

Slipping Layer for Thermal Donor

David G. Foster, Eastman Kodak Company, Rochester, NY/USA

Abstract

Resistive-head thermal dye transfer printing is a digital printing method in which thermal energy is used to create photographic quality output by the transfer of dyes from a donor ribbon to a receiver that are in intimate contact. Dye donor elements consist of support, dye layers, adhesive layers, laminate overcoat layers, and slipping or heat-resistant layers. Slipping (or slip) layers are coated on the opposite side from the dyes on the thermal donor. The primary function of the slipping layer is to facilitate transport of the donor under the thermal printhead. These layers have several characteristics, including the ability to provide low and constant friction over the entire printing temperature range, to be noncontaminating and nonabrasive to the printhead, and noninteractive with the other layers when spooled. Slipping layers typically contain lubricants, polymeric binders, solvents, and other addenda to achieve photographic quality printing. Work over the past few years has focused on the redesign of the slipping layer for enhanced performance features. The result is a layer that provides enhanced lubrication, improved retransfer protection from the dye side to the slip side upon spooling, improved fold performance in the printing operation, and cleaner printheads during printing.

Introduction

Thermal dye transfer (TDT) printing, also referred to as dye diffusion thermal transfer (D2T2), is an imaging system that was developed and has been used at Kodak since 1984. Thermal printing employing TDT is used in consumer, home, government, professional, entertainment, and commercial printing applications. In the TDT process, electronic images are subjected to color separation and converted into electronic signals. These electronic signals are transmitted to a thermal printer where images are created by printing yellow, magenta, cyan, and laminate patches from the dye donor to the receiver. Based on the amount of heat that is generated from the printhead, as a function of the color needs of the particular image, dye is transferred from the donor to the receiver during the printing process. Thermal donors are multilayered material structures that are coated on a thin polyethylene terephthalate (PET) support. Donors generally contain alternating patches of cyan, magenta, and yellow dyes that are coated in a gravure coating process. Dye donor layers commonly contain dyes, binders, plasticizers, and other addenda to facilitate thermal printing. In addition to the dye layers, several other layers are incorporated. An adhesive layer is coated on each side of the PET support to assist in adhesion of the functional layers, as well as to act as a barrier and antistat. A slipping layer is coated on the side opposite the dyes and acts to facilitate the transport of the donor through the printer and is in direct contact with the thermal printhead during the printing process. The

laminate layer is coated on the dye side of the material and is the last to be printed in the printing sequence. The laminate acts to protect the print from environmental attack, including UV radiation, ozone, and dirt. It is because of the laminate layer that thermal prints may be completely immersed in water without loss of image quality. Laminate options include both glossy and matte finishes for images.

Design of a New Slip Layer

As thermal printing evolved to include new printers, faster print times, and expanded applications, it became necessary to redesign the slipping or heat-resistant layer to maintain printing quality in these multiple applications. The goal was to formulate a single slip layer that could be used in various printers for various print sizes and configurations. To accomplish this goal there was a need to create a more robust slip layer coating that would resolve the material, cost, coating, and printing concerns with previous slip layers.

A deficiency in the performance of the slip layer causes intermittent rather than continuous transport across the thermal printhead. The dye transferred will not appear uniform, but rather as a series of alternating light and dark bands called "chatter marks." It is desirable for the slip layer to provide smooth transport of the donor across the printhead in a wide range of printing conditions and temperatures. Variable print forces along either the length or width of a print can cause image defects. Differences in print forces are peculiarly magnified in regions of abrupt temperature change. At the transition from D-max (maximum print density) to D-min (minimum print density), the force may spike upward from D-max to a peak force and then return to D-min. This differential is referred to as "pops" because an audible popping noise can be heard in extreme cases during printing. Slip layers are in direct contact with the printhead during printing and are responsible for keeping the printhead clean.

Slip layers typically contain lubricants, binders, cleaning agents, solvent, and other components to facilitate printing. Previous slip layer formulations contained natural waxes that were of varying color and quality, head cleaners that could be costly and difficult to coat, and siloxanes that although they were very good lubricants, tended to facilitate retransfer.

Over three hundred lubricants from multiple classes of compounds were screened and multiple binder options were tested in the course of this work. The new slip layer was formulated using a synergistic combination of lubricants from a friction perspective and in terms of headwear buildup. Additional benefits include reducing folds especially when used with fast printers, and dye retransfer prevention from the dye donor layer to the slipping layer during production. The new slip layer formulations included a polyvinyl acetal binder and the combination of three lubricants.

The three commercially available lubricants are all solids at room temperature. Details of these materials will be discussed later.

Friction

Friction testing was used as the primary screening test for all lubricants examined. Friction testing was done using a custom-made fixture that measures the torque required to advance media during printing called a strain gauge. Kodak has been using this device for over 10 years, and has published data from this device in several patents [1]. Good slip performance requires low torque to advance media at all printing conditions (D-min, D-max, etc). Uniform torque is desirable to avoid wrinkles and folds in the ribbon.

The procedure used to measure friction testing is to place the dye side of the donor in contact with a dye-receiving layer of the same area. This assembly was clamped to a stepper motor driving a 60-mm-diameter rubber roller. Next, a TDK Model L-231 thermal head, thermostatted at 28 °C, was pressed against the slipping layer side of the assembly with a force of 24.75 Newtons (5.56 lbs-force) pushing it against the rubber roller. The imaging electronics were activated causing the donor/receiver assemblage to be drawn between the printhead and roller. At the same time the resistive elements in the thermal printhead were pulsed for 128 μ s/pulse at 134 μ s intervals during the 4.575 ms/dot printing time. A test pattern shown in Figure 1 was generated incrementally increasing the number of pulses/dot from 0 to 32 (D-min to D-max). The voltage supplied to the printhead was approximately 13 V, resulting in a maximum total energy of \sim 1.45 mJ/dot.

The test pattern consisted of two large dark-density bars followed respectively by two lighter density bars, and at the end, a series of eight smaller density bars. The first dark-density bar is the warm-up bar and serves to prepare the thermal printhead for printing the test image. No data is collected during the printing of the warm-up bar stage. The first light bar represents the toe region of a density scale and is the mean of all the data points collected when printing the low-density bar. The next bar is a D-max bar (called the Hot bar), and two values are measured during the printing of this bar. The first is the Initial Hot value, which is achieved when the printhead first starts printing this D-max bar. The Final Hot value is data collected at the end of printing the D-max bar. The next bar is a D-min or Cold bar where no power is delivered to the printhead. This is the average value of printing a D-min or white region of an image. The final area is a series of eight D-max bars separated by D-min regions. This area measures a rapid series of narrow D-max lines interspaced with D-min. The printhead is cycling on and off rapidly. This rapid change associated with printing this area pushes the limits of the slip layer. The Pops parameter (named for the sound made by the thermal printers, cited earlier) averages the high-density/low-density values to generate this response.

Results in the course of screening lubricants suggested that many lubricants when used alone did not perform well enough and that a synergistic combination of lubricants that satisfies the needs of printing both D-min and D-max regions was necessary. In addition, as will be discussed in later sections, siloxanes cause retransfer and natural waxes tend to cause printhead buildup. As a result, the focus of this work quickly turned to finding a combination of synthetic lubricants that were solids at room temperature. Fortunately, three such lubricants were found that

could satisfy the constraints of the system. The first lubricant is a fully saturated homopolymer of polyethylene available commercially as Polywax 400. The second is a polymerized alpha-olefin available commercially as Vybar 103, and the final lubricant is a solid polymer-derived alpha alkene, maleic anhydride, and monoisopropyl maleate; such a polyolefin is available commercially as Ceramer 1608.

Table I. Strain Gauge Data from Friction Testing

	Description	Cold	Toe	Initial Hot	Final Hot	Pops
1	Ceramer 1608 (0.0646 g/m ²)	1.89	4.23	6.51	6.60	8.35
2	Vybar 103 (0.0646 g/m ²)	3.48	2.74	2.00	1.91	2.11
3	Polywax 400 (0.0646 g/m ²)	2.08	2.81	5.08	4.06	18.63
4	Ceramer 1608 (0.0215 g/m ²), Vybar 104 (0.0215 g/m ²), Polywax 400 (0.0215 g/m ²)	1.82	1.95	1.39	1.31	1.31

The data shown in Table I illustrate the synergistic combination of these three lubricants. The table has strain gauge friction testing results for an experiment where the lubricants were tested singly and then in combination. All slip layer coatings tested have 0.38 g/m² of polyvinyl acetal binder and a total of 0.0646 g/m² of total lubricant. Coatings 1–3 in the table have 0.0646 g/m² of the three lubricants coated singly. The fourth coating in the table has each of the three lubricants coated at 0.0215 g/m² and the total lubricant load is 0.0646 g/m². As seen from the data, none of the three lubricants alone acts to lower friction in a thermal printer as well as the case in which they are all coated together. This is true even when the total level of lubricant is maintained at the same level [2, 3]. One additional feature of slip layer #4 is that the noise generally experienced during the printing of the Pops parameter was significantly reduced, demonstrating the even friction delivered across all densities from D-max to D-min.

Retransfer

The propensity for one-time (1X) retransfer of the dye to the slip layer occurs when the donor spool is coated. Because the dye-donor element is a roll-format product, the slip layer and the dye layer will be in direct contact when the material is coated on a large roll. The retransfer of interest is from the dye side to the slip layer side, because then the large manufacture roll is further divided into smaller rolls, the dye that originally transferred to the slip side of the coating can retransfer back to the dye side (2X retransfer), but in a different place on the dye coating, thereby contaminating it with unwanted dye. For example, in the large rolls, magenta dye from the magenta patch can retransfer to the slip side, and then upon the making of smaller rolls from this large roll, the magenta dye can retransfer from the slip side to the yellow

patch, resulting in contamination of the yellow dye patch with magenta dye. The result can be defective color produced during dye-transfer printing caused by unwanted dye mixed with the desired dye.

Table II illustrates results for 1X retransfer. Various slip layers were tested by making separate coatings of slip and dye in which the opposite side was bare PET support without any coating to avoid having 1X retransfer when the test coatings were initially coated and spooled. In the test procedure, the samples were placed so that the slip side sample and the dye side sample faced each other. These samples were then mounted in a screw press at ~300 psi for seven days at room temperature. Samples were interleaved with receiver to provide uniform pressure and were removed from the fixture and placed against a sheet of thermal receiver for readings. The $L^*a^*b^*$ values were read using a Byk-Gardner unit with an integrating sphere. The a^*b^* vector length in the table refers to the length of the vector along the axis in CIELAB 3-dimensional color space. Short vector lengths indicate less dye retransfer, and long vector lengths indicate more dye retransfer. The most desirable situation is to have a vector length of zero. The data of the table is a small but representative sampling of the entire data set. All slip layers contained 0.38 g/m² of polyvinyl acetal binder. The first slip layer in the table is made with polydimethyl siloxane lubricant (0.0084 g/m²), Candelilla Wax (0.021 g/m²), and polymethylsilsesquioxane (0.055 g/m²) coated out of diethyl ketone and methanol solvents. The second slip layer contains Ceramer 1608 (0.0215 g/m²), Vybar 104 (0.0215 g/m²), and Polywax 400 (0.0215 g/m²); the third contains a methylstyryl-modified silicone fluid (0.0215 g/m²) and an organo-modified silicone fluid (0.0215 g/m²); the fourth slip layer contains dimethylsiloxane-ethylene oxide block copolymer (0.0215 g/m²) and methylstyryl-modified silicone fluid (0.0215 g/m²); and the fifth contains dimethylsiloxane-ethylene oxide block copolymer (0.0215 g/m²) and polydimethylsiloxane-co-methyl(3-hydroxypropyl)siloxanes grafted with polyethylene/propylene glycol (0.0215 g/m²), all coated out of toluene, methanol, and cyclopentanone. As the data suggests, slip layer #2 has a significantly shorter a^*b^* vector length, indicating that this slip layer has significantly less retransfer than all the others in the table and, it should be noted, less than all the other slip layers investigated.

Table II. Effect of Slip Layer Components on Retransfer

Slip Layer Number	a^*b^* Vector Length
1	1.10
2	0.40
3	1.45
4	3.00
5	4.10

Head Wear

Another important requirement of slip layers is their ability to keep the printhead clean without damaging the head. Testing for this parameter involves coating large quantities of various slip layers and printing for long periods of time in order to provide sufficient time for the slip layer and printhead to interact. A specialized image (Figure 1) is used for this testing that consists of multiple bars of various densities. The image is printed such that sections of the printhead experience only one of the density bars for the entire length of the testing. In this way one is able to understand the long-term effects of printing different densities on the printhead as well as the overall slip layer and printhead interaction. In the course of this work, numerous potential slip layers were tested in this manner. Many contaminated or damaged the printhead very quickly.

A thermal printhead consists of a heading bar in the center where the printhead transfers heat to the donor. Heat transfer in this process occurs on the slip side of the donor through the support to the dye side where dye transfer occurs by Fick's Law diffusion to the receiver. As a result, keeping the printhead clean and free of debris is very important. Head wear testing consisted of loading the printer with the test donors and periodically taking micrographs of the printheads during testing; typically this is done every 500 planes to ensure that changes are observed quickly. A plane is defined as printing a single color patch of the donor. Thus, a full color image contains four total planes: cyan, magenta, yellow, and laminate. Micrographs are taken of the printhead at areas corresponding to each of the eight bars on the image (Figure 1). In this way areas of the printhead experience only one of the bars throughout the entire experiment. Generally the heat line, which is where the heat for printing is generated, gets contaminated with slip layer components. The area after the heat line also becomes contaminated as the slip layer cools and moves over the unheated area of the printhead. The area in the top of Figure 2a has the appearance seen with many of the printheads that were tested and in this case was the slip layer described in Table II, slip layer #1. It represents the printhead in the D-max position after 40,000 planes, which is equivalent to 10,000 prints. The heat line, which is the dark area in the center of the image, was analyzed and found to contain the components of the slip layer used in this experiment. One common defect that occurs when the heat line becomes heavily contaminated with slip layer is scratching of the printed image. Figure 2b is a similar micrograph of the slip layer described in Table II, slip layer #2, of a printhead after 40,000 planes or 10,000 prints. A clean heat line is observed even after extended printing, thus enabling longer times between printhead cleaning or when replacement was necessary.

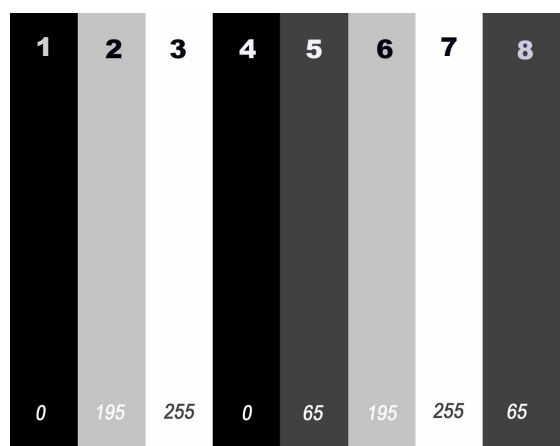


Figure 1. Image used for head wear testing

(a) Slip Layer as described in Table II, Slip #1



b) Slip Layer as described in Table II, Slip #2

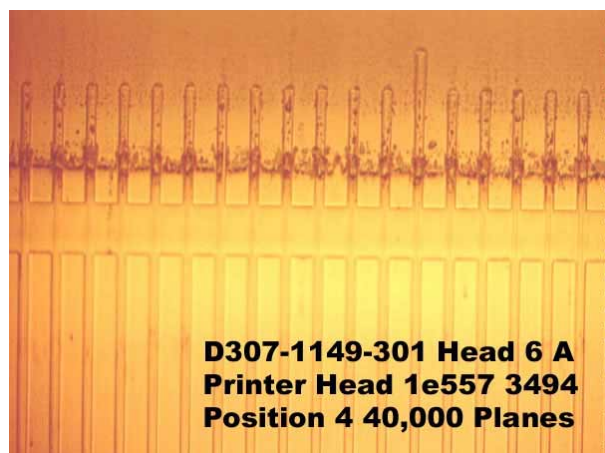


Figure 2. Results of printing of position 4, the D-max printing position

Conclusions

As thermal printing evolved to include new printers, faster print times, and expanded applications, it became necessary to redesign the slipping or heat-resistant layer to maintain printing quality in these multiple applications. This was accomplished by designing a slip layer with a synergistic combination of synthetic lubricants that provide a robust slip layer that provides even friction during all stages of printing, significantly lower retransfer, fewer folds, and cleaner printheads during printing.

References

- [1] R.P. Henzel, "Slipping Layer Containing Functionalized Siloxane and Wax for Dye-Donor Element Used in Thermal Dye Transfer," U.S. Patent 4,866,026, September 12, 1989.
- [2] D.G. Foster and M.L. Gray, "Slipping Layer Containing Wax Mixture for Dye-Donor Element Used in Thermal Dye Transfer," U.S. Patent 7,078,366, July 18, 2006.
- [3] D.G. Foster and M.L. Gray, "Slipping Layer Containing a Branched Olefin for a Dye-Donor Element Used in Thermal Dye Transfer," U.S. Patent 7,109,147, September 19, 2006.

Author Biography

David G. Foster is a Senior Research Scientist at Eastman Kodak Company, where he has been employed for over 25 years. For the last 7 years he has worked in thermal media research. In 1999 Dr. Foster received the Distinguished Inventor Award at Kodak; he holds over 35 U.S. Patents and has authored numerous scientific publications and presentations. He is currently an Adjunct Professor in Chemical Engineering at the University of Rochester where he teaches courses in Fluid Dynamics and Transport Phenomena. Dr. Foster has a B.S. in Chemistry from Rochester Institute of Technology and Ph.D. in Chemical Engineering from the University of Rochester.