National Textile Center
FY 2007 New Project Proposal

Project No. C07-PH01

Competency: Chemistry

Microencapsulated Inks for Digital Ink Jet Textile Printing

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Changes from Previous Submission:
The proposal has been refocused on oxidative, rather than reductive, systems and preliminary results outlining the success of this methodology have been included. Experimental details on the proposed oxidative discharge, illuminating chemistry and encapsulation methodology have been expanded.

Objective:
The objective of this project is to develop an environmentally safe, microencapsulated ink system in which the ink components are isolated from each other and from the digital ink jet (DIJ) apparatus. Due to the deleterious nature of oxidative/reductive chemicals to the hardware, discharge printing has not been successfully adapted for DIJ applications. At the conclusion of this project we expect to have developed a dye encapsulation technology that abrogates corrosive effects on DIJ equipment. This technology may find applications for the delivery of other core materials to textile surfaces by related digital printing methods, *e.g.* electrophotography.

Relevance to NTC Mission:
Progress in the chemistry and technology of DIJ printing will permit a more responsive supply-chain that allows access to a new family of mass-customized products and will benefit the manufacturer, retailer and consumer. This project will promote technological leadership and economic competitiveness of the US digital printing industry by developing the scientific knowledge base necessary for the creation of a microencapsulated ink delivery system that: 1) expands design capabilities, 2) meets the stringent demands of digital printing, 3) is environmentally benign, and 4) may evolve into a new proprietary technology.

State of the Art:
DIJ printing – The National Textile Center (NTC) has funded several projects related to DIJ textile printing [1-7] and has played a significant role in the development of this technology. These projects have focused on direct printing styles (*e.g.*, photographic, diminutive, and non-repeated imaging). Due to the complex nature of the ink formulation and its effect on the printing hardware, specialty printing styles (*e.g.*, discharge, devoré/burn-out, and creped effects), available with conventional printing technologies, have not been addressed in previous NTC projects. Currently, only one discharge system is commercially available for DIJ printing, but product evaluation at the *Center for Excellence of DIJ Printing for Textiles at Philadelphia University* has revealed significant limitations, including inadequate substrate ink penetration leading to inconsistent discharge, short operating-life of the print heads, limited time between printing and curing, and off-gassing during curing.
Discharge printing – Traditionally, discharge screen printing using reduction involves dyeing a ground shade with azo colorants. Occasionally, the discharged pattern remains white; however, the ground shade is usually replaced with an illuminating color. Currently, it is not possible to achieve the overall appearance of traditional discharge/ illuminating methods with *direct* DIJ printing because of the limited penetration of colorants and restricted gamut of hues available *via* process colors. Reductive agents used in discharge processes, *e.g.*, sulfoxylates (hydrosulfates stabilized with formaldehyde), suffer significant drawbacks such as corrosive effects to printing equipment as well as health and safety concerns for operators and the environment. These concerns have fostered research into novel discharge systems using safer, non-formaldehyde-based alternatives, which enable reactions to occur more rapidly, at lower pH, and/or introduce modified curing conditions [8-12]. Recent patents specify a number of creative approaches for discharging, *e.g.*, using bacteria and ozone, but most are incompatible with DIJ delivery [13, 14].
Microencapsulation – Encapsulation technology has rapidly progressed from its debut in carbonless paper, through flavors and essences, to biomedical applications in drug delivery and medical imaging [15]. Driven by the need to develop textiles with enhanced-performance properties, *e.g.*, flame retardance, anti-microbial protection, etc., with

or without value-added novelty behavior, *e.g.*, thermochromism and skin-care, encapsulation in the textile industry has grown since the 1990's [16]. Liposomal entrapment has been investigated to delay uptake of water soluble dye by fibers [17] and to control exhaustion [18]. Water-soluble dyes have also been encapsulated using the double emulsion/solvent evaporation technique [19]. These examples indicate that dye packaging systems can be successfully developed for digital printing in the textile industry; however, no literature reports exist indicating that such systems can withstand the stringent demands of DIJ Printing.

Approach: The proposed microencapsulated system requires the chemistries of the (1) discharge, (2) illumination, (3) encapsulation material, and (4) ink formulation to function without interfering with other components of the ink(s) or damaging the DIJ equipment. The design and integration of these chemistries in a way that meets the mechanical demands of DIJ printing, in conjunction with the engineering of an efficient release mechanism that triggers the entire process, are major challenges of this project and constitute significant scientific risk.

***Discharge Chemistry*:** Since oxidative discharge typically results in fewer deleterious by-products than traditional reduction of azo moieties, it will serve as our model system. Suitable colorant-oxidant combinations must be selected and tested in order to identify complementary pairs whose reaction will result in efficient discharge. High molar extinction coefficients and capacity for significant changes in absorption following discharge made triphenylmethane (TPM) ground-shade dyes an obvious choice in preliminary discharge studies in our laboratory. TPM dyes, C.I. Acid Green 3 and C.I. Acid Blue 83, were treated with micromolar concentrations of alkaline H_2O_2 at room temperature (RT), resulting in robust discharge [20]. Encouraged by this initial success, additional TMP colorants will also be examined for oxidative discharge, along with dyes from other structural categories. Table 1 shows a collection of dye classes, oxidative agents and bleach activators whose interactions will be evaluated for extent and rate of discharge at RT. The oxidative agents listed in Table 1 were chosen for their commercial availability and demonstrated safety (*in situ* formation of peroxides using bleach activators). Dyes and oxidative agents will be combined in solution, and any resulting reaction will be monitored by UV-Vis absorption spectroscopy. Analysis of spectral shifts and/or loss in visible-region absorptions over time will indicate degree of discharge and kinetics. Structural identification of reaction products will be determined by GC/MS, ^{1}H, and proton-decoupled-^{13}C NMR spectroscopy. This structural data, augmented by molecular modeling, will provide valuable input for development of structure-activity relationships (SARs). Should technological/creative circumstances dictate a need for additional dyes, these SARs would then form a vital portion of a "developmental toolkit" for the design and synthesis of novel dyes for use in this discharge methodology. Toxological considerations of oxidants, dyes and their degradation products will be evaluated using chemoinformatics.

Table 1	
Dyes Classes	**Oxidative Agents**
Triphenylmethane	Hydrogen peroxide
Xanthene	Peroxyacetic acid
Acridine	Sodium Percarbonate
Diphenylmethane	3-chloro-peroxy benzoic acid
Bleach Activators	Carbamide peroxide
TAED	
NOBS	

***Illuminating Dye Chemistry*:** Colorant-oxidant pairs and illuminating chemicals must be combined in a formulation to give both complete discharge and rapid development of the illuminating hue. Oxidative color chemistry is well known, albeit mostly for non-textile uses, and illuminating shades typically develop at near neutral pH and RT [21]. Preliminary results in our laboratory using the primary intermediate (base) 1,4-phenylenediamine and three secondary intermediates (couplers) 2-methylresorcinol, 1,3-aminophenol, and 4-amino-2-hydroxytoluene for illuminating shades have shown that oxidative colorants form at RT on silk substrates in less than fifteen minutes [20]. Based upon these results, additional combinations of the primary and secondary intermediates shown in Table 2 will be studied. Solution studies of base/coupler pairs will be used for reaction product identification and kinetics. Methodology using the printed substrates will be adapted from the 2005 report of the SCCP of the European Commission [22]. The alkaline oxidizing agent will be combined with a 1:1 ratio of primary and secondary intermediates, applied at RT (Zimmer sample printer) and allowed to react for 5, 10, 15, and 30 min. For comparison purposes, substrates with/without ground color will be studied. Following extraction with methanol and collection of insoluble surface dye, the colorant will be analyzed by GC/MS to determine identity and concentration of reaction products. Following purification on silica, reaction products will be further characterized using ^{1}H and proton-decoupled ^{13}C NMR spectroscopy.

Table 2	
Primary Intermediate (Base)	**Secondary Intermediate(Coupler)**
1,4-phenylenediamine	2-methylresorcinol
Toluene-2,5-diamine	Resorcinol
4-aminophenol	4-amino-2-hydroxytoluene
	1,3-phenylenediamine
	3-aminophenol

***Encapsulation Methodology and Release Mechanism*:** Microencapsulation not only provides a means of isolating, separating, protecting and storing the active core materials, it also imparts uniform particle size and surface characteristics that facilitate and simplify ink formulation. While the encapsulation technique determines the particle size and polydispersity, the wall material dictates the release mechanism of core chemicals and ink stability. The optimal capsule must be jettable through a 30 μm nozzle, *e.g.*, 1-2 μm diameter, but large enough to maximize the

loading fraction of the active core chemicals without destabilizing the microcapsule structure. Methods of releasing the core material(s), *e.g.*, mechanical, chemical, thermal, ultrasound, UV, *etc.*, must be sufficiently rapid to facilitate, not impede, the desired chemical reactions, to provide a means of vertical penetration of the discharge/illuminating ink minimizing lateral wicking and satellite droplet formation, and to leave the substrate undamaged. Once the core material is released, the polymeric material of the capsule must remain unreactive, non-toxic, and not affect the hand and/or appearance of the printed material. Further, the varied chemical nature of the dyes and oxidative agents suggests a comprehensive approach in which more than one encapsulation method is employed and the components are pre-mixed as a cocktail in a single ink or formulated into multiple inks.

Polysaccharide shells (starch, chitosan, and gum arabic (with gelatin)) present many useful properties for the intended application (safety, low cost, high degree of sustainability, lack of particle aggregation and the ability to encapsulate a variety of materials), and would therefore be an ideal encapsulation material for this project [23 a-f]. *Encapsulation:* Natural polysaccharide will be emulsified with either a lipophilic oxidant or primary/secondary intermediates in oil under high-turbulence conditions (sonication) and passed directly into a steam jet cooker apparatus. Particles will be isolated by dilution in water, followed by drum-drying. *Characterization of particles:* Particle size will be determined by a combination of dynamic light scattering and SEM. *Optimization of Particle Attributes:* Thickness of the starch coating, a factor requiring fine control to facilitate release, can be altered by the method used to isolate the capsules (hot- or cold-dilution), composition of the starch (amylase:amylopectin ratio, anionic/cationic character) and mixing intensity during dilution (degree of shear). Should issues concerning shelf life, ink suspension or encapsulation emerge, capsules/core material could further be coated with parylene (a transparent, fungal- and bacterial-resistant coating formed by vapor deposition) which is used extensively in the medical device industry [24]. *Release Mechanism:* A variety of diverse release mechanisms will be explored; however, mechanical rupture methods have many practical advantages. Release aids, such as incorporation of amylase to degrade the starch, will be investigated as needed. *Encapsulation alternatives:* Should any components not be amenable to encapsulation using starch, *e.g.*, the oxidative agent, complex coacervation using chitosan will be explored as an alternate method [25]. A solution of sodium sulfate (20% w/v) containing the species to be encapsulated will be added dropwise to a stirred, aqueous solution of chitosan (0.25% w/v) in acetic acid (2% v/v) with 1% polysorbate 80. Following sonication with continued stirring for one hour, formed microspheres will be washed by repeated centrifugation and dried. Weight percent of core materials, coating thickness, and microsphere diameter will be optimized by manipulating stirring rate and insonation.
Chemistry /Ink Formulation: Ink formulations for DIJ printing on textiles present significant challenges [26]. Encapsulation of various chemically active components will actually simplify ink formulation because of the homogenous hydrophilic/hydrophobic profile, size and surface texture of the capsules. Utilization of multiple print heads for delivery of discrete encapsulated oxidative agents and illuminating dyes is the simplest and most flexible method. However, the formulation of a single ink composed of microcapsules with different core materials delivered from a single print head is a feasible approach that will be researched.

Mid-Project Review Goals:
At the mid-project review, oxidants for discharge will have been identified and the bleaching mechanism for a variety of ground shades will have been elucidated. A preliminary microencapsulation protocol that is both complementary to core materials and meets the demands imposed by DIJ printing will have been developed.

Outreach to Industry:
Translational research will be conducted between the *Center for Excellence of DIJ Printing for Textiles at Philadelphia University* and the following industrial partners: Oxidative/reductive chemistry (Larry Vale / larry.vale@degussa.com / Degussa Corp.-Peroxygen Applied Tech); Encapsulation equipment (Lee Van Dixhorn / LVDixhorn@hydro-thermal.com / Hydro-Thermal Corp); Ink formulation (David Clark / david.clark@cibasc.com / Ciba Specialty Chemicals Corporation USA, Antonio Lopez / lopez.antonio@dystar.com / DyStar L.P, Ming Xu/mingxu@sublimation.com / Sawgrass Technologies, Zhenwen Fu / zfu@rohmhaas.com / Rohm and Haas); DIJ equipment (Masaaki Fujita / fujita@mimaki.co.jp / Mimaki USA, Hue P. Le / hueple@aol.com / PicoJet Inc.).

New Resources Required:
Custom laboratory steam jet cooker and auxiliary components (Hydro-Thermal Corp); ARES Rheometer (TA Instruments); Starch Consultant [subcontract]; Graduate student stipend (Philadelphia University); Graduate/undergraduate student(s) (Drexel University [subcontract]); Chemicals and equipment (Philadelphia University and Drexel University [subcontract]); Hardware/software for chemoinformatics (Philadelphia University).

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