Xerographic Toners for Textile Printing

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Fabric printing is a bottleneck in the textile-apparel supply pipeline. It is commonly believed that digital printing systems will replace the current methods of printing textiles. Xerography is one of the digital printing technologies being investigated for textile printing at the Georgia Institute of Technology. The research reported in this paper has focused on developing polymerbased xerographic toners giving required printed fabric properties. The suitability of toners produced through mechanical grinding processes for xerographic textile printing is discussed. Three classes of polymeric binders (amorphous polyester, three thermosets, and five polyamides) were studied. The potential of these binders was evaluated using crockfastness (rub fastness) and fabric flexural rigidity tests. Materials that could be ground to the required particle size were too rigid. Thus the printed fabrics had high flexural rigidities and, in many cases, unacceptable wet crockfastness ratings. The potential of a more flexible resin, which could not be ground to the required particle size, was assessed by applying toners via a solvent medium. The flexible resin gave the required textile properties.

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Introduction

The textile industry has developed quick response systems to remove time from the textile-apparel supply pipeline; however, fabric printing is a bottleneck. Printing lag time prevents true manufacturing on demand. Some of the disadvantages of screen printing, the predominant method of printing textiles, are:

- 1. long changeover time for style and color changes,
- 2. screen production is time consuming and expensive, and
- 3. information is stored on screens requiring large storage space.

In 1999, time from design to sample production was typically eight to ten weeks at a cost of about \$6000-8000 per sample. It is widely accepted that screen printing will be unable to meet the requirements of demand activated manufacturing. Even with technologies such as computer-driven lasers to facilitate screen production, the lag time associated with screen printing is still too long. It is commonly believed that digital printing systems driven by computers storing information will

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replace screen printing. Some of the paper digital printing systems having potential for textile printing are xerography, ink jet, electrostatic, ion deposition, thermal transfer and TonerJet[®]. Polymeric materials are often used in these processes as binders to fix colorants to the fabric.

Textile digital printing research is being conducted at the Georgia Institute of Technology.¹⁻⁷ Xerographic digital printing is one of the technologies being investigated because it offers many potential benefits for printing on textile materials. For example, because xerographic toner is a dry solid containing colorant, excellent color registration is obtainable without chemical pretreatment of the fabric against color bleeding. Because no water is required, this process is one of the few "environmentally friendly" methods of textile printing in existence.¹ However, there are many obstacles to be overcome. Although xerographic printing is a highly developed technology for printing on paper, printing on textiles presents new challenges. Unlike most paper substrates, textile fabrics have irregular surfaces and often have high porosities. Toner transfer to the fabric is unacceptably low and varies significantly from fabric to fabric.4

In 1989, Carr and co-workers¹ investigated the use of xerography for textile printing. Because no toner had been specifically designed for textile printing, fabrics were xerographically printed using toners made for paper printing. The binders for these paper toners were

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TABLE I. Toner Composition

Toner	Toner Composition	Carrier
Colorocs	Polyester resin, styrene-acryl resin, solvent dye, polypropylene wax	Colorocs
Shell-epoxy	Epon resin 2004, coreactant RSC 2295, epicure P-101, luperton pink EP	Vertex Image
H.B. Fuller-epoxy	Bispenol A epoxy resin, benzophenone tetracarboxylic dianhydride, fanal pink	Vertex Image
Ruco-polyester	Rucote 102, Rucote NI-2, pink E, fanal pink, octaflow-ST-70	Vertex Image
Polyamide-1	Polyamide from dimer acid and ethylenediamine plus TOFA as chain terminating agent. MAGENTA RT-235-D pigment, FF4102 charge control agent, Carbo-sil	Vertex Image
Polyamide-2	Polyamide from dimer acid and ethylene-diamine, hexamethylene-diamine, chain plus stearic acid as terminating agent. MAGENTA RT-235D pigment, FF 4102 charge control agent, Carbo-sil	Vertex Image
Polyamide-3	Polyamide from dimer acid and aromatic-diamine with amino acid incorporated. Carbon Black Regal 330 (CABOT Corporation). Charge controlling agent-Copy Blue PR (Hoechst High Chem Pigment)	Vertex Image
Polyamide-4	Polyamide from dimer acid and aromatic-diamine. Carbon Black Regal 330 (CABOT Corporation). Charge controlling agent-Copy Blue PR (Hoechst High Chem Pigment)	Vertex Image

TABLE II. Material Properties

						T _g (°C)	
Toner	Tribo-electric Number (μC/g)	Particle Size Average (µm)	Initial Modulus (GPa)	Breaking Strain (%)	Tensile Strength (MPa)	Before Cross-linking	After Cross-linking
Colorocs	+10.2	10.4	1.75	0.19 ^a	2.65ª	60	b
Shell-epoxy	+12.6	10.5	С	С	С	58.7	64.3
H.B. Fuller-epoxy	+6.0	7.3	0.50	1.15ª	2.97	54.8	103.4
Ruco-polyester	+1.5	11.5	С	С	С	57.7	d
Polyamide-1	+9.0	15.0	0.11 ^{e,f}	50 ^{a,f}	6.9 ^{a,f}	54 ^f (DMS)	b
Polyamide-2	+8.5	12.0	0.20 ^{e,f}	g	g	59 f (DSC)	b
Polyamide-3	+15.5	10.8	0.26 ^{e,f}	g	g	46 f (DMS)	b
Polyamide-4	+12.6	11.5	0.43 ^{e,f}	g	g	46 ^f (DMS)	b
Aldrich 140	h	h	0.03 ^{e,f}	1000 ^{a,f}	i	gʻ	b

a. measured using Instron

b. does not crosslink

c. toner could not be converted into specimen required for Instron test

d. could not be measured using DSC because the curing process involves several simultaneous chemical and physical transformations

e. measured using DMA

f. property of binder

g. too brittle to be measured using Instron

h. too flexible to be ground into required particle size

i. not available

based on styrene-acrylic copolymers. The printed fabric had extremely poor textile properties. For example, rub fastness, referred to as crockfastness by the textile industry, was unsatisfactory. Also, the printed fabrics were too stiff.

The binder (adhesive) component of the toner holds the colorant on the surface of the fiber. It typically accounts for more than 90% of the toner mass and is the cause of most of the deterioration of the desired textile print properties in xerographic printing. If the binder is too stiff, properties of the printed fabrics may be negatively affected. Two of these properties are fabric handle and drape. Fabric handle⁸ refers to the feel of the material and so depends on the sense of touch. Drape⁸ very broadly is the ability of a fabric to assume a graceful appearance in use. Many fabrics are expected to drape gracefully. There is no adhesive in the unprinted fabric to hold the fibers and filaments together; instead the fabric is held together as a result of friction between the fibers/yarns in the fibrous assembly. Both fabric handle and drape are related to the freedom of movement of the fibers in the textile structure. Thus, the introduction of some external hindrance, such as binder, to the independent movement of fibers can negatively alter fabric handle and drape of the resultant printed cloth.

Because the binder causes most of the problems associated with the deterioration of printed fabric properties, the binder problem must be solved before the xerographic method of digital fabric printing can become truly feasible. A binder giving desired fabric properties while meeting the requirements of xerography is needed. Among the many desirable properties of the ideal binder being sought for xerographic printing of textiles are: 1) low melt viscosity and good flowing characteristics for good film formation, 2) good adhesion with the fiber and colorant, and 3) good mechanical properties (i.e., low initial modulus, high breaking strain and low tenacity).

This article discusses the suitability of several binders for producing textile-specific toners. Three classes of polymeric binders (amorphous polyester, three thermosets, and five polyamides) were studied. The toners were produced through mechanical grinding processes.

Experimental

Two component developer systems (toner plus carrier) were used for making the xerographic prints on a Colorocs color printer. Two types of carrier were used to obtain satisfactory triboelectric numbers. One was Colorocs carrier, normally used with the Colorocs print-

TABLE III. Toner Composition and Crockfastr	ess Results for Prints Produced Using Toner Solutions
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			Crockfastne		stness
Toner	Toner Composition	T_g (°C)	Toner Deposition (mg/cm ²)	Dry	Wet
Colorocs	Polyester resin, styrene-acryl resin, solvent dye,				
	polypropylene wax, chloroform, tetrahydrofuran (THF)	60	0.3	4.5	3.5
			0.5	4	3
			0.7	3.5	2.5
Polyamide-1	Polyamide from dimer acid and ethylenediamine plus				
	TOFA as chain terminating agent.				
	MAGENTA RT-235-D pigment, chloroform	54	0.1	4.5	3.5
			0.3	4.5	3
			0.5	3	3
			0.7	3	3.5
			1.0	3	3
			1.5	3	3
Aldrich 140	Dimer-acid based polyamide, solvent,				
	MAGENTA RT-235-D pigment, chloroform	9	0.1	5	4.5
			0.3	4.5	4.5
			0.5	5	4.5
			0.7	5	4.5
			1.0	4.5	4.5
			1.5	4.5	4.5

ers, and Vertex Image, Inc supplied the other. A model CP 4007 Colorocs color printer with a resolution of 300 dpi was used to produce the xerographic prints. The printer was designed so that the substrate, typically 0.21 m in width and approximately 0.28 m long, runs in a straight path through the machine. The curing unit was insufficient to properly cure the prints on the fabrics. The curing unit was removed, and the printed samples were cured in a convection oven. Most of the prints were cured for 3 min at an oven temperature of 200° C; however, in some cases, curing times of 5 and 10 min were used.

The performance of toners based on three classes of polymeric binders was studied. These were amorphous polyester, thermoset binders, and low T_g polyamide binders. Toner composition and material properties are given in Tables I and II. The polyester toner, referred to as Colorocs, is a typical color paper toner. It is an amorphous thermoplastic toner designed for xerographically printing on paper and consists of polyester resin, styrene-acrylic resin, colorant, and polypropylene wax. The binder is a mixture of polyester and styrene-acrylic resins, and the polypropylene is used as internal lubricant and fuser release agent. A magenta solvent dye and a black pigment are used as colorants.

Three thermoset toners (two epoxy-based and one polyester-based) were studied. After consultation with resin suppliers, the binders were selected based on their potential of meeting the flexibility and colorfastness requirements of textile printing. The toners are designated as H.B. Fuller-epoxy, Shell-epoxy, and Ruco-polyester, named after the resin suppliers.

Five polyamide binders were selected for producing toners for the xerographic printing study; however, one of them was too flexible to be ground into toner. The binders and the toners including their components are listed in Tables I and III. The polyamides successfully converted into toner were produced from fatty acids. These toners are designated as polyamide-1, polyamide-2, polyamide-3, and polyamide-4. The polyamide-1 and polyamide-2 toners were selected from several aliphatic polyamide binders available from Union Camp Corporation. These polyamide materials were selected because of their good grindability. The colorant used in the toners was MAGENTA RT-235-D pigment from CIBA, and the charge control agent used in the toners was FF4102 from BASF.

Polyamide-3 and polyamide-4 toners were made from aromatic polyamide binders produced at the Institute of Paper Science and Technology.⁹ These polyamides were selected because of their good flexibility and clarity in film form. Thus the study included both aliphatic and aromatic polyamide binders. Polyamide-4 toner was made of pure dimer-acid based polyamide while polyamide-3 was made from a dimer-acid based polyamide resin. The pigment used in these two toners was carbon black.

The thermoplastic pigmented resin, Aldrich 140 obtained from the Aldrich Company, was too flexible to be ground into toner using conventional grinding equipment. Attempts were made to grind the material using cryogenic grinding equipment, but this resin could not be converted into the fine powder form required for xerographic toners. Aldrich 140 resin is also in the family of dimer-acid based polyamide and was selected because of its thermal and mechanical properties. To simulate a print produced from this resin, it was applied to fabrics via a solvent medium (chloroform). The resin was colored with MAGENTA RT-235-D pigment from CIBA. Polyamide-1 and Colorocs toners were also applied on the fabrics by solvent medium for comparison with Aldrich 140. Polyamide-1 was dissolved in chloroform, but Colorocs toner was dissolved in tetrahydrofuran (THF).

Cotton, cotton/polyester blends, rayon, nylon, and silk fabrics were used in this study. Descriptions of the fabrics are given in Table IV. Definitions of textiles specific terms can be found in the literature.¹⁰

One of the important properties that a printed fabric must have is good rub fastness referred to as crockfastness. One standard crockfastness test (dry crock-fastness) involves rubbing the print with a dry rubbing cloth. A second standard test (wet crockfastness) uses a wet rubbing cloth containing 65wt% water on a dry basis.

TABLE IV. Fabric Description

Fabric	Description	Weight (g/m ²)	Weight (oz/dy²)	Warp Count (yn/in)	Filling Count (yn/in)	Weave	Supplier
Spartan Mills Cotton	Heavy cotton	218	6.43	98	54	4 shift satin	Spartan Mills, Inc.
Spring Industries Cotton	Light cotton	135	3.98	108	88	1/1 plain	Spring Industries, Inc
PET/cotton	65/35 P/C	123	3.63	106	76	1/1 plain	Spring Industries, Inc
Rayon	212 bright filament viscose	93	2.74	144	80	2/2 twill	Testfabrics, Inc.
Filament Nylon	306A nylon 6,6 semi-dull taffeta	59	1.71	104	84	1/1 plain	Testfabrics, Inc.
Silk	Crepe de chine	72	2.12	150	102	1/1 plain	Testfabrics, Inc.
Rubbing Cloth	Bleached, desized	110	3.25	80	84	1/1 plain	Testfabrics, Inc.

TABLE V. Crockfastness Results for Xerographic Prints

Toner	Fabric Type	Dry Crockfastness	Wet Crockfastness
Colorocs	Heavy cotton	4-5	2-3
	Nylon filament	5	5
	Silk	5	5
Shell-epoxy	Heavy cotton	5*	3-4*
H.B. Fuller-epoxy	Heavy cotton	5*	4-5*
Ruco-polyester	Heavy cotton	5*	3-4*
Polyamide-1	Heavy cotton	3.5	3.5
	Light cotton	3.5	3
	65/35 P/C	3.5	3
	Rayon	3.5	3.5
	Silk	2.5	4.5
Polyamide-2	Heavy cotton	2.5	2.5
	Light cotton	2	2.5
	65/35 P/C	2	2
	Rayon	2	2
	Silk	2	3
Polyamide-3	Heavy cotton	1.5	1.5
	Light cotton	2	1.5
	65/35 P/C	2.5	1.5
	Rayon	2	2.5-3
	Silk	2	3-3.5
Polyamide-4	Heavy cotton	3	2
	Light cotton	2.5	1.5
	65/35 P/C	3.5	2-2.5
	Rayon	2	2.5-3
	Silk	2	4

* Curing time is 10 min

These tests attempt to simulate the conditions of wearing and washing a fabric. Standard dry and wet crockfastness were measured using an American Association of Textile Chemists and Colorists test method (AATCC Test Method 8-1988) (ratings are: 1: entirely unacceptable, 2: unacceptable, 3: borderline acceptable, 4: good, 5: excellent (no color transfer)). Wang⁵ investigated the effects of toner deposition and found that the amount of toner deposition on the fabric has a surprisingly small effect on crockfastness ratings for the range of depositions used in his work.

A FRL Cantilever Bending Tester was used to measure fabric flexural rigidity. The test method was obtained from American Standard Test Method (ASTM D1388-64).

Differential scanning calorimetry (DSC) was performed on a Seiko SII DSC 220C, and thermogravimetric analysis (TGA) was performed on a Seiko SII TG/DTA 320. Measurements of the tensile modulus were carried out on injection-molded specimens at room temperature using an Instron-5567 (2 in./min). Dynamic mechanical analysis (DMA) was performed on a Seiko SII DMS 210 to measure glass transition and initial modulus of the resins. Some tensile properties were obtained from resin manufacturers.

Results and Discussion

Crockfastness results for the xerographic prints are summarized in Table V. Fabric flexural rigidity is shown in Fig. 1, and tensile properties of the toners are summarized in Table II. First consider the results for Colorocs toner. The dry crockfastness results (4-5) are good to excellent; however, wet crockfastness shows rather poor results (low crockfastness numbers) for cotton fabrics. This is important because cotton



Figure 1. Fabric Flexural Rigidities of Heavy Cotton Fabric Xerographically Printed with Various Toners

fabric represents a large percentage of the fabric printed by the textile industry. As shown in Fig. 1, the fabric rigidity of the Colorocs prints is unacceptably high. The high rigidity is associated with the high modulus and low elongation of the Colorocs toner.

In an effort to improve the wet crockfastness of xerographic prints on cotton, an investigation⁴ was conducted to determine if crosslinking the toner would improve the wet crockfastness ratings. The thermoset toners gave acceptable wet crockfastness results (see Table V) for cotton fabric; however, the curing time had to be increased from 3 to 10 min. These curing times are too long to be practical in industrial printing processes. In addition, increasing curing time caused yellowing of the fabric. Although the resin manufactures had indicated the thermoset resins were flexible, the fabric rigidities of fabrics printed with the thermoset toners were higher than that for the Colorocs toner, as shown in Fig. 1.

A study was conducted to determine the feasibility of using polyamide resin to produce textile-specific toner via grinding.⁷ Five polyamide resins were selected; however, attempts to grind the most flexible polyamide (Aldrich 140) into the required particle size were unsuccessful. Among the four polyamide toners produced via grinding, only polyamide-1 gave mostly acceptable dry and wet crockfastness ratings (see Table V). It was the most flexible (lowest initial modulus) of the toners. All of the other toners were very brittle. They had poor crockfastness ratings as well as unacceptable fabric flexural rigidities (similar to the Colorocs toner). Although the Polyamide-1 toner gave much lower fabric flexural rigidity, the fabric was still too stiff.

There are many factors that may influence crockfastness and fabric flexural rigidity. The mechanical properties including initial modulus, breaking strain, and breaking stress, are dominant factors. When toner is applied to fabric, if the toner film is more flexible than the fabric, the flexibility of the prints is primarily determined by the fabric. If the fabric is more flexible than the toner film, then the toner film has more influence on the flexibility of the print. Another factor is the penetration of the toner because the location of the toner and how it binds the fabric structure together will affect overall flexibility of the print. Toner penetration is influenced by factors such as viscosity, fusing temperature and fusing time. It can also be affected by the method of application.

Because all of the fabrics printed xerographically with the test toners were too stiff due to insufficient flexibility of the resins, tests were conducted to assess the effect of using a more flexible resin (Aldrich 140) on crockfastness as well as fabric flexural rigidity. Using solvents, toner was applied to the fabric. The exact amount of toner was added to the solvent to get the desired deposition. In Fig. 2, the flexural rigidities of light cotton fabric printed using three different toner solutions are shown. Because toner penetration is greater when toner is applied via solution, the fabric flexural rigidities of the solvent prints are higher than those for the xerographic prints (compare Figs. 1 and 2). In Fig. 2, it is obvious that prints made using Aldrich 140 toner are the most flexible, and prints made by Colorocs toner are the most rigid. These results were expected since Aldrich 140 resin is the most flexible resin and has a break strain of 1000%. Polyamide-1 resin is less flexible than Aldrich 140 resin, but more flexible than Colorocs toner. Thus the Polyamide-1 prints have a larger fabric flexural rigidity than the Aldrich 140 prints, but lower than the Colorocs prints. It can also be seen in Fig. 2 that when deposition is increased, the fabric flexural rigidity of Aldrich 140 toner does not increase as fast as those of polyamide-1 and Colorocs toners. Subjective evaluation of the prints indicated that the Aldrich 140 toner gave acceptable crockfastness and



Figure 2. Fabric Flexural Rigidities of Heavy Cotton Fabric Printed with Various Toner Solutions

fabric flexural rigidity. Alternate methods for producing textile-specific toners from flexible resins such as Aldrich 140 should be investigated.

Conclusions

The approach used in this research to produce textilespecific toners involved grinding of melt mixtures of binder, pigment and charge control agent to achieve the required particle size for xerography. The binder had to be sufficiently brittle for successful grinding, and materials that could be ground were too rigid. Thus fabrics printed with these toners had high fabric flexural rigidities, and in many cases, unacceptable wet crockfastness ratings.

Fabrics printed with Aldrich 140 toner via a solvent medium had good dry and wet crockfastness and fabric flexural rigidity ratings. Alternate methods for producing textile-specific toners from flexible resins such as Aldrich 140 should be investigated.

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