# Xerographic Printing of Textiles: Polymeric Toners and Their Performance

# W. W. CARR,<sup>1</sup> D. S. SARMA,<sup>1\*</sup> L. COOK,<sup>1</sup> S. SHI,<sup>1</sup> L. WANG,<sup>1</sup> P. H. PFROMM<sup>2</sup>

<sup>1</sup> Georgia Institute of Technology, School of Textile and Fiber Engineering, Atlanta, Georgia 30332

<sup>2</sup> Institute of Paper Science and Technology, 500 10th Street NW, Atlanta, Georgia 30318

Received 8 February 1999; accepted 11 November 1999

ABSTRACT: Xerographic printing of a number of common fabrics was investigated. The role of the polymeric binder used for the formulation of the commercially available and custom-made toners was investigated. Fabric performance tests (crockfastness), friction tests, and morphological investigations using scanning electron microscopy were performed. The intricate relations of toner and fabric properties with the results of an important overall industrial performance test for fabrics (crockfastness) are discussed. Both cohesive and adhesive toner failure can be important. Improved toner performance was achieved with a thermoset polymer as the toner binder. However, curing times for the thermoset polymer used are not sufficiently short for high-speed industrial printing. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2425–2434, 2000

Key words: xerography; textiles; toner; fastness; printing

# **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 1998, time from design to sample production is typically 8 to 10 weeks at a cost of approximately \$6000-8000 per sample. It is widely accepted that screen printing will be unable to meet the requirements of demand activated manufactur-

Contract grant sponsor: National Textile Center, Wilmington, DE.

Journal of Applied Polymer Science, Vol. 78, 2425–2434 (2000) © 2000 John Wiley & Sons, Inc.

ing. Even with technologies such as computerdriven lasers to facilitate screen production, the time lag associated with screen printing is still too long. It is commonly believed that digital printing systems driven by computers storing information will replace screen printing. Some of the paper digital printing systems that may have potential for textile printing are xerography, ink jet, electrostatic, ion deposition, thermal transfer, and TonerJet<sup>™</sup>. 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.<sup>1</sup> Xerography is one of the technologies that have been investigated. Technical barriers associated with xerographic textile are (1) lack of textilespecific toners; (2) number of toner transfer steps; (3) low toner transfer efficiency to fabrics; and (4) unavailability of machinery specifically designed for textile printing. Thus, research is needed in several areas for xerography to become a largescale commercial method of printing textiles. The

Correspondence to: P. H. Pfromm (peter.pfromm@ipst.edu). \* Present address: Trident International, Brookfield, CT.



Figure 1 Basic principle of the xerographic process.

research reported in this article has focused primarily on developing polymer-based xerographic toners giving required printed fabric properties.

The xerographic process will be discussed briefly herein. More details can be found in an earlier publication.<sup>2</sup> The six primary steps of the xerographic process are shown schematically in Figure 1. The first step involves electrically charging the surface of the photoconductor (PC). This is typically achieved using a corona, which ionizes the surrounding air, resulting in the flow of ions to the surface of the PC and thereby forming a charged surface layer. The second step, imaging, is to form a latent electrostatic image on the PC. Copiers use reflected light from an original to form a latent image, whereas printers use photodiodes or lasers driven by a computer to form a latent image. In both cases, the PC becomes electrically neutralized in the areas exposed to the light. The third step is to develop the latent electrostatic image into a visible image with a colored polymeric material (toner). The toner is commonly applied using a dual-component development system composed of toner (polymer, pigment, and additives) and carrier (polymer-coated magnetic beads). The toner particles are much smaller (5-20 microns in diameter) compared with the carrier beads (50–150 mi-

crons in diameter). Mixing the two materials (toner and carrier) causes them to become triboelectrically charged and to attract each other. The smaller toner particles electrostatically adhere to each carrier bead. The developer system brings the mixture of toner and carrier in close proximity to the latent electrostatic image, and the toner moves from the carrier bead to the latent image due to the stronger electrical force of the latent image. The fourth step (transferring) is the process in which the developed image on the PC is transferred to the substrate being printed. This is accomplished by passing the printing substrate between the PC and a transfer corona, which charges the backside of the substrate. The charge on the substrate has opposite polarity to that of the toner and thus attracts the toner to the printing substrate. In the fifth step (fusing), the toner is heated and fixed to the substrate. Various fusing techniques (hot roll, cold roll, radiant, or solvent) are used depending on the toner and substrate properties. In the final step (cleaning), residual toner and charge remaining on the PC are removed.

The xerographic process has been recognized as a revolutionary technology that could be used in many applications.<sup>3–5</sup> In 1989, Carr et al.<sup>6</sup> investigated the use of xerography for textile printing. In textile applications, the toner must have properties compatible with xerography, and at the same time, must meet several textile requirements. Since 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 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.

Since the study reported by Carr et al.,<sup>6</sup> color printers have reached the market place. The toners used for color printing are primarily based on polyester. In the study reported in this article, the performance of a typical polyester paper toner used for color printing was evaluated for printing fabric. The textile performance of the polyester toner, referred to as Colorocs in this article, varied significantly with type of fabric used in the printing. In the rubbing test, dry crockfastness was usually acceptable; however, wet crockfastness ratings varied greatly with fiber and fabric and were usually lower than for dry crockfastness. Lower wet crockfastness ratings are also usually reported for screen-printed fabrics. Little information is available in the literature concerning the mechanisms for color transfer during the rubbing (crocking) of fabrics. This article discussed an investigation conducted in an effort to better understand the variation in the performance of the polyester toner on fabrics and to study the failure mechanisms occurring during crocking.

# **EXPERIMENTAL**

#### Materials

#### **Toner and Carrier**

A two-component developer system (toner plus carrier) was used for making the xerographic prints on a Colorocs color printer. The magentacolored Colorocs toner was selected for this study. It is a thermoplastic toner designed for xerographically printing on paper and consists of polyester resin, styrene-acrylic resin, solvent dye, 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 is used as the colorant. Colorocs carrier, normally used with the Colorocs printers, was used mixed with the toner to produce developer.

#### Fabric

Cotton, polyester, nylon, and silk fabrics were used in this study. Descriptions of the fabrics are given in Table I. Definitions of textiles specific terms can be found in the literature.<sup>7</sup>

#### Instrumentation and Equipment

#### Printer

A model CP 4007 Colorocs color printer (Colorocs, Suwanee, GA) with a resolution of 300 dpi was used to produce the xerographic prints. This is a commercial paper printer that uses an LED printhead and four colored (cyan, magenta, yellow, and black) polyester-based (thermoplastic) toners. 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 on the Colorocs Printer was insufficient to properly cure the prints on the fabrics. To facilitate time and temperature curing studies, the curing unit was removed from the printer, 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.

#### **Toner Deposition**

The effects of toner deposition on fabric properties were investigated. Grid voltage, which relates to the surface charge on the photoconductor belt, and toner concentration in the developer were varied to obtain a range of toner depositions. Fabric samples were stored overnight at standard conditions (65% relative humidity, 70°F) to reach equilibrium moisture regain (water sorption). The samples were then weighed, printed, and cured. The printed samples were stored overnight at standard conditions, and then weighed again. The amount of toner/paste deposition was taken as the difference of fabric weight after and before printing. The toner/paste deposition per unit area was calculated from toner/paste deposition divided by print area. Wang<sup>8</sup> investigated the effects of toner deposition on fabric properties and found that the amount of toner deposition on the fabric has a surprisingly small effect on crockfastness ratings within the range experienced in our work.

# Standard and Special Crockfastness Tests

One of the important properties that a printed fabric must have is good rub fastness, referred to as crockfastness. One standard crockfastness test (dry crockfastness) involves rubbing the print with a dry rubbing cloth. A second standard test (wet crockfastness) uses a wet rubbing cloth containing 65 wt % water on a dry basis. 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 (AATCC) test method (AATCC Method 8-1988).<sup>9</sup> The standard crockfastness tests were conducted using an AATCC Crockmeter, model cm-1. Standard crockfastness ratings are: 1, entirely unacceptable; 2, unacceptable; 3, borderline acceptable; 4, good; and 5, excellent (no color transfer).

#### Thermal Analysis

Differential scanning calorimetry (DSC) was performed on a Seiko SII DSC 220C, and thermogravimetric analysis was performed on a Seiko SII TG/DTA 320.

#### Surface Morphology

Surface morphology was observed under a scanning electron microscope (SEM) (Stereoscan 430, Leica Cambridge Ltd., 10 kV, 2.39 A filament current, 200 nA probe current). A sputter coater (International Scientific Instrument) was used for sample preparation (90 s, 1.3 kV, 40 mA, Au-Pd target).

#### Wettability and Melt Flow

A polarized optical microscope (Leitz Laborlux 12 POL, magnification  $100\times$ , with heating stage, manufactured by W. Nuhsbaum, Inc., McHenry, IL) was used to study the wetting characteristics of the toner melt on single fibers, the melt flow behavior of the toners, and the wetting properties of toners on fabrics.

Fine single fibers of cotton, polyester, nylon, and silk were separated from their yarns in the fabrics. Each single fiber was placed on a glass slide on which there was a thin layer of toner powder. A second glass slide was placed on it, and they were rubbed together for about 1 min. After observing toner powder attached to the surface of the single fiber, the fiber was attached to a clean glass plate using scotch tape on both ends and leaving the middle part of the fiber suspended in air. The change of the morphology of the toner particles on the fiber surface was observed under  $\times 200$  magnification with a heating rate of 3°C/ min under the polarized optical microscope. Digital images were taken every 10 min.

#### Surface Free Energy

A dynamic contact angle (DCA) tensiometer and an FTÅ200 (First Ten Ångstrom, Inc., Portsmouth, VA) contact angle measurement instrument were used to measure solid surface free energy.

Small specimens of cellulose acetate films (15  $\times$  20 mm) were washed with deionized water and dried at room temperature. Deionized water and ethylene glycol were selected as the testing liquids. Surface free energy measurements were performed in triplicate and averaged for each substrate film at room temperature using a DCA tensiometer (sample stage speed of 198  $\mu$ m/min)

For direct contact angle measurements, the toner powder was applied to a glass slide and

evenly distributed until a layer of toner powder with smooth surface was formed. The glass slide was placed on a heating stage at approximately 150–190°C for 5 min until the toner powder was fused and then cooled at room temperature. Surface free energy measurements were performed at room temperature on the FTA 200 surface energy analyzer with two liquids: deionized water and ethylene glycol.

## **Mechanical Properties**

Tensile test specimens of Colorocs toner were made using an injection-molding machine (Sheffer Corp., Cincinnati, OH). Measurements of the tensile modulus were performed at room temperature using an Instron-5567. The strain rate was 2 in/min.

# **RESULTS AND DISCUSSION**

Table I gives an overview of the crockfastness data obtained in this work. Also shown are the fabric weight per area and the toner deposition. The dry crockfastness test generally shows good results (4-5, good to excellent). However, wet crockfastness (to simulate washing) with water shows rather poor results (low crockfastness numbers), except for silk and filament nylon. Immediately the question arises why prints on silk (a natural polymeric fiber with high water sorption and an intricate fine structure) and nylon (an artificial polymeric fiber with low water sorption and no fine structure) both show very good performance when tested wet. Although cotton fabric is the focus of this article, other fabrics were tested to obtain more information on the failure mechanisms of the prints.

The results shown in Table I led to a detailed investigation of several issues that could be suspected of influencing the crockfastness of a printed fabric. SEMs of many samples were taken to elucidate the surface morphology of the fibers and prints. Friction and surface energies were investigated. Finally, based on the results of the above investigations, toners with the capability for chemical crosslinking were tested, and shown to have superior properties for xerography of textiles, with the drawback of time needed to complete the crosslinking step.

#### Spreading/Wetting of Various Fabrics by the Toner

It could be suspected that the wetting/spreading of the toner melt on the fabric material contributes to poor crockfastness. The toner might form small domains on the fabric, rather than spreading and providing a large amount of interfacial area for adhesion, and opportunities for geometric entrapment.

The surface energy of Colorocs toner determined by contact angle measurements (water and ethylene glycol) was 20.8 dynes/cm.<sup>10</sup> The spreading coefficient of Colorocs toner was 24.3 dynes/cm on a cellulose acetate film. This film was used to simulate cotton fibers. The spreading coefficient indicates that the toner melt will likely wet cotton fibers spontaneously. Therefore, wetting/spreading is not a likely cause for poor crockfastness of cotton fabrics.

An optical microscope equipped with a hot stage was used. Toner particles that adhered to single fibers of the various fabrics were observed when the fibers were heated to 100°C. It was noted that the toner particles did melt and spread out along the fibers. This is additional evidence that wetting/spreading is not a problem with the fabrics and toners used.

#### **Apparent Coefficient of Kinetic Friction**

Friction plays an important role in the crockfastness test. It could be suspected that poor crockfastness results might be due to the surface morphology of the fabrics. In addition, the amount of toner and the morphology of the deposited toner may influence the crockfastness results. Because wet crockfastness was found to be poor (except for silk and filament nylon), whereas dry crockfastness ratings were largely acceptable, the frictional properties of printed and unprinted wet and dry fabric samples were evaluated.

The apparatus as described elsewhere<sup>8</sup> was used for the friction tests. The major components of the apparatus include an aluminum platform, a Plexiglas sled, a Teflon wheel, and an Instron-5567. The system measured the apparent friction between fabrics mounted on the aluminum platform and the Plexiglas sled. An Instron tester pulled the sled along the platform at constant speed (500 mm per min) for a distance of approximately 110 mm and measured, using a 50-N load cell, the resulting apparent frictional force.

In the wet/dry friction tests, normal pressure on the rubbing cloth/fabric, length of the rubbing path, cycle number, and water pickup were the same as in crockfastness tests. There was one difference between the friction tests and the crockfastness tests. The crockmeter moved at a

Vehicle). Also Shov	vn: Tightly Woven Cottor	n Printed wi	ith a Thermoset	Resin-Based T	oner (H. B. Fuller	Epoxy-Based)	
Toner	Fabric Type	ID No.	Fabric Weight (grams/m <sup>2</sup> )	Toner Deposition (Mg/cm <sup>2</sup> )	Dry Crockfastness	Wet Crockfastness (Water)	Wet Crockfastness (Hexadecane)
Colorocs (polyester-based, thermoplastic)	Cotton tightly woven Nylon 306a filament	15 10 7	218 59 72	0.29 —	4-5 5	2-3 5	2–3 5
	Silk	11 3	72	0.42	5	ũ	Ũ
H. B. Fuller (epoxy-based, thermoset)	Cotton tightly woven	58	218	I	IJ	4-5	Ω
Curring: 200 °C, 3 m Note: Crockfastness	nin in air for all toners. rating below three is unaccept	able.					

speed of 1200 cm/min whereas the sled used in the friction tests moved at 50 cm/min; however, Naik and Carerra<sup>11</sup> showed that in the case of fabric-to-sled friction, the coefficient of friction did not change with sliding speed.

The following procedure was used in conducting the friction tests:

- 1. Conditioned fabrics were cut in the designated orientation for testing. In this experiment, warp directions were always used for both testing fabrics and rubbing cloths.
- 2. The fabric portion that was in contact with the rubbing cloth was left with no glue. The rubbing cloth was weighed, then attached to the sled using acrylate glue to fix the cloth to the one side of the sled. For the wet fabric friction tests, the liquid was dropped on the rubbing cloth until the liquid pickup reached the desired amount. The amount of liquid needed in the rubbing area (25  $\times$  110 mm) was calculated from the fabric weight. The liquid was dispersed uniformly with a pipette.
- 3. Two Kevlar 49 threads were tied to two screws in the sled. One thread was clamped in the Instron jaw, and the other was used to pull the sled back to its original position at the end of each cycle.
- 4. The platform was aligned so that the sled moved perpendicular to the Instron crossbar. A Teflon wheel to redirect the pulling thread to the Instron was placed directly below the Instron jaw.
- 5. A weight of 3350 g was placed on top of the sled to produce the same pressure as in standard crockfastness tests (7.2 psi).
- 6. The Instron was started (110 mm distance at constant speed).
- 7. The Instron was stopped and the sled was returned to the starting position by manually pulling on the Kevlar return thread.
- 8. Repeat items 6 and 7 10 times.

The apparent coefficient of kinetic friction for dry unprinted (blank) and printed cotton, silk, and filament nylon samples is shown in Figure 2. For unprinted and printed dry samples, the apparent coefficient of kinetic friction was relatively constant over 10 cycles. The results do not show evidence that a significant difference exists in the dry frictional properties of the printed or unprinted fabrics.



**Figure 2** Apparent coefficient of kinetic friction for unprinted and Colorocs-printed dry and wet fabrics (legend: cot, cotton; nyl, nylon). One set of data (fabric 50% wet) is shown where the fabric, not the crocking cloth is wet.

Testing of wet samples at standard conditions (65 wt % of water pick up in the rubbing cloth) showed a strong dependence on the number of test cycles (Fig. 2). However, after 10 cycles, the values of the dry fabrics were approached for ny-lon and silk, whereas the value for cotton (printed and unprinted) remained somewhat above the dry test.

In wet crockfastness tests, a wet crocking cloth (see Experimental) is rubbed against an initially dry fabric sample. It was found that the initial apparent coefficient of kinetic friction was higher for wet crockfastness tests than for the dry crockfastness test. This was true for all fabrics, printed or unprinted. The reason is probably the surface tension of water present at the interfaces in wet rubbing.<sup>12</sup>

The apparent coefficient of kinetic friction for the wet crockfastness test decreased over 10 cycles to somewhat above (cotton) or down to the value for the dry tests. This can be attributed to distribution of the water between the crocking cloth and the fabric sample with the number of cycles. This was verified with a test in which the relatively large fabric was saturated with water, so that redistribution of water between fabric and rubbing cloth would not dry the interface between rubbing cloth and fabric to be tested.

In Figure 2, data for a friction test at 50 wt % water saturation of the fabric shows no change with the number of cycles (as opposed to the data for 65 wt % water saturation on the rubbing cloth). It is therefore apparent that presence of water does increase the coefficient of friction between crocking cloth and fabric. The increase of the coefficient of kinetic friction for the wet crocking test may explain poor wet crocking results for

cotton. However, no significant differences were found that would explain the good wet crockfastness for silk and filament nylon versus the inferior results for cotton, based on friction.

To determine whether an increase in friction would result in a lower crockfastness rating, we performed tests with increased normal force. Crockfastness tests for Colorocs printed cotton with an increase of the standard normal pressure on the crocking arm from 7.2 to 15.7 PSI showed that the dry and wet crockfastness ratings were unchanged (4–5 and 2–3, respectively). The increase in normal force on the fabrics rubbed against each other should have resulted in poor dry crockfastness—if increased apparent friction would be the main reason for poor performance. This was not the case.

It can be concluded that water plays an additional role in reducing crockfastness, beyond an increase in apparent friction. Simple increase of the normal force in the dry crockfastness test did not cause poor results for fabrics that performed poorly in the wet crockfastness test.

Wet friction tests were performed with hexadecane to test whether swelling in conjunction with higher friction was responsible for the poor performance of cotton. The lower surface tension of hexadecane compared with water would be expected to lower the apparent coefficient of kinetic friction somewhat relative to the presence of water. In addition, nonpolar hexadecane cannot swell cotton fibers as significantly as water. The initial (cycle 1) apparent coefficients of kinetic friction for blank cotton and filament nylon fabrics were as expected lower for hexadecane than for water but still increased compared with dry tests.

#### Influence of the Type of Liquid on Crockfastness

In a set of special tests, hexadecane replaced water in the wet crockfastness test. The liquid pickup was kept at 65 wt %.

Crockfastness tests with hexadecane instead of water showed essentially similar results to water (Table I). This is despite the significant differences (polarity, viscosity, surface tension) of the two liquids. The conclusion from this data, supported by the results from friction tests discussed above is that liquids play a role in the crockfastness beyond hydrodynamic issues (friction), and swelling of the fibers.



**Figure 3** SEMs for tightly woven cotton fabric printed with magenta Colorocs toner. (a) unprinted; (b) printed, before crockfastness test; (c) unprinted, after dry crockfastness test; (d) printed, after dry crockfastness test; (e) unprinted, after wet crockfastness test (water); (f) printed, after wet crockfastness test (water); (g) printed after wet crockfastness test (hexadecane).

#### Surface Morphology Via SEM

The morphology of cotton fibers (virgin, unprinted tightly woven cotton) is shown in Figure 3(a). The cotton fibers show their typical fine structure (flat fibers, fibrils).<sup>13</sup> Figure 3(b) shows the cotton fibers after application of Colorocs xerographic toner in the experimental printer. The printed fabric was exposed to 200°C for 3 min (standard postprinting treatment). Especially at intersections of fibers the toner can be seen as a film connecting the fibers. The toner layer on the fibers obscures the fine structure of the fibers. Figure 3(c) demonstrates that unprinted virgin cotton fibers experience little damage during the dry crockfastness test. This, together with Figure 3(d) (printed fibers after dry crockfastness test) supports the good results for dry testing (see Table I).

Little damage to the fibers occurs. Some cracking of the toner layer is visible, but loose debris is very limited. Figure 3(e) (unprinted) and 3(f) (printed) show the significant damage inflicted on the hydrophilic cotton fibers during the water wet crockfastness test. In Figure 3(f), a large amount of toner fragments can be seen. Toner fragments can be identified as particles with rather sharp edges due to the brittle nature of the toner. Figure 3(f) shows that the fibers are damaged, and that toner is physically detached from the fiber surfaces.

Figure 3(g) shows the tightly woven cotton after wet crockfastness test with hexadecane. The а crockfastness ratings for water wet and hexadecane wet tests were similarly low. Figure 3(g) shows no fibrillation of the fibers. This is evidence that the presence of water and the associated swelling reduces the ability of cotton fibers to resist mechanical abrasion. Despite the fact that fibrillation is absent in the hexadecane wet test, a significant amount of toner debris can be seen. The conclusion from the morphological evidence for cotton is that the failure of the toner is both cohesive (toner fragmentation) and adhesive (removal of toner from the fibers), followed by transfer of the toner fragments from the fabric sample to the rubbing cloth.

The SEMs for silk fibers are shown in Figure 4. Silk is also a hydrophilic natural fiber, similar to cotton in some respects. The fine structure of virgin silk fibers can be seen in Figure 4(a). Just as in the case of tightly woven cotton, the applied toner coats the fibers [Fig. 4(b)] as expected from the wetting experiments. Dry crockfastness of silk was good, and no significant damage was observed, as in the case of cotton [Fig. 4(c,d)]. The appearance of silk after wet crockfastness tests with water [Fig. 4(e,f)] is very similar to the cotton fibers. Surprisingly, however, the crockfastness results were outstanding, despite the serious damage and fibrillation. No significant amount of loose toner particles is observed. This supports the conclusion that although cohesive failure of the fibers occurred, the toner still adhered to the silk and was not removed from the fabric, resulting in good fastness ratings. In Figure 4(g), no fibrillation is evident, since the hexadecane is not expected to swell and weaken hydrophilic fibers. Although some debris is seen, the crockfastness is still outstanding. The toner fragments may have formed since the stresses induced by the crockfastness test were fully brought to bear on the toner layer, and not dissipated by the damage and fibrillation to softened fibers, as is the case for water wet tests



**Figure 4** SEMs for silk fabric printed with magenta Colorocs toner. (a) unprinted; (b) printed, before crock-fastness test; (c) unprinted, after dry crockfastness test; (d) printed, after dry crockfastness test; (e) unprinted, after wet crockfastness test (water); (f) printed, after wet crockfastness test (water); (g) printed after wet crockfastness test (hexadecane).

Unprinted filament nylon fabric is shown in Figure 5(a). The smooth and cylindrical fibers with no distinguishable fine structure are typical of man-made materials. The appearance of these fibers did not change during printing and in any of the tests applied herein [Fig. 5(b)]. The fibers remain smooth and cylindrical, and no significant debris is seen. This is reflected in the crockfastness ratings (Table I). It can be concluded that no failure of either the fibers or the toner occurred in these tests.

The results of the morphological studies show the intricate set of properties that must be present to produce a well-performing xerographic print on a fabric. Fiber damage does not necessarily lead to inferior print performance, if toner adhesion is good. Because cotton was the main





**Figure 5** SEMs for nylon fabric printed with magenta Colorocs toner. (a) unprinted; (b) printed, after dry crockfastness test.

target of this study, it was decided to attempt to improve print performance by using a thermoset resin. The chemical crosslinking of the resin after application to the fabric was expected to improve the cohesive strength of the toner layers that form during the printing and thermal fusing steps. Because the toners do wet and coat the fibers, an improvement in cohesive strength might not only prevent toner fracture, but possibly also detachment of toner. The toner was hoped to physically entrap the fiber as a strong coating.

# Improving Toner Performance: Use of a Thermoset Toner

A bisphenol-A epoxy resin manufactured by H. B. Fuller was chosen as a thermoset toner vehicle.

The toner contained benzophenone tetracarboxylic dianhydride for crosslinking, and fanal pink as the pigment. The thermoset toner was tested by DSC (Seiko SII DSC 220C, 20°C/min). The glass transition temperature increased from 55°C



**Figure 6** SEMs for tightly woven cotton fabric printed with a thermoset resin based toner (H. B. Fuller). (a) printed, after dry crockfastness test; (b) printed, after wet crockfastness test (water); (c) printed, after wet crockfastness test (hexadecane).

(before crosslinking, first heat) to  $103^{\circ}$ C after crosslinking. The onset of crosslinking was observed at 111°C, and the curing enthalpy was -50.4 mJ/mg. A simple rubbing test with a methyl ethyl ketone saturated swab on an ovencured toner sample fused on a glass slide showed that at 3–5 min curing time at 200°C crosslinking was sufficient.

Table I shows the excellent crockfastness properties of this toner. This was a first confirmation of our hypothesis that a crosslinked toner would show an improvement over thermoplastic materials.

Figure 6 shows SEMs of samples of tightly woven cotton printed with the H. B. Fuller toner. Figure 6(a) shows the expected smooth coating of toner on the fibers, which is not significantly damaged by the dry crockfastness test. The water wet crockfastness test [Fig. 6(b)] produces some damage and fibrillation to the fibers. However, large areas of intact toner can be seen virtually encapsulating the fibers. If hexadecane is used in the wet crockfastness test [Fig. 6(c)] the cotton fibers are not fibrillated, and the appearance is very similar to the dry crockfastness test.

The very good crockfastness results for the thermoset toners, together with the morphological studies indicate that a thermoset toner vehicle does solve some of the problems of low wet crockfastness for xerography of textiles.

# **CONCLUSIONS**

The textile print property most difficult to obtain for xerographic printing of textiles is the wet crockfastness (simulating washing of the fabric). The most significant issue seems to be the failure of the toner/fiber interface. Good properties can be obtained even if the fibers sustain serious damage in the test, as long as the toner adheres well, or if the toner is physically crosslinked.

A major obstacle to industrial application of xerography on textiles is the time (several min-

utes) to allow the toner to wet/spread, and potentially crosslink, after application to the fabric. The desired speed for full-scale fabric production (50-100 yards per minute) would require very large curing zones after the print is applied to the fabric. Rapidly crosslinking systems would be required for industrial application of xerography for textiles. The production of small samples of new patterns, however, could be easily performed by xerography.

The support for this project by the National Textile Center is gratefully acknowledged. The H. B. Fuller Company supplied pigmented toners. Carrier materials were supplied by Vortex Image Products, Inc. Tightly woven cotton was supplied by Spartan Mills. The support of these companies is gratefully acknowledged.

# REFERENCES

- 1. National Textile Center, 1998 Annual Report; Wilmington, DE, 1998.
- Carr, W. W.; Sarma, D. S.; Cook, F. L.; Shi, S.; Wang, L.; Pfromm, P. H. J Electrostatics 1998, 43, 249.
- 3. Carlson, C. F. Photographic Age 1949, March, 10.
- 4. Bulls, C. U. S. Pat. 4,724,468, 1988.
- 5. Mammino, J. U. S. Pat. 4,064,285, 1977.
- Carr, W. W.; Cook, F. L.; Lanigan, W. R.; Sikorski, M. E.; Tincher, W. C. Text Chem Color 1991, 23, 33.
- 7. Tortora, P. G. Understanding Textiles, 4th ed.; Maxwell MacMillan Publishing: New York, 1992.
- Wang, L. M. S. Thesis, Georgia Institute of Technology, School of Textile and Fiber Engineering, 1996.
- 9. American Association of Textiles Chemists and Colorists Technical Manual; AATC, Research Triangle Park, NC, 27709, 1995.
- Shih, S. M. S. Thesis, Georgia Institute of Technology, School of Textile and Fiber Engineering, 1996.
- 11. Naik, A.; Carrera, E. Textile Month, December 1, 1994.
- 12. Kenins, P. Textile Res J 1994, 64, 722.
- Warner, S. B. Fiber Science; Prentice Hall: New York, 1995.