of Digital Inkjet Printing for Textiles at Philadelphia University. The following industrial partners of the Center have agreed to participate in this research: Ciba Specialty Chemicals Corporation USA, Mutoh America, Inc., MacDermid Colorspan, DuPont, Wasatch Computer Technology, Mimaki USA, and Rohm and Haas.

New Resources Required:

No requirement of major equipment is anticipated in the first year.

References:

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3. Lesney, M.S., "Concocting combinatorials: Chemistry in Drug Development" Today's Chemist at Work, 2002, 28.
4. Greaves, A.J. & Gasteiger, J., "The use of self-organizing neutral networks in dye design" Dyes & Pigments, 2001, **49**, 51.
5. Garg, A., Bhat, K.L. & Bock, C.W., "Mutagenicity of aminoazobenzene dyes and related structures: A QSAR/QPAR Investigation" Dyes & Pigments, in press (2002).