

# Application of Dimer Acid-Based Polyamide for Xerographic Toners for Textiles Printing

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**ABSTRACT:** Xerographic printing of textiles was explored. A number of fabrics were printed using commercially available and synthesized polymers as toner vehicles. The polymers were characterized using standard methods (DSC, DMA, tensile tests). The performance of the prints was evaluated using textiles-specific tests (crockfastness, flexural rigidity). It was found that the initial modulus is a reasonable predictor of the performance of the printed fabrics. However, the requirements on toner vehicles for good textile performance (low initial modulus, flexibility) contradict the requirements for production of toner powders by grinding (brittle behavior). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2399–2407, 2001

**Key words:** polymer engineering; polymer composite materials; textile printing; xerographic toner

## INTRODUCTION

It is widely accepted that currently used textile printing technologies will not meet the requirements of quick response and demand-activated manufacturing. Recognizing the need for new textile printing technologies, the National Textile Center sponsored research<sup>1</sup> to investigate the use of digital printing technologies for textile printing. Xerography was selected as one of the technologies to be studied. It has the potential of meeting demand-activated manufacturing requirements, allowing style and color changes with minimum downtime for changeover. However, there are several technical barriers<sup>2</sup> that must be overcome before xerography can have an impact on commercial textile printing.

The major technical barriers associated with the use of xerography to print textiles are: (1) lack of toners designed to give desired textile properties, (2) low toner transfer efficiency to fabrics, and (3) unavailability of machinery specifically designed for textile printing. Thus, research is needed in several areas for xerography to become a large-scale commercial method of printing textiles. The research reported in this study focused primarily on developing polymer-based xerographic toners that give required printed fabric properties.

Earlier studies<sup>3</sup> on xerographic printing of fabrics used toners designed for xerographic printing on paper. It was shown that fabrics could be printed using xerography; however, adhesion to textile fibers was poor, demonstrating that the requirements for paper printing are quite different from those for textile applications. Because space limitations in office copiers/printers necessitate fusing of toner on paper in milliseconds, the binders used in toners for xerographic printing on

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paper are typically amorphous thermoplastics that consist of styrene/acrylate copolymers. In that somewhat longer fixation times can be used in textile printing, thermoset polymers were considered as potential binders for textile toners in a subsequent study.<sup>2</sup> Epoxy-based and polyester-based thermoset toners were produced to evaluate the potential of crosslinkable polymers as binders for textile-specific toners. These thermoset toners were evaluated along with a typical amorphous, thermoplastic polyester-based toner used in paper color printing. The thermoset toners gave good crockfastness properties (a textiles-specific friction test) when applied on fabric, but the curing time was too long, causing yellowing of the fabric. The hand property (flexibility and feel) of the printed fabric was unacceptable. The amorphous, thermoplastic polyester-based toner used for color paper printing had better properties than those of the toners used in the earlier study,<sup>3</sup> but was still unacceptable. Wet colorfastness on cotton and the hand property were unacceptable.

Xerographic toners for paper printing are usually produced by grinding a blend of polymer, colorant, and additives. The grinding process requires the polymers, which are typically amorphous thermoplastics, to have glass-transition temperatures ( $T_g$ ) above approximately 40°C. The relatively high  $T_g$  facilitates converting the material into the needed particle size (5 to 20  $\mu\text{m}$ ) and reduces blocking during storage; however, the high  $T_g$  makes the toners too stiff to give the desired hand on fabrics. Similarly, the binders used in the thermosets are amorphous with  $T_g$ 's sufficiently high to allow converting the material into the desired particle size. As a result, the toners based on amorphous thermoplastics and thermosets are too stiff to give the needed printed fabric hand properties.

### Xerography

The six primary steps of the xerographic process, shown schematically in Figure 1, are briefly described here. More detail can be found elsewhere.<sup>2</sup>

In the first step (charging), the surface of the photoconductor (PC) is electrically charged. Typically, this is accomplished using a corona that ionizes the surrounding air, causing ions to flow to the surface of the PC and thereby to form a charged surface layer. In the second step (imaging), a latent electrostatic image is formed on the PC. In copiers, reflected light from an original is

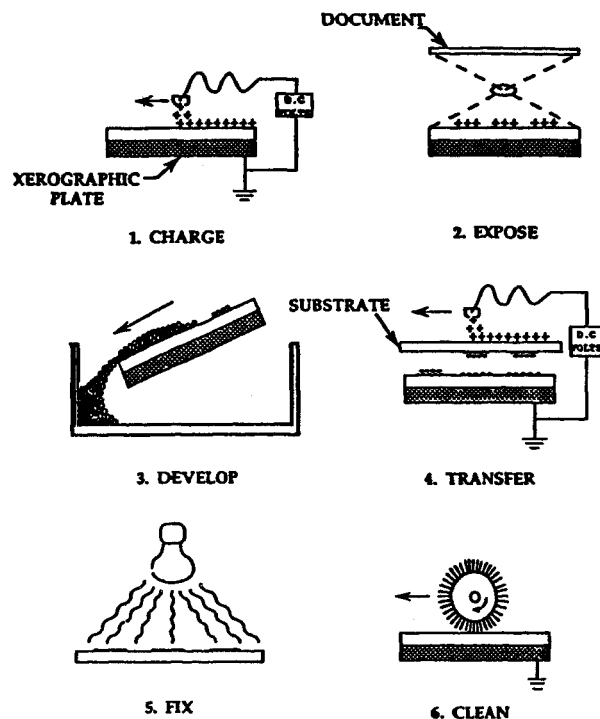


Figure 1 The xerographic process.

used to form a latent image, whereas in printers, photodiodes or lasers driven by a computer are used to form a latent image. In both cases, the PC becomes electrically neutralized in the areas exposed to the light. In the third step (developing), the latent electrostatic image is developed into a visible image with a colored polymeric material (toner). Dual-component developing is the most commonly used method and involves a toner (polymer, pigment, and additives) and carrier (polymer-coated magnetic beads). Mixing of the toner and carrier causes them to become triboelectrically charged and to attract each other. Several of the smaller toner particles (5–20 microns in diameter) electrostatically adhere to each carrier bead (50–150 microns in diameter). When the developer system brings the mixture of toner and carrier in close proximity to the latent electrostatic image, the toner moves from the carrier bead to the latent image because of the stronger electrical force of the latent image. In the fourth step (transferring), the toner moves from the PC to the substrate being printed. The printing substrate passes between the PC and a transfer corona, which charges the backside of the substrate in opposite polarity to that of the toner. Thus the toner is attracted to the printing substrate.

In the fifth step (fusing), the toner is fused to the surface of the substrate. Fusing is accom-

**Table I Mechanical, Thermal, and Triboelectrical Properties of Toners**

Resin	$T_g$ (°C)	$T_m$ (°C) by DSC	Initial Modulus (mPa) by DMA	Breaking Strain (%) by Instron	Tensile Strength (mPa) by Instron	Viscosity (cps mPa <sup>-1</sup> s <sup>-1</sup> ) at 160°C	Triboelectric Charge (μC/g)	Average Particle Size (μm)
Polyamide-1	54 (DMA) 10-15 <sup>a</sup>	98	0.11 <sup>b</sup>	50	6.9	2900 <sup>a</sup>	9.0	15.0
Polyamide-2	59 (DSC)	100	0.20 <sup>c</sup>	d	d	250 <sup>a</sup>	8.5	12.0
Polyamide-3	46 (DMA) 30 <sup>e</sup>	113	0.26 <sup>c</sup>	d	d	—	15.5	10.8
Polyamide-4	46 (DMA)	127	0.43 <sup>c</sup>	d	d	—	12.6	11.5
Aldrich 140	9 (DMA)	95	0.03 <sup>c</sup>	1000	—	—	—	—
Colorocs	57.9 <sup>f</sup>	—	1.75 <sup>b</sup>	0.19 <sup>f</sup>	2.65 <sup>f</sup>	—	8.5	10.4

<sup>a</sup> Data obtained from Union Camp Corp.

<sup>b</sup> By tensile test.

<sup>c</sup> By DMA.

<sup>d</sup> Too brittle to be measured.

<sup>e</sup> Obtained from IPST.

<sup>f</sup> From Wang<sup>9</sup>.

plished by various techniques (hot roll, cold roll, radiant, or solvent), depending on the toner and substrate properties. In the final step (cleaning), residual toner and charge remaining on the PC are removed.

### Dimer Acid-Based Polyamides

As discussed above, a lower  $T_g$  appeared desirable, based on our previous studies. Because lowering the  $T_g$ 's of the amorphous thermoplastic and thermoset polymers used in previous work did not appear feasible, the use of semicrystalline thermoplastics is explored in this investigation. Another study<sup>4</sup> showed that flexible clear films could be produced from semicrystalline dimer acid-based polyamide. Dimer acid-based polyamide is made by polycondensation from di- or polyfunctional amines and dibasic acids (dimer acid). The crystallinity of dimer acid-based polyamides was shown to be similar to that of nylon.<sup>4</sup> The melting temperatures and  $T_g$ 's for the polyamides used here are shown in Table I. As expected,<sup>4</sup> the  $T_g$  of the resins made using aromatic diamines (polyamide-1 and -2) is higher than the  $T_g$  for resins containing aliphatic amines (polyamide-3 and -4) as a result of the increased rigidity introduced by the aromatic group.

It was hoped that a small amount of crystallinity might allow a polymer with a  $T_g$  near room temperature to remain sufficiently brittle for conversion into the needed particle size, and at the same time be sufficiently flexible to meet the hand requirements of textile printing. An investigation of dimer acid-based polyamide as a potential tex-

tile specific toner for xerography was conducted and is reported here.<sup>5</sup>

### Objective of This Work

The objective of the work was to evaluate the feasibility of producing, by conventional grinding methods, xerographic toners from dimer acid-based polyamides with sufficiently low  $T_g$  to give desirable textile hand properties for printed fabrics. This involved the conversion of blends of binder, colorant, and additives into the required particle size, and then determining whether the toners had properties compatible with the xerographic printing process while fulfilling textile-printing requirements.

## EXPERIMENTAL

### Materials and Methods

#### Resin and Toner Characterization

Thermogravimetric analysis (TGA) was performed on a Seiko SII TG/DTA 320 (Seiko, Japan). Differential scanning calorimetry (DSC; Seiko SII DSC 220C) was used to measure the glass-transition temperature  $T_g$  and the melting temperature  $T_m$  of resins. Two heating cycles were used. The temperature range was -50 to 150°C at a heating rate of 5°C/min. The first cycle involved heating up and cooling down at the same rate to eliminate the heat history of the resins. The second heating cycle was used to obtain the results.  $T_g$  was not easily identified in the DSC

measurements; thus, dynamic mechanical analysis (DMA, 1 Hz) was used to measure  $T_g$ . The  $T_g$  determined from DMA will often be higher than that determined from DSC. For brittle samples, the initial force was 10 N, and the F0 gain was in the range of  $10 \pm 5$  N. For flexible samples, the initial force was 100 N, and the F0 gain was in the range of  $100 \pm 50$  N.

The films used in the dynamic mechanical and tensile tests were produced on a heated hydraulic Carver Laboratory press (Instron, Canton, MA). The hot stage was preheated. Then, a metal frame was placed on aluminum foil and 5 g of resin was put into the frame and covered with additional foil. The frame with the aluminum foil covers was sandwiched between two Teflon boards. When the temperature exceeded the melting temperature of the resin, the hot stage was pressed together to produce the film. After cooling, the Teflon boards were removed, the aluminum foil was removed, and the film was cut from the metal frame. The films had a thickness of about 0.25–1 mm.

Measurements of the tensile modulus were carried out at room temperature using an Instron-5567 (Carver, Wabash, IN). The strain rate was 2 in./min. ASTM D882–73 was followed, except for the film size in heat-pressed films (6 in.). Tensile-test specimens of Colorocs toner were made using an injection-molding machine (Sheffer Corp., Cincinnati, OH).

A Malvern MasterSizer Micro Plus (Malvern Instruments, Southborough, MA), with a 0.05- to 556- $\mu\text{m}$  size range, was used to measure toner particle size distributions.

The triboelectric properties of the developer (toner and carrier) were measured using an apparatus built in our laboratory. This technique measures the charge per mass of the developer in units of microcoulombs per gram ( $\mu\text{C/g}$ ).<sup>9</sup>

### Printer

To produce the xerographic prints, a model CP 4007 Colorocs color printer (Colorocs, Suwanee, GA) with a resolution of 300 dpi was used; 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 Fabrication

The possibility of producing a toner by conventional grinding depends largely on the resin (binder) properties.<sup>6</sup> Toughness (crack resistance) is one of the important factors. The size reduction of brittle materials poses no problem. In tough materials, excess strain energy brings about plastic deformation rather than the propagation of new cracks and mechanical size reduction. On the other hand, toughness is a required property of the binders for xerography on most textiles.

The  $T_g$  of a polymeric material is one indicator of grindability. Usually materials with a high  $T_g$  will be easier to grind. If the  $T_g$  is similar to or lower than the grinding temperature, the segments in the polymer chain are mobile and brittleness is reduced. One can process the polymer below  $T_g$  through cooling (cryogenic grinding). When comparing two different polymers with regard to size reduction, even similar  $T_g$ 's may not be indicative of similar grinding characteristics because of differences in the chemical structure. Generally, if the polymer backbone is stiff (e.g., having a higher aromatic content) the material is more grindable.

Softening and melting point also are indicators of size-reduction properties. Because significant heat is often generated in the grinding process, this may lead to softening and problems in grinding.

Agglomeration must also be avoided in grinding. This is often associated with absorbed water in the polymer, which also influences the mechanical properties. Drying may be necessary.

Several components are usually melt-mixed to produce toner.<sup>7</sup> After pregrinding the particle size is reduced to the range of 10  $\mu\text{m}$  by ultrafine grinding. The particles are then classified. External additives (e.g., to avoid blocking) may be added into the powder to formulate the final toner. These steps are summarized here:

1. *Mixing.* Toner resin, pigment, and charge control agent were physically mixed using a two-roll rotator built in our lab.



**Table II Toners and Their Composition**

Colorocs toner	Polyester resin, styrene-acrylic resin, solvent dye, and polypropylene wax.
Polyamide-1 (commercial resin)	Polyamide from dimer acid and ethylene-diamine, TOFA as chain terminating agent. Magenta RT-235-D pigment, FF4102 charge control agent, Carbo-sol.
Polyamide-2 (commercial resin)	Polyamide from dimer acid and ethylene-diamine, hexamethylene-diamine, stearic acid as chain-terminating agent. Magenta RT-235-D pigment, FF4102 charge control agent, Carbo-sol.
Polyamide-3 (synthesized resin)	Polyamide from dimer acid and aromatic-diamine with amino acid incorporated. Carbon black Regal 330 (Cabot Corp.). Charge control agent, Copy Blue PR (Hoechst High Chem Pigment).
Polyamide-4 (synthesized resin)	Polyamide from dimer acid and aromatic-diamine. Carbon black Regal 330 (Cabot Corp.). Charge control agent, Copy Blue PR (Hoechst High Chem Pigment).
Aldrich 140 (commercial resin)	Polyamide from dimer acid. Magenta RT-235-D pigment.

2. *Melt mixing.* A Haake Rheocord 90 twin-screw extruder (Thermo Haake, Paramus, NJ) was used to melt-mix the toner resin, pigment, and charge control agent into a uniform compound.
3. *Pregrinding.* Heavy-duty grinders were used to grind the well-mixed compound to particle size of about 500  $\mu\text{m}$ .
4. *Grinding.* A Trost TX jet mill (Plastomer Products Division, Newtown, PA) was used to grind the toner particles to 10–20  $\mu\text{m}$ .
5. *Classification.* No.140 and No.170 sieves were used to classify the particles collected from the jet mill.

Polyamide-1 through polyamide-4 were successfully processed into toners. Colorocs toner samples were readily available. The Aldrich 140 material was found to be too soft for grinding into toner powder with the means available to us.

### **Toners and Carriers**

Six thermoplastic toners were used in this xerographic printing study (Table II). Four of them were based on polyamides produced from fatty acids (polyamide-1 to polyamide-4). The other two thermoplastic toners were Colorocs toners (Colorocs magenta and Colorocs black), which are used with the Colorocs printers and copiers for xerographic printing on paper.

The polyamide-1 and polyamide-2 toners were selected from several aliphatic polyamide binders available from Union Camp Corp. These polyamide materials were selected because we expected good grinding properties. The pigment used in the toners was Magenta RT-235-D (Ciba

Pigment). The charge control agent used in the toners was FF4102 (BASF).

Polyamide-3 and polyamide-4 toners were made from aromatic polyamide binders produced at the Institute of Paper Science and Technology.<sup>8</sup> Thus, the study included both aliphatic and aromatic polyamide binders. Polyamide-4 toner was made of pure dimer acid-based polyamide, whereas polyamide-3 was made from a modified dimer acid-based polyamide resin. The pigment used in these two toners was carbon black.

Colorocs magenta and Colorocs black were used in the experiments as controls for comparison with the printing results for the polyamide-based toners. They are typical of polyester toners used for color printing on paper.

Additionally, a toner based on the thermoplastic pigmented resin Aldrich 140 was applied on fabrics by dissolving the resin in a chloroform and applying this solution to the fabric. Polyamide-1 and Colorocs toners were applied in this way also as reference. We selected the Aldrich 140 material because its thermal and mechanical properties were promising. However, we could not grind this resin into the particle size required for xerography.

The Colorocs carrier and a carrier supplied by Vertex Image Inc. were used.

### **Toner Deposition**

The effects of toner deposition on fabric properties were investigated previously.<sup>9</sup> Similar procedures were used here. 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 sam-

**Table III** Fabrics and Their Properties

Fabric	Description	Weight (g/m <sup>2</sup> )	Weight (oz/yd <sup>2</sup> )	Warp Count (yn/in.)	Filling count (yn/in.)	Weave	Supplier
Cotton	Tightly woven cotton (heavy weight)	218	6.43	98	54	4 shift satin	Spartan Mills, Inc.
Cotton	Cotton, prepared to print (light weight)	135	3.98	108	88	1/1 plain	Spring Industries
50/50 PET/cotton	Prepared to print	123	3.63	106	76	1/1 plain	Spring Industries
Rayon	212 Bright Filament Viscose	93	2.74	144	80	2/2 twill	Testfabrics, Inc.
Silk	Crepe De Chine	72	2.12	150	102	1/1 plain	Testfabrics, Inc.
Cotton rubbing cloth <sup>a</sup>	Bleached, desized	110	3.25	80	84	1/1 plain	Testfabrics, Inc.

<sup>a</sup> The cloth used in crockfastness tests to rub the fabric to be tested.

ples 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, after which they were 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.

### Fabrics

Six types of fabrics were used in this study (Table III). Definitions of textiles-specific terms can be found in the literature.<sup>10</sup> Rubbing cloth refers to the cloth needed in crockfastness tests, which are discussed next.

### Crockfastness Tests

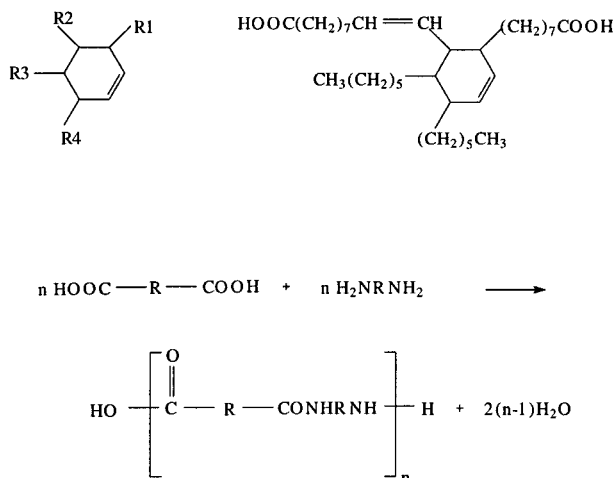
One of the important properties that a printed fabric must have is good rub fastness, referred to as crockfastness. One standard crockfastness test (dry crockfastness) involves rubbing the printed sample with a dry rubbing cloth. A second standard test (wet crockfastness) uses a wet rubbing cloth containing 65wt % water. 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>11</sup>). The stan-

dard crockfastness tests were conducted using an AATCC Crockmeter, model cm-1. The transfer of color from the printed sample to the rubbing cloth is visually evaluated against standards. Standard crockfastness ratings are: 1, entirely unacceptable; 2, unacceptable; 3, borderline acceptable; 4, good; 5, excellent (no color transfer).

## RESULTS AND DISCUSSION

As discussed earlier, one of the resins (Aldrich 140) was not processed into toner because grinding with our available methods was not successful. The low  $T_g$  and high breaking strain (see below) of this material indicate the potential difficulties for grinding.

As mentioned earlier, the thermal and mechanical properties of the polymers used as binders are listed in Table I. The  $T_g$  is similar for the materials, except for the low  $T_g$  of the Aldrich 140 resin. The materials that were processed into toners cover a range of initial moduli. Covering a range of moduli seemed important to us, to investigate the influence of mechanical properties on the performance of the toners on fabrics. The weight-average molecular weight ( $M_w$ ) of polyamide-1 was reported by the manufacturer (Union Camp Corp.) to be 2800–3500 g/mol. Polyamide-2 was reported to have a somewhat lower  $M_w$  than that of polyamide-1. The  $T_g$ 's measured by us for polyamide-1 and -2 (DMA) did not correspond well to that reported by the manufac-

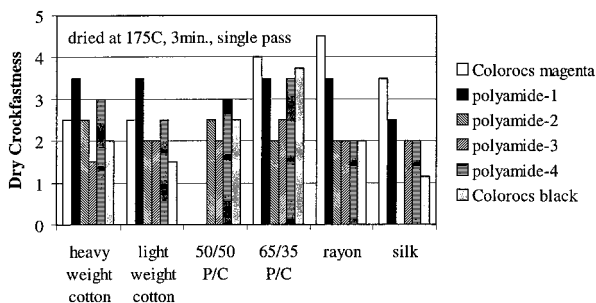


**Figure 2** Structure and polymerization mechanism for dimer acid-based polyamides. Top: general structures of dimer acids. Bottom: polycondensation mechanism to produce polyamide.

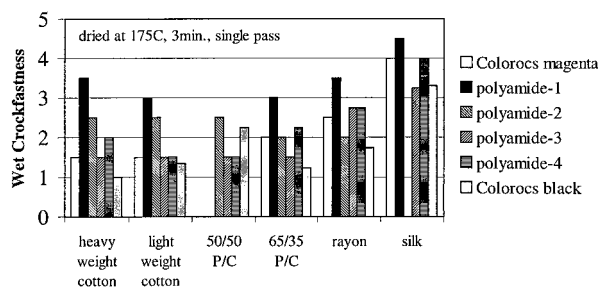
turer for polyamide-1. The manufacturer's  $T_g$  correlates reasonably well to an empirical relation between  $T_m$  and  $T_g$  ( $T_g = \frac{2}{3}T_m$ ) that is often used. Our high  $T_g$ 's may be attributed to crosslinking by trimer acid that was reported to be present in these resins.

Figures 2 and 3 show the dry and wet crockfastness results for our series of toners. The Colorocs toner (designed for paper printing) is shown as a reference.

Dry crockfastness results (Fig. 2) show that polyamide-1 is acceptable in all cases, except for silk, where the rating of 2.5 is slightly below acceptable. Polyamide-1 has the lowest initial modulus (Table I) and consistently shows the best performance in wet crockfastness (Fig. 3). This may indicate that the mechanical properties of the toner resin play an important role in



**Figure 3** Dry crockfastness of xerographic prints with various toners on textiles. Polyamide-1 shows consistently good performance.



**Figure 4** Wet crockfastness of xerographic prints with various toners on textiles. Polyamide-1 shows consistently good performance.

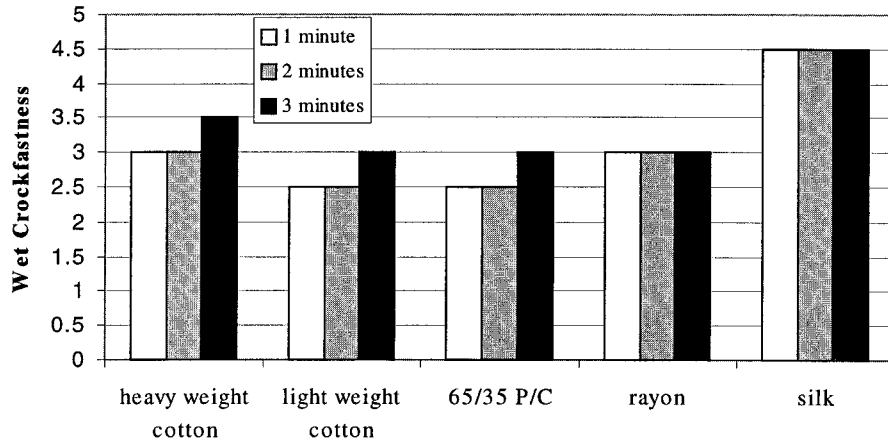
the abrasion resistance as tested by crockfastness.

The influence of the drying or fusing time of the prints at the fusing temperature was investigated. Figure 4 shows, as an example for polyamide-1, that variations of the crockfastness were generally minor with this range of fusing times.

It was pointed out earlier that the resin with the highest breaking strain and the lowest initial modulus could not be ground into toner (Aldrich 140). However, this resin appeared as a promising candidate for superior print performance because of its mechanical properties. We therefore applied this resin, the other promising candidate (polyamide-1), and the Colorocs magenta toner from solution onto the light cotton fabric. Figure 5 shows the superior performance of the Aldrich 140 resin that we expected, based on mechanical properties. This is further evidence that the mechanical properties are a good predictor of print performance.

The hand or feel of a fabric can be quantified, to some extent, by measuring the flexural rigidity. Hand is of concern because of the need to fulfill the tactile and other properties (drape) that are expected by the consumer. We tested the flexural rigidity of lightweight cotton fabric, because a lightweight fabric contributes less than does heavyweight fabric to the flexural rigidity and is thus most likely to reveal the differences between toners.

The flexural rigidity data shown in Figure 6 were gathered as a function of the mass of toner deposited per area of fabric. The toners were applied by xerography and from a solution. The solution deposition had to be used for Aldrich 140 because grinding into toner powder was not successful; thus, we also applied two other toners from solution, to be able to compare the materials with Aldrich 140.



**Figure 5** The variation of wet crockfastness for polyamide-1 with fusing time at 175°C was not significant.

At low deposition, little difference is found between toners because the fabric exerts the main influence. At higher deposition, the toner properties are revealed as significant, and the Aldrich 140-based toner shows the lowest flexural rigidity, as might be expected, recalling that Aldrich 140 has the lowest initial modulus and highest breaking strain of the resins tested here (Fig. 7).

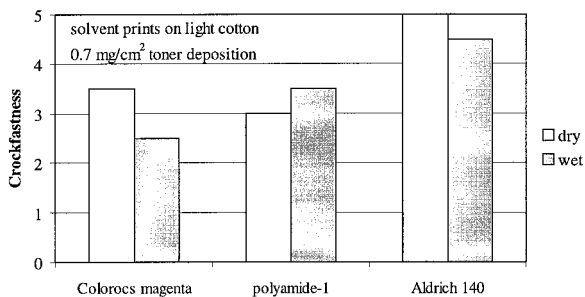
It can be seen that solvent deposition results in a much higher flexural rigidity when comparing the same toner. This could be the result of increased flow of toner into the fabric, whereas xerography deposits the toner more on the surface. Even though the Aldrich 140 was applied by the solvent method, the flexural rigidity was still far lower than that of other binders, even at higher depositions. This clearly illustrates that low modulus is important in producing xerographic toners for textiles.

such as crockfastness and flexural rigidity in xerographic printing of textiles. Low initial modulus combined with high breaking strain gave the best textile print properties. However, the material shown to give the optimum textile print properties, when applied using a solvent technique, was too flexible to be mechanically ground with our grinding methods. Other grinding methods might be more successful. It also appears worthwhile to investigate techniques other than the mechanical grinding used here to produce the particle size needed for optimized toners for xerographic printing of textiles.

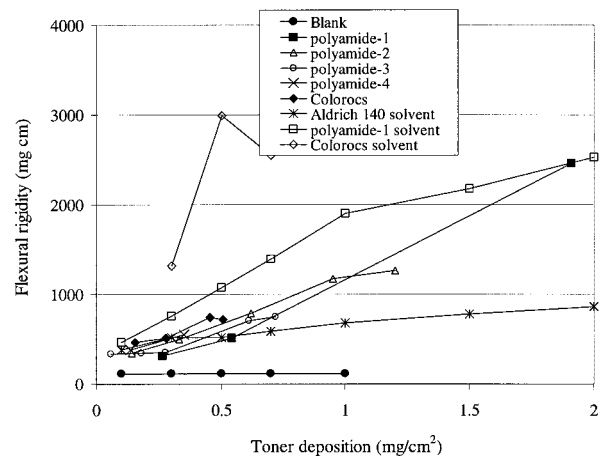
The authors thank the National Textile Center for support of this project; Dr. Nelson Lawson of Union Camp Corp. for valuable discussions; and John F. Cooper for generous help with grinding of toners. The authors gratefully acknowledge the following companies: Vor-

**CONCLUSIONS**

Toner resin properties ( $T_{gr}$  and tensile properties) greatly influence required textile print properties



**Figure 6** Dry and wet crockfastness of solvent prints using Colorocs magenta, polyamide-1, and Aldrich 140.



**Figure 7** Flexural rigidity as a function of toner deposition on light cotton fabric.



tex Image Products for supplying carrier materials; Spartan Mills and Spring Industries for supplying fabrics; and Union Camp Corp. for supplying some resins.

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