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Novel Phase Change Inks for Printing Three-Dimensional Structures

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Abstract. *Based on recent progress, nonimpact printing techniques can deliver the next generation of materials for an extensive set of novel applications. A novel hot melt ink composition, useful for three-dimensional (3D) printing comprising different waxes, tackifier and plasticizer resins, rheology modifiers, and gas releasing agents, was designed. The behavior of the inks was comparable to commercial hot melt inks without gas releasing agents. The hot melt ink properties promise a possibility of use in a conventional phase-change printer in order to create 3D printed structures. Differential scanning calorimetry was used to evaluate thermal properties of the ink components and the extensive study of the thermal behavior of the proposed gas releasing agents has been carried out. The rheology behavior of inks was measured, and printability analysis, such as image detail, definition of dots (height, sharpness of the edges), dot formation, and spreading were investigated. Rub resistance tests were also used together with tape adhesion tests for ink adhesion monitoring.* **©** *2006 Society for Imaging Science and Technology.* [DOI: 10.2352/J.ImagingSci.Technol.(2006)50:6(550)]

INTRODUCTION

The ability to form a raised three-dimensional (3D) image makes possible the use of modified processes, inks, and substrates in fine art work, such as children's books, business cards, postcards, and other special type printing processes. If the raised image attains the required height and firmness, it can be used in printing of Braille characters. Production of 3D images on a substrate can be accomplished by old fashioned embossing techniques,[1] hectographic or spirit duplicating masters,[2] raised xerographic printing with thermally intumesced electroscopic powders,[3] three-dimensional imaging paper,[4,5] thermographic processes,[6] a special printing process that works by building parts of light curable photopolymer in layers,[7] or heat transfer printing with a thermally expandable ink layers.[8]

The main idea of ink writing techniques lays in the deposition of colloidal, nanoparticle, or organic based inks to create raised structures. Inks are typically formulated from colloids, polymeric materials, or polyelectrolytes suspended or dissolved in a liquid or heated to create a stable, homogeneous ink with the desired and reproducible rheological (or flow) behavior.[9]

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Cima[10] and Sachs[11] from Massachusetts Institute of Technology pioneered the concept of using ink jet printing to assemble a broad array of materials by means of this printing technique. In their approach, a low viscosity binder is printed onto a powder coating to fuse materials together in a pattern. 3D printing, direct ink jet printing, and related approaches such as hot melt printing,[12–14] involve patterning materials using a typical ink jet print head, similar to one used in desktop printers. This approach requires wax-based inks that are heated during droplet formation and then solidify upon impact cooling.

There is a continuous drive toward the development of new printing techniques suitable for smaller scale printing jobs, which can deposit certain amounts of various polymer based materials that would create three-dimensional structures on different types of substrates. The aim of this work is to formulate a hot melt ink capable of creating raised images. The ink, along with thermoplastic polymers, will contain particular chemical substances, blowing agents, which will decompose at elevated temperatures, releasing gas bubbles. The decomposition will take place rapidly after deposition of the ink on the substrate. The gas bubbles will stay entrapped in the ink droplet because of the ink solidification process. The blowing agent and thermoplastic polymers have to be selected according to the temperature in the print head and have to be inert and nonreactive with other chemicals present in the formula.

HOT MELT (PHASE-CHANGE) PRINTING TECHNOLOGY

With phase-change printing technology, hot melt printers employ wax-like hot melt ink, rather than the liquid or dry ink used in other processes. The phase-change inks (hot melt inks or thermal waxes) are brought into contact with the substrate and using a piezoelectric ink jet head.[15] Thus, the hot melt ink printer is a variant of drop-on-demand ink jet printers, where the liquid for the printing is obtained by melting the hot melt inks when in contact with the ink loading system.[13–20] The simplicity of this technology leads to low equipment cost, cleanliness of the image, and high reliability.[21]

Spectra, Inc., one of the leaders in ink jet head manufacturing, has elaborated a model for the interaction of a hot melt ink drop with a substrate in early stage of hot melt ink development. According to this model, if a drop is ejected at

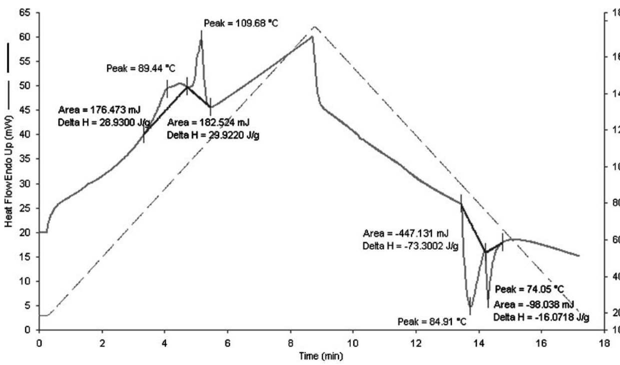

Figure 1. DSC plot of melting and freezing profiles of Xerox Cyan ColorStix™ hot melt ink.

Table I. Composition of experimental hot met ink.

Component	Function	Melting Temperature (°C)
Carnauba/PE wax alloy	Ink vehicle	111
Polyamide resin	Imparts adhesion	103
High molecular weight alcohol	Lower viscosity	109
Hydrogenated rosin ester	Tackifier	69

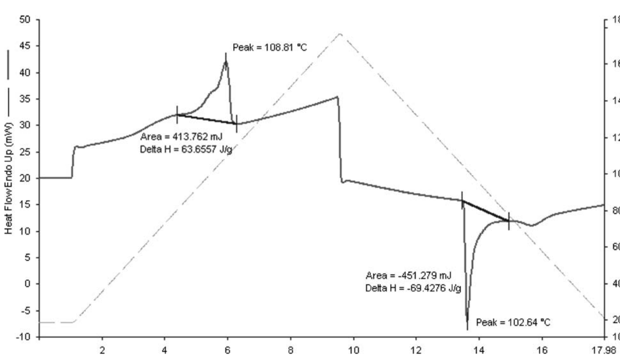

Figure 2. DSC plot of melting and freezing profiles of experimental hot melt ink.

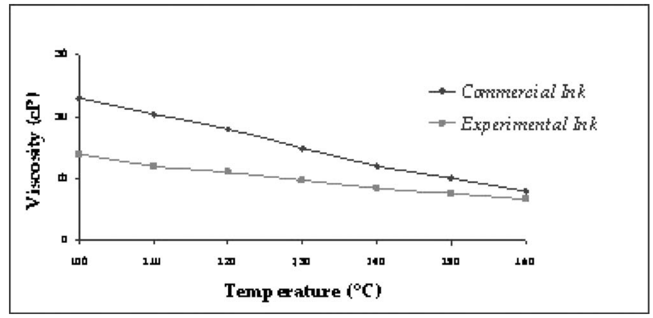

Figure 3. Viscosity measurements of commercial and experimental hot melt ink.

Table II. Melting and solidifying temperatures of commercial and experimental hot met ink.

Ink	T_m (°C)		T_s (°C)		Viscosity at 130 °C (cP)
Commercial hot melt	89.5	109.7	74.1	85.0	15
Experimental hot melt	108.8		102.6		11

Table III. Decomposition temperatures of different blowing agents. (Exo—exothermic mechanism; Endo—endothermic mechanism.)

Name	Composition	Decomp. T (°C)	Decomp. Type
Hydrocerol BIH	Sodium bicarbonate	145	Endo
Celogen® OT	OBSH	179	Exo
Ficel HFVP	OBSH/ADC	183	Exo
Celogen® AZ	ADC	238	Exo

125 °C and travels about 1 mm, the drop temperature decreases by less than 1 °C. At 1 cm of travel distance, one expects only about 5 °C cooling. Even at 10 m/s drop velocity, hot melt ink droplets do not produce impacts with much laterial distribution. The droplet then hits the substrate without unnecessary spreading.[22]

The hot melt ink jet inks have to stay solid at ambient temperature, liquefy at the moment of printing, and promptly solidify when reaching the substrate. When reaching a surface, the molten ink drop solidifies immediately, and prevents the ink from spreading or penetrating into the printed substrate. The quick solidification ensures that the image quality is good on a wide variety of recording media.[18–23]

Conventional hot melt inks are formulated using four main components: an ink binder comprising a wax with a melting point in the range of 50–90 °C, which works as a ink vehicle, a resin, representative of tackifiers and adhesion promoters and different additives, such as antiscratch additives, adhesion and surface additives, antioxidants, biocides, plasticizers, and corrosion inhibitors designed to improve the ink's performance. Generally, hot melt ink contains a pigment or a dye functioning as a coloring component.[24]

The most important properties of conventional hot melt inks are the following ones: melting point of 100–130 °C, sharp melting transitions as characterized by differential scanning calorimetry (DSC), a viscosity of 10–20 cP at 130 °C, nontoxicity, transparency in the solid phase, good lightfastness, and wide color gamut size. Inks also have to be capable of dissolving printing colorant such as dyes or implement the pigments, and remain intact during long term heating in air and in contact with the print head. Additionally, no offset transfer or blocking of finished prints at 70 °C or below should occur. Hot melt inks should also possess good adhesion to various paper substrates as well as

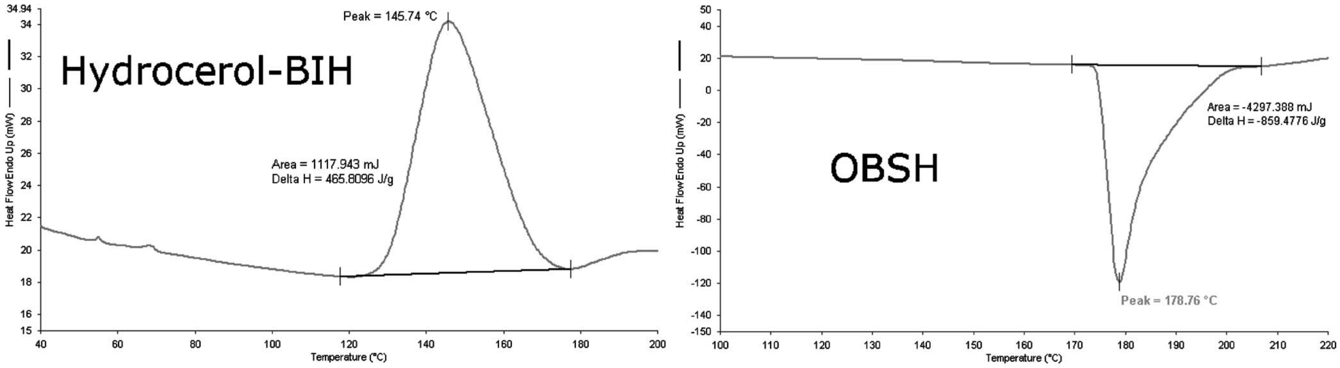

Figure 4. Thermal analysis of sodium bicarbonate and blowing agents *p*, *p*′-oxybis (benzenesulfonylhydrazide), respectively.

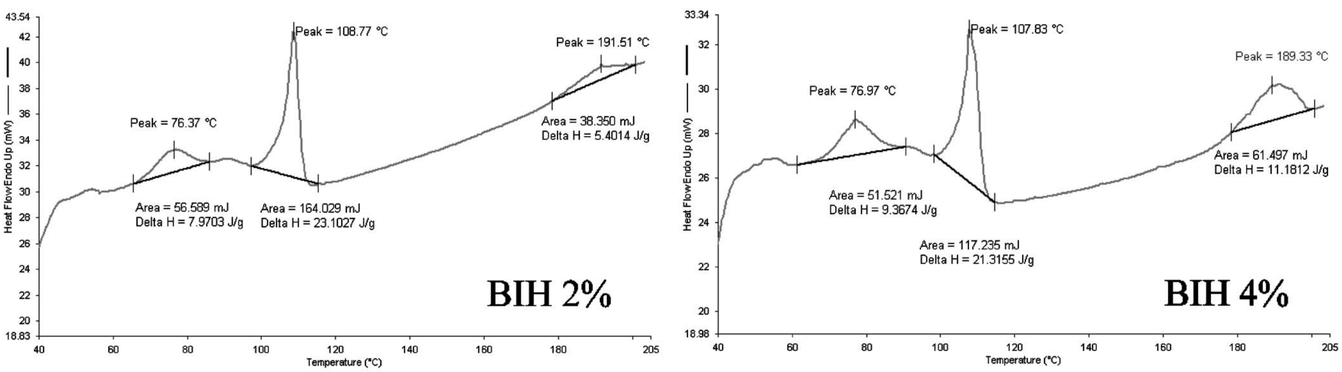

Figure 5. Thermal analysis of the experimental ink with 2% and 4% of BIH, respectively.

transparency materials and flexibility towards bending when printed on different flexible substrates.[16,25,26]

BLOWING AGENTS

The structure of cellular gas-filled polymers can be formed using three possible methods: by foaming a polymer system; by introducing gas-filled microspheres into a system; or by extracting material by a post-treatment which results in the cell or pore formation. The most general classification, which divides blowing agents into chemical and physical blowing agents, is based on the mechanism by which a gas is liberated to the system.[27,28] Chemical blowing agents (CBAs) are individual compounds or mixtures of compounds that liberate gas as a result of chemical reactions, including thermal decomposition, or as a result of chemical reactions of CBAs, or interactions of CBAs with other components of the ink formulation.[27,29]

There are many options available when selecting a blowing agent. There are eight key materials used as blowing agents around the world. These may include: sodium bicarbonate; *p*-toluene sulfonylhydrazide; azodicarbonamide (ADC); and *p*, *p*′-oxy-bis(benzenesulfonylhydrazide) (OBSH).[30]

EXPERIMENT

Various thermoplastic resins, waxes, and alcohols, solid at ambient temperature, were used for formulation of inks for 3D structures. All of the inks were prepared the same way. The ingredients were mixed in a Lightnin® high speed mixer equipped with a mixing blade. The components were placed into a kettle, heated to about 85 °C, and the stirring was commenced. The kettle was heated to 120 °C and stirring continued until a homogenized state of the mixture was achieved. The formulations were then cooled to ambient temperature at which they transitioned from the flowable to the non-flowable state. A Perkin Elmer Pyris 1 DSC was employed for ink calorimetric analysis. A Brookfield digital viscometer DVLV II with spindle No. 1 was used to measure hot melt inks' flow viscosity. Ink temperatures were maintained between 100 and 160 °C during the measurement. The FTA32 Video 2.0 software from First Ten Ångstroms, Inc. was used to capture images of solid ink droplets and provided the printability analysis in terms of droplet height, contact angle, base area, etc.

RESULTS AND DISCUSSION

A very important property is the sharp melting point of the phase change ink. The differential scanning calorimeter was used to obtain the range of melting temperatures for commercially produced hot melt inks used in phase-change desktop printers. Figure 1 represents melting and freezing profile of a commercial hot melt ink. For this purpose we used Xerox Cyan ColorStix™ ink.

We formulated an experimental hot melt ink, which

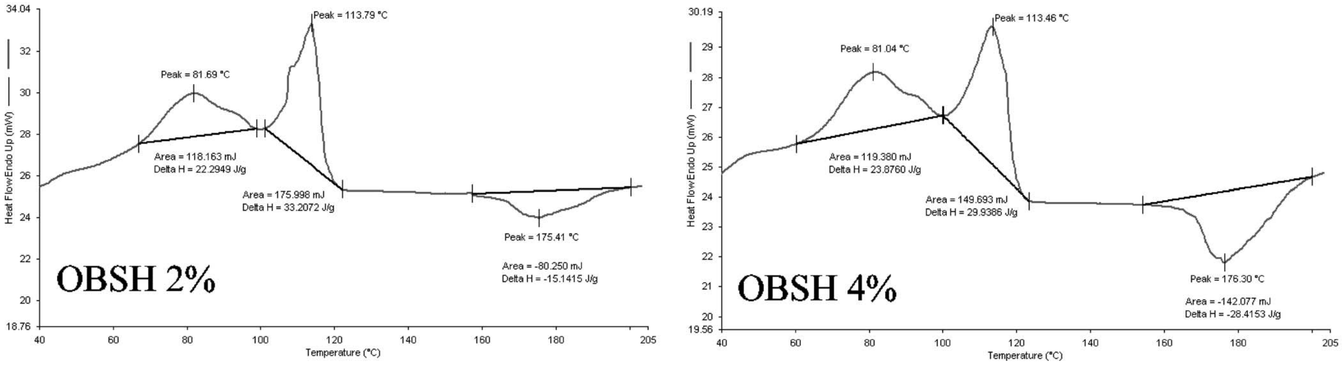

Figure 6. Thermal analysis of the experimental ink with 2% and 4% of OBSH, respectively.

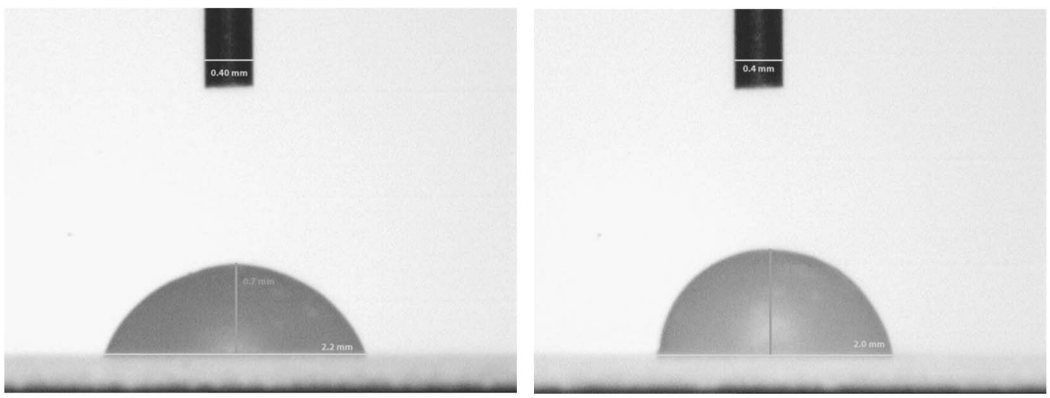

Figure 7. FTA 32 Video 2.0 projection for experimental ink without and with OBSH.

possesses very similar properties to the commercial one. The composition of the ink includes commercially available resins, waxes, and high molecular weight alcohols. The approximate formula of experimental ink can be seen in the Table I.

Differential scanning calorimetry was performed in order to check the melting and freezing profiles of the experimental ink (Fig. 2). Viscosities of both types of the ink were compared (Fig. 3).

The main melting (T_m) and solidifying (T_s) temperatures for both hot melt inks are shown in the Table II. The commercial ink shows two peaks in the melting area and also two peaks in the solidifying area. Generally, melting points of these inks vary in the range of 90–110 °C. The experimental ink showed satisfactory hardness and adhesion to the substrate. The viscosity of the ink at 130 °C was in the acceptable range as well (10–15 cP).

In the second stage of the project, the screening of suitable chemical blowing agents were carried out. The decomposition temperatures of the selected blowing agents must be higher than the ink melting temperature, and also they should not chemically interact with other components of the ink formulation. The blowing agent and thermoplastic polymers were selected according to the temperature in the hot melt printer print head (~135 °C) (Ref. 21) and the chemical compatibility with all of the ink ingredients. Various blowing agents based on different chemistry were analyzed. The corresponding decomposition temperatures are shown in the Table III.

The two most appropriate chemical blowing agents were selected according to the thermal analysis: Hydrocerol BIH (sodium bicarbonate encapsulated in polyethylene) and Celogen OT (OBSH). Also, they represent two different types of decomposition, exothermic and endothermic, as shown in the graphs in Fig. 4.

In the next steps we combined the previously mixed experimental ink with the selected blowing agents. The melting points of the ink components and the decomposition points of the blowing agents are shown in the following figures. Figures 5 and 6 show thermal trace of the ink composition with two different blowing agents incorporated in them. For better proof of the presence of the blowing agents they were added in two amounts; 2% and 4% of the ink composition.

The hot melt ink formulation has a melting temperature well segregated from the decomposition points of the blowing agents. In addition, an appearance of the peak at 76 °C was observed in the graphs (Figs. 5 and 6). We presume this peak corresponds to one of the chemicals used in the formula. The hot melt ink formula including the sodium bicarbonate (BIH) blowing agent shows a shift in the de-

Table IV. Printability analysis of droplet on paper substrate.

	Ink	Ink+OBSH
Contact angle (deg)	69.42	83.34
Base (mm)	2.21	2.07
Base Area (mm^2)	3.41	3.08
Height (mm)	0.72	0.94
Sessile Volume (ml)	~1	~1

composition temperature of the blowing agent. The point shifts from 145 to 191 °C. The gap created by the shifting seems to be too large for the intended function. This phenomenon was observed with almost all tested blowing agents, except OBSH. The OBSH possesses the same decomposition point, whether mixed with the ink or not. It was found that the low molecular weight alcohols present in the ink formula most likely interact with one of the components in the ink formula in the previous works.[14] It is expected that the shifts in the blowing agent decomposition could be caused by similar interactions.

FTA32 Video 2.0 software was used to capture images of the final ink droplets (Fig. 7). The simulated droplets were created by deposition of molten inks on the regular paper substrates using micropipettes.

The images of droplets were taken after solidification of the ink. Fta32 Video 2.0 also provided the printability analysis in terms of droplet height, contact angle, and base area (Table IV).

Figure 7 and Table IV clearly show the increase in height of droplet which consequently possesses a higher contact angle. It is predictable that the high temperature of the heating system after printing will release the gas within the deposited structure.

CONCLUSIONS

The formulation of novel hot melt inks, which are suitable for use in a desktop phase-change printer, has been carried out. These inks have been modified with particular chemical substances, blowing agents, in order to obtain raised images on a substrate. Blowing agents present in the ink decompose right after the ink deposition and form gas bubbles, which are entrapped in the solidifying ink droplets. This new approach proposes use of the ink for creation of three dimensional structures at a smaller scale.

Differential scanning calorimetry was used in evaluating the thermal behavior of novel phase change inks. The modified ink formula containing the selected blowing agent possesses the properties essential for this type of hot melt printing process, e.g., melting point of 100–130 °C, sharp melting and freezing transitions, and viscosity of 10–20 cP at 130 °C. It was found that while the linear alcohols reduce the melt viscosity of inks, they might also interact with the added blowing agents and cause the shift in their decomposition temperatures to higher values.

In order to print the three-dimensional structures with a conventional phase change printer, the printer must be further customized. In addition to important ink properties, based on the type of the substrate the surface tension of the ink needs to be modified to achieve proper ink/substrate interaction.

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