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TITLE: COLORATION SYSTEMS FOR QUICK RESPONSE MANUFACTURING

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GOAL: To develop textile coloration processes consistent with demand activated manufacturing.

ABSTRACT

Major effort this year has been directed toward development of material systems that can be used for printing of textile substrates using ink-jet and xerographic print engines. Material properties required for performance in the print engines and characteristics required for textile applications have been identified. Material selection has been guided by computer simulation of polymer properties based on the group contribution methodology. A number of promising candidate materials have been selected and synthesis of a number of these materials has been conducted. Screening tests have been identified for candidate materials and test equipment is in place for determination of critical properties. Print engines specifically selected for both ink-jet and xerographic printing of textiles are in place for actual test of promising material systems.

INTRODUCTION

Color is one of the major factors in consumer selection of textile products. Prediction of consumer preference for color is an inexact art at best and it is a major contributor to poor consumer acceptance of textile products and, consequently, to end-of-season inventories. For this reason coloration of textiles as late in the textile production chain as possible is highly desirable. Rapid movement of textile coloration and finishing processes from traditional textile companies to apparel manufacturers is already evident. An excellent example of this movement is the recent entry of apparel firms into garment dyeing and "wrinkle resistant" garment finishing. This trend can be expected to continue and even the involvement of retail firms in dyeing and finishing may be anticipated.

This major relocation of dyeing and finishing in the textile production pipeline will require development of new coloration and finishing processes. Textile printing technology presents a clear challenge to this change in textile production but the change will provide significant benefits. For example, in cutting parts for garments assembled from printed fabric the printed pattern must match at seams. If the parts are cut from already printed fabric, the packing of parts in the marker is never optimum for fabric utilization. The ability to prepare an optimum marker and then print the fabric with the pattern oriented on each part so that matching at seams is achieved will result in a significant reduction in fabric waste.

The printing of fabrics, particularly for apparel applications can be expected to follow the same pattern that is now underway in paper printing in which a significant shift from large printing operations to PC based "desktop publishing" is clearly occurring. The purpose of the current research effort is the development of coloration techniques consistent with these new demand activated manufacturing systems of the future. Recent work has been directed in two major areas--garment dyeing and new printing technologies.

NEW PRINTING TECHNOLOGIES

Two relatively new technologies have made major impact in color printing on paper in the graphics arts and in the computer color printing arenas--xerographic printing and ink-jet printing. Both of these technologies are capable of taking an electronic image from a computer generated design or drawing and producing a color print in minutes. Some of the ink-jet and xerographic printers are capable of producing images on textiles but the printed fabric does not have properties acceptable for textile applications.

Xerography is favored for high speed single color (black) printing, although ink-jet systems are making in-roads in this area. Color printing has been dominated by ink-jet systems largely because of the small size that can be achieved for color printing systems.

Xerographic printing on textiles has been largely limited to use of existing color toners (designed for paper) to print a computer image on specially coated papers and to transfer the image to a textile substrate using standard thermal transfer presses. These prints suffer from poor fastness properties and very stiff fabric hand.

Most current work in the utilization of these new technologies for textile printing have centered on ink-jet systems. Stork has produced a "proofing" or strike-off machine based on binary ink-jet technology. In this system a continuous stream of ink drops is produced by mechanical stimulation at a frequency of several thousand hz of a ink stream (see Figure 1).

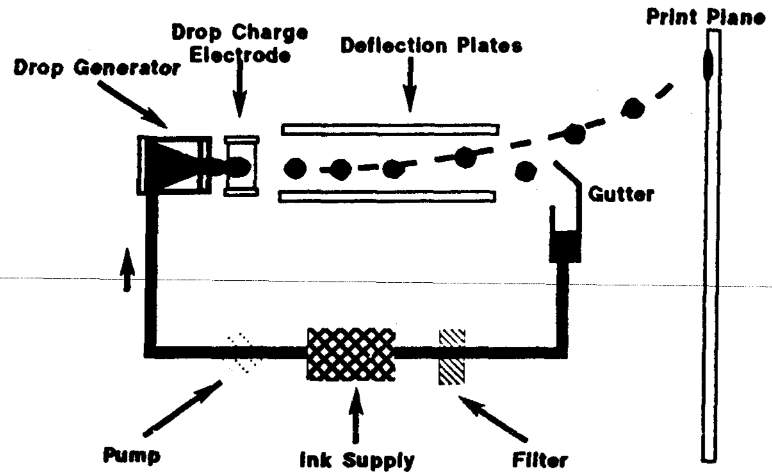

Figure 1

A charging electrode is placed just at the drop formation point and drops are selected for application to the media by placing a charge on the drop. If a drop is not needed at that time it is not charged. A deflection electrode is positioned so that charged drops are deflected to the media but uncharged drops pass straight to a waste collector.

The other major developments in ink-jet technology for textile printing use the drop-on-demand system. In these systems the drop formation process is usually driven by a piezoelectric transducer or by a thermally generated vapor bubble. This is believed to be the basis of the Canon-Kanebo textile printing machine and the basis for an ink-jet machine using a special plastisol for t-shirt printing.

Pattern design, computer image manipulation, and physical transfer systems for these new printing technologies have all been well established by the printer manufacturers. All of these systems work well for printing on textiles. The major barriers to widespread use of these systems in textile printing lie in the speed of printing and the poor performance of the materials used in existing systems designed for printing on paper. Much of the research work has been directed, therefore, at development of materials that are compatible with existing xerographic and ink-jet printing and have properties required for textile substrates.

RESEARCH ON COLORATION METHODOLOGIES

All of the existing systems for ink-jet and xerographic printing on textiles utilize either reactive dyes or resin pigment systems. Both of these approaches have significant deficiencies. Reactive dye printing (ink-jet) requires both a pretreatment and an after treatment of the textile substrate. This greatly increases the cost of the printed fabric. Resin pigment systems used in xerography suffer from the inherent limitations in color saturation caused by scattering of light by the pigment particles. This reduction in saturation increases the problem of producing a wide range of color from 3 or 4 primary colors. One phase of the current work has been directed toward looking at the possibility of using dyes that are soluble in the resin binder. Such a system avoids the problems associated with both reactive dyes and pigments.

Three highly saturated magenta, cyan, and yellow dyes that are soluble in resin compositions of interest as toners or ink-jet systems have been obtained from a leading dyestuff manufacturer. These dyes can be incorporated in the resins, produce clear films and give highly saturated film color.

RESEARCH ON MATERIALS FOR INK-JET PRINTING

Drop formation in ink-jet printing involves a complex interaction between inertial, viscous and surface tension forces. The drop formation process has been extensively modelled by the ink-jet print engine manufacturers. The controlling parameter is the ratio of the Reynolds number to the Weber Number and ranges of viscosity and surface tension for ink-jet liquids have been determined. In general, low viscosity and high surface tension favor drop formation. In systems designed for electrostatic deflection of the drops, the electrical conductivity is also important. This property can usually be controlled by addition of a suitable cation generator to the ink.

Most of the effort in ink-jet printing has been directed toward use of UV curable resin systems. A wide variety of interesting monomers are available commercially with structures shown below:

```
                                                    A
                                                    |
R--A        A--R'--A        A--R"--A           A--R'"--A
                                |                   |
                                A                   A
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where R, R" and R '" are a variety of organic groups (ethers, esters, urethanes, etc) and A represents a vinyl reactive group, usually acrylic acid. It is thus possible to produce a wide range of structures by suitable selection of the various building blocks.

In typical experiments, the monomer combination, a UV initiator and one or more of the dyes described above are mixed and poured into a thin cavity in a teflon block and cured using a standard laboratory UV lamp. Cure times of 1 to 5 minutes are required. The films are then removed from the block and tested. The initial modulus, tensile strength and stress at 10% elongation are the important properties examined. Several compositions that have been tested show interesting properties. The compositions with interesting properties will be selected for further study with the laboratory ink-jet printer described below.

An advanced design ink-jet printing machine made by Toxot Science & Applications has been selected as a test bed for development of materials and systems for printing on textiles. This machine is based on the continuous jet principle (see Figure 1) but instead of a binary system (drop on substrate or drop in gutter) the ink drops can be placed in any of 24 positions on the substrate by electrostatic deflection. Drops that are not charged are captured by the gutter. The machine prints with a resolution of 120 dots per inch and is capable of printing 0.2 inches from a single nozzle by electrostatic control of drop placement. The drop generator produces 62,500 drops per second so that at high speed 4 square inches per second can be printed from a single nozzle. The system can use both dyes and pigments (particle sizes up to 0.5 microns). The device is equipped with systems for very quick change of ink sources so that screening studies can be efficiently conducted. Thus, both the hydrodynamic characteristics of the selected fluids and the properties on the substrate can be evaluated. A more advanced version of the ink-jet engine will also be purchased to permit printing from 16 nozzles (printing 2.5 inch wide fabrics) in multiple colors. This will permit complete evaluation of printed fabric properties and studies on color gamut achievable with the available colorants.

RESEARCH ON ELECTROPHOTOGRAPHY

Efforts have continued to produce a toner satisfying both textile and electrophotographic requirements. Toners are typically produced by incorporating pigments in a molten polymer and then producing fine particles by a several stage grinding process. This is possible with the brittle resins used in paper printing but will be difficult or impossible with the very flexible resins required for textile printing. Flexible polyesters have been made by suspending small droplets of an organic phase in water and conducting interfacial polymerization between a diacid chloride and a diol at the droplet surface. This system may be capable of producing fine particle resins with dyes already incorporated that can be spray dried and used directly in toners. This would avoid the problem of grinding these flexible polymeric materials. A number of candidate polyesters have been produced by this technique for property evaluation.

Work continues in seeking and evaluating commercial materials and sources that have promise in textile printing. H. B. Fuller, who provided materials used as toners in earlier studies, was visited in an effort to obtain further cooperation in toner production , characterization and development. Toner Research Services, a consulting and research laboratory specializing in electrophotographic developer systems, has agreed to participate in the project providing assistance in toner production and development, as well as guidance in the electrophotographic research. Toner Research Services has agreed to produce a series of toners including polyamides, polyesters, epoxies and acrylics. Electrophotographic and textile properties of the toners will be evaluated and the relationships between polymer properties and textile properties will be studied. The results will be used as a guide for modifying test toners and/or synthesizing polymers for new toners.

A trip was also made to Delphax in Canton, MA, to discuss the use of their "ion deposition" electrophotographic system for textile printing.

MOLECULAR MODELING

Much of the work on synthesis of new toner and ink-jet materials is guided by the polymer molecular modeling studies. Polymer molecular modeling software from Biosym technologies Inc., running on a Silicon Graphics Iris Indigo workstation, is being used for the molecular modeling work. Predictions regarding several properties of candidate polymers have been made using two different structure-property relationship modules, namely Synthia and QSPR. These approaches are based on group contribution methodology. The properties of primary interest in screening polymers include the glass transition temperature, the melting point (if any) and moduli at room temperature.

Several polymers have been modeled. The first set of polyesters modeled were based on hydroxy terminated oligo(ethylene oxide) as well as alkane glycols reacted with terephthaloyl chloride. Interfacial polymerization was attempted for two candidate systems with tetramethylene glycol or hexamethylene glycol with terephthaloyl chloride. However, successful polymerization could not be achieved due to side reactions. Subsequent simulations were conducted on polyesters based on bisphenol-A with alkane dicarboxylic acids of varying methylene lengths. Polymers based on the bisphenol-A unit have been synthesized and are currently being characterized.

Characterization capabilities now include detailed thermal analysis (DSC, DT/TGA) and molecular weight determination by multi-angle laser light scattering. These capabilities were established as a part of the work on this project.

RESEARCH ON GARMENT DYEING

One of the major problems in garment dyeing is the requirement that multiple layers of fabric must be dyed to acceptable shade. This may include shell fabric that has been thermally bonded to interlining fabrics or nonwovens as well as seams between garment parts. Uniform penetration of these multiple fabric layers and dyeing to the same shade as the other garment parts is a difficult challenge.

A number of men's 100% cotton white shirts, purchased at retail, were scoured in an alkaline detergent bath to remove possible finishing agents and then dyed in a medium yellow and a light blue shade on a Unimac Model 160 garment dyeing machine. A number of different types of reactive dyes were used in the dyeing process to determine if different reactive dye types could enhance or reduce the difference in shade between multiple and single fabric layers in the shirts. Color of the various dyed shirt parts was measured on an ACS SpectroSensor II and the color differences between the collars, cuffs and plackets of the shirts and the bodies of the shirts were calculated using the CMC(1:2) color difference equation Results for different reactive dye types are shown in Table 1.

The first observation is that the dyeings were more uniform than had been expected. The dyeings with reactive dyes of type 2 and 3 were very close to acceptable. There is also a very clear difference in the ability of different reactive dye types to dye multiple layers of fabric to the same shade as the single fabric layers. This strongly indicates that dye selection will be critical in any attempt at successful garment dyeing. Dyeings in three shades have been conducted with a fourth type of reactive dye specifically recommended for garment dyeing. Quantitative results are not yet available for these dyeings but visual comparison indicates surprisingly good color uniformity.

TABLE 1
COLOR DIFFERENCES BETWEEN PARTS OF GARMENT DYED SHIRTS

	COLOR DIFFERENCES		
PART	REACT TYPE 1	REACT TYPE 2	REACT TYPE 3
BLUE DYEING			
Cuff	2.0	0.9	1.7
Collar	4.7	1.0	0.7
Placket	1.5	1.0	0.9
YELLOW DYEING			
Cuff	2.3	1.3	0.8
Collar	3.3	1.3	1.1
Placket	1.0	1.0	1.6

Similar types of dyeings have been conducted on 65/35 cotton/polyester men's shirts and as expected, very poor shade uniformity was obtained. It is clear that finishing of garments after dyeing will be required for blends having a permanent press finish. Fortunately the rapid development of "wrinkle free" garment finishing processes will make the possibility of garment dyeing and finishing a reality in the near future.