

Production of 3D Structures in Printing

Veronika Chovancova*, Alexandra Pekarovicova* and Paul D. Fleming III*

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Abstract

The ability to form a raised three dimensional image makes possible the use of modified processes, inks and substrates in fine art work, such as children's books, business cards, postcards, and 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 three dimensional (3D) images on a substrate can be accomplished by old fashioned embossing procedures, a process using hectographic or spirit duplicating masters, or raised Xerographic printing with thermally intumesced electroscopic powders. It may also be done employing three-dimensional imaging paper with randomly distributed fibers with uniformly dispersed unexpanded synthetic thermoplastic polymeric microspheres, thermographic processes, special printing processes, which work by building parts of light curable photo-polymer in layers, or heat transfer printing with thermally-expandable ink layer.

Results from our laboratory show a modified formula of hot melt ink that can be used in 3D thermal wax printing process to create raised images on the substrates. An extensive study of thermal behavior of the components of proposed phase change ink has been carried out.

* Western Michigan University
Center for Ink and Printability
Department of Paper Engineering, Chemical Engineering and Imaging
Kalamazoo, MI 49008

Introduction

3D images can be produced by many ways. Old fashioned procedures employ special devices – e. g. embossers. These can create raised image output when attached appropriately to computers. The speed of these generators ranges from 25 characters per second to 60 characters per second. There are several disadvantages related with the embossers. First of all, the cost of these embossers is somewhere around \$20, 000 or more and their embossing speed is very slow when compared to conventional or digital printers with digital printing inks. Additionally, paper that is used for embossing needs to be of a special grade (Braille, 1996).

Another old style process is used to produce hectographic or spirit duplicating masters. Hectographic or spirit duplicating was a broadly used process, especially because of its low costs of a copy or equipment, and also because there was no special training required to operate or service the equipment. Usually, a spirit duplicating master includes a substrate, typically paper, carrying a hectographic ink mirror image of the material to be duplicated. The hectographic ink on the master contains a spirit or alcohol soluble dye which when pressed into momentary printing contact with a sheet of paper transfers dye from the master to the sheet (Dadowski, 1979).

Raised xerographic printing with thermally intumesced electroscopic powders presents different way of creating 3D structures. Intumescent electroscopic powders with foamable microspheres are blended with the powdered ink or toner in the ink reservoir of a copying machine. The image is formed and transferred to a paper carrier in the Carlson process (Carlson, 1942). The heat used in thermoadhesively attaching the toner to the paper also causes great intumescence of the intumescent powder, resulting in a raised image. Immense benefit of this process lays in the price (Jacob, 1984).

In another approach, the recording material is first magnetized, and then it is induced by a magnetic field forming 3D dots. A magnetized thermoplastic recording material is heated to be liquefied in a small bath, and injected toward the printing paper surface through a nozzle. The hotmelt thermoplastic recording material is induced onto the paper surface by means of a leakage magnetic field from a gap in the magnet arranged on the back side of the paper surface where it is deposited and solidifies. The characteristics for recording material include a certain viscosity at high temperatures, the formulation has to include material with properties that enable it to be subjected to the external magnetic force, and also the material should have good adherence to the substrate. The material consists of ethylene-vinyl acetate copolymer (EVA), paraffin wax and, of course, magnetic particles (diameter $\sim 0.5 \mu\text{m}$) used for magnetization (Otake, 1990).

Bruce Campbell's group at Eastman Kodak Company worked on unique three dimensional imaging papers with randomly distributed fibers and uniformly

dispersed unexpanded synthetic thermoplastic polymeric microspheres, which after exposition to heat are capable of producing a raised image by expansion of the caliper of the paper. This could be achieved by incorporating the unexpanded synthetic thermoplastic polymeric microspheres into dry cellulose fibers. A signal in the form of heat reaches the substrate; subsequently the caliper of the paper expands in areas heated above the expansion temperature of the microcapsules and thus provides a raised image (Campbell, 1992).

A similar approach was offered by Torii (Torii, 1999), in which a heat transfer printing sheet comprises a substrate sheet, and a thermally expandable ink layer. The ink layer contains thermally expandable microcapsules as expanding agents, and a binder resin. The process for producing raised images includes the steps of superposing, on an image receiving sheet, a heat transfer printing sheet, heating image wise the thermally expandable ink layer and bringing the heat transfer printing sheet into pressure contact with the image receiving sheet, releasing the heat transfer printing sheet from the image receiving sheet. By this the thermally expandable ink layer is separated from the heat transfer printing sheet and transferring it to the image receiving sheet. Applying light to the thermally expandable ink layer, which has been transferred image wise to the image receiving sheet it is possible to obtain raised images (Torii, 1999).

Thermography is the process of spreading special thermal powders on the wet ink of a print application and heating it in order to melt the powder into a single solid mass, which is raised above the printed surface. The powdered resins are applied to a printed surface on which the printing ink is still wet. Sheets of suitable material such as paper bearing image areas overlaid with powder particles, which typically are made of thermoplastic resin, are transported through a heating chamber. Here, the powder particles are heated sufficiently to fuse them together into raised image portions fixed to the sheet. This also enables the powder to stick to the printed areas. Any powder on non-image areas and any excess powder on the image areas are suctioned off the substrate before the heating takes place. The heat is produced with electric heating elements that are placed inside an oven or tunnel. The powdered substrate passes into the heat tunnel where the powder melts onto the heated substrate and is fused with the wet ink. The substrate must be raised to the temperature of the melting point of the powder in order for the process to work correctly. Generally, the temperature of the sheet itself must be raised to above 200 F, and the heating temperature used for economical production needs to be in the range of about 1000 F to 1200 F. The sheets then are passed through a cooling station in which, an air flow from above cools them to solidify the fused image portions (Van Pelt, 1997).

A method of screen printing raised 3D images involves the use of a stencil attached to the print side of the print screen. The stencil is made from a pre-fabricated, photosensitive thick film having a precision controlled thickness. The print screen is coated with a photosensitive emulsion, and the combination of the print screen and the attached photosensitive stencil blank are exposed to UV

light in order to harden the non-exposed emulsion and stencil material. The screen and stencil are thereafter washed to remove the non-hardened emulsion and stencil material, thereby creating openings in the screen coating and stencil material to form a three dimensional image volume. Pigmented paste is screen printed through the one or more image openings in the coated screen and the associated one or more image volumes in the stencil to form a raised image on the substrate. Complex images can be built using a plurality of raised image layers. The raised image layers have a generally planar surface and sharp edges perpendicular to the planar surface (Meola, 2000).

Another process used for building three-dimensional objects works by building parts of ink in layers. Raised printing is the deposit of ink containing a raising agent on paper to cause the words or images being raised above the plane of the paper. This creates the effect of the words or images standing out from the page in order to emphasize their content. The method includes the steps of depositing a light curable photo-polymer material on the area selected for the printing effects and curing the area. The amount of material to be deposited corresponds to the area selected for the printing effects and the height of the raised area relative to the medium on which the photo-polymer material is deposited. Curing is carried out using ultra violet (UV) or infrared (IR) radiation (Gothait, 2003).

Very interesting approach has been recently introduced by 3D Systems, Inc. In their work they introduced ultra-violet light curable hot melt ink compositions that can be used either in a solid object printer to produce strong and desirable parts or in the adhesive industry to produce adhesive and their film coatings. In particular, the UV curable phase change compositions is comprised of urethane (meth)acrylate resin, a wax, a low molecular weight diluents, a photoinitiator and a polymerization inhibitor. These mixtures of various waxes and polymers are solid at ambient temperatures, but convert to a liquid phase at elevated jetting temperatures in the print head. Such phase change materials have melting points of about 65°C and a viscosity of about 13 cP at jetting temperature (130°C to 140°C) (Schmidt, 2005).

3D Ink Writing Systems

Three dimensional writing techniques can be divided into two categories:

- Droplet based inks
- Continuous inks

The main idea of ink writing techniques lays in the deposition of colloidal, nanoparticle, or organic based inks to create structures. Because of the containing self-supporting characteristic 3D periodic structures propose the great challenge for designing inks. Inks are typically formulated from colloidal, polymeric, or polyelectrolyte suspended or dissolved in a liquid or heated to

create a stable, homogeneous ink with the desired and reproducible rheological (or flow) behavior (Lewis, 2004).

3D printing, direct ink-jet printing, and related approaches such as hot melt printing (Seerden, 2001), 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. Cima (1995) and Sachs (1992) from Massachusetts Institute of Technology (MIT) pioneered the concept of using ink-jet printing to assemble materials.

Hot Melt (Phase-Change) Printing Technology

With thermal transfer printing and thermal wax transfer printing technology, phase-change inks (hot-melt inks or thermal waxes) are brought into contact with the substrate and a thermal head. The hot melt ink printer is a variant of DOD ink jet printers, where the liquid for the printing is obtained by melting the hot melt inks. Thermal transfer and hot melt printers utilize wax-like hot melt ink, rather than the liquid or dry ink used in other processes. The simplicity of thermal transfer printers leads to low equipment cost, cleanliness and high reliability (Atkinson, 2000, Khunova, 2001, Pekarovicova, 2000, Pekarovicova, 2001, Pekarovicova, 2002a, Pekarovicova, 2002b, Pekarovicova, 2003).

The thermal head is digitally addressed (Kipphan, 2001). The process is generally binary, although some higher-end models are capable of producing multi-level dots on special thermal paper. This print image is stored as a pattern of dots, at 300 dots per inch, and is reproduced by precisely timed and controlled exposure of the ink sheet to heating elements on a Thermal Print Head (TPH).

Phase-Change Inks

Inkjet printers use a few kinds of inks, either liquid inks with very low viscosity or solid inks with the phase-change ability occurring during the printing process. The hot melt inkjet inks have to stay solid at ambient temperatures, liquidify at the moment of printing and promptly solidify when reaching the substrate. Upon hitting a recording surface, the molten ink drop solidifies immediately, thus preventing the ink from spreading or penetrating into the printed media. The quick solidification ensures that the image quality is good on a wide variety of recording media (Pekarovicova, 2000, Pekarovicova, 2003).

Composition of Phase-Change Inks

Conventional hot-melt inks are composed from 4 main components: an ink binder comprising a wax with a melting point in the range of 50°C to 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 (Pekarovicova, 2003).

Blowing Agents

The structure of cellular gas-filled polymers can be formed using two possible ways. Either 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 scheme is based on the mechanism by which gas is liberated by blowing agents (BAs).

Chemical blowing agents (CBAs)

Chemical blowing agents 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 formulations (Klempner, 1991, Shutov, 1986, Reedy).

There are many options available when selecting a blowing agent. There are eight key materials used as blowing agents around the world. These include: azodicarbonamide (ADC); p, p'-Oxybis(benzenesulfonylhydrazide) (OBSh); p-toluene sulfonylhydrazide (TSH); 5-phenyltetrazole (5-PT); p-toluene sulfonylsemicarbazide (PTSS); dinitrosopentamethylene tetramine (DNPT); sodium bicarbonate (SBC); and zinc carbonate ($ZnCO_3$) (CBA, 2001).

This research is focused on a formulation of hot melt inks for inkjet printers with various demands on its physical state. The ink is supposed to be in solid state at the ambient temperature, liquid in the moment of printing and to solidify again right afterward creating an image on a substrate. The ink along with thermoplastic polymers should contain particular chemical substances, e.g. blowing agents, which will decompose at elevated temperature, releasing gas bubbles. The blowing agent and thermoplastic polymers have been selected according to the temperature in the print head. After melting and printing, additional heat will be applied to decompose blowing agents, forming needed gases to create raised film.

Experimental

Materials

Various thermoplastic resins, waxes and alcohols, solid at ambient temperature,

were used for formulation of inks for 3D structures.

Mixing

All of the inks were prepared the same way. The ingredients were mixed in 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 130°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.

Calorimetry

Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC) was employed for ink calorimetric analysis.

Viscometry

Brookfield digital viscometer DVII with spindle # 3 was used to measure hot melt inks flow viscosity. Ink temperatures were maintained at 130°C during the measurement.

Printability

Fta32 Video 2.0 software from First Ten Ångstrom, Inc. was used to capture images of droplets and provided the printability analysis in terms of droplet height, contact angle, base area, etc.

Results and Discussion

This project was focused on a novel formulation of hot melt inks with various demands on its physical state. The ink, along with thermoplastic polymers, should contain particular chemical substances, e.g. blowing agents, which will decompose at elevated temperature releasing gas bubbles. The temperature must be higher than the ink melting temperature and also should not chemically react with other components. The blowing agent and thermoplastic polymers were selected according to the temperature in the print head (130-140°C), the viscosity requirements (~ 20 cPs @ 130°C) as well as the chemical compatibility of all ink components.

In order to be able to use such a composition in standard inkjet printer the ink has to melt and reach low viscosity in the printing head before ejection. Very important parameter here is the sharp melting point of the phase change in. In addition, the presence of blowing agent in the formula proposed a question of the decomposition point. After melting and printing process, additional heat is applied to decompose blowing agents, forming needed gases.

The selection of suitable blowing agents was carried out. The most fitting chemical blowing agent has the following chemical composition: p,p'-

Oxybis(benzenesulfonylhydrazide). OSBH (**Figure 1**) is prepared by chlorosulfonation of diphenylether with chlorosulfonic acid and subsequent reaction with hydrazine in the presence of a base.



Figure 1: Chemical Structure of *p, p'*-Oxybis(benzenesulfonylhydrazide)

The blowing agent decomposition takes place at a temperature of approximately 179°C and the process is exothermic as shown in the graph below.

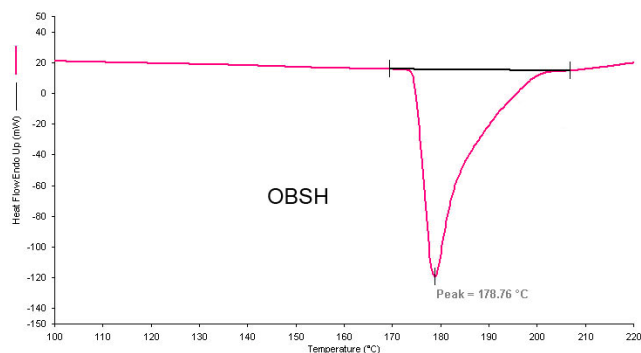


Figure 2: Thermal Analysis of *p, p'*-Oxybis(benzenesulfonylhydrazide) Blowing Agent

The following components were used in the formulations of hot melt ink (**Table 1**):

Table 1: Formula #1 (Sample #5). Pbw- parts per weigh, [%]- weight percent of material in the formulation

S.No.	Component	Function	pbw	%
1	Paraffin wax	Ink vehicle	20.0	19
2	EVA	Imparts adhesion	10.0	10
3	Polyamide resin	Imparts adhesion	30.0	29
4	Low molecular alcohol I	Lower viscosity	40.0	39
5	Blowing Agent	Gas release	2.8	3
	Total		102.8	100.0

When a small volume of the molten ink was dropped onto a piece of paper, the resulting solidified ink drops were too brittle and did not have sufficient adhesion to the substrate. Alternations in the formula were then made (**Table 2**). To improve adhesion we increased the amount of polyamide resin and discarded the EVA component from the formula.

Table 2: Formula #2 (Sample #6) Pbw- parts per weigh, [%]- weight percent of material in the formulation

S.No.	Component	Function	pbw	%
1	Low molecular PE wax	Ink vehicle	3.5	3.1
2	Polyamide resin	Imparts adhesion	68.0	59.4
3	Low molecular alcohol I	Lower viscosity	40.0	34.9
4	Blowing Agent	Gas release	3.0	2.6
	Total		114.5	100.0

The ink possessed improved hardness and better adhesion after deposition. Unfortunately, there was loss of adhesion observed over time. Also, oily marks were discovered underneath the printed areas.

Another modification was made to the formula (**Table 3**). The use of hydrogenated rosin resin as a tackifier was considered. In order to reach low viscosity target we increased the low molecular alcohol ingredient parts.

Table 3: Formula #3 (Sample #22) Pbw- parts per weigh, [%]- weight percent of material in the formulation

S.No.	Component	Function	pbw	%
1	Carnauba wax	Ink vehicle	4.0	3.9
2	Polyamide resin	Imparts adhesion	20.0	19.6
3	Low molecular alcohol I	Lower viscosity	25.0	24.5
4	Low molecular alcohol II	Lower viscosity	25.0	24.5
5	Hydrogenated rosin ester	Tackifier	25.0	24.5
6	Blowing agent	Gas release	3.0	2.9
	Total		102.0	100.0

The resultant ink showed satisfactory adhesion and hardness. Viscosity of the ink at 130°C was in the acceptable range as well (15-20 cPs). **Figure 3** shows the thermal trace of the ink composition. The melting temperatures of all the ink components are listed in the **Table 4**.

Table 4: Melting Temperatures of Ink Ingredients

Component	Melting Temperature (°C)
Carnauba wax	85
Polyamide resin	127
Low molecular alcohol I	63
Low molecular alcohol II	56
Hydrogenated rosin ester	77
Blowing agent	179

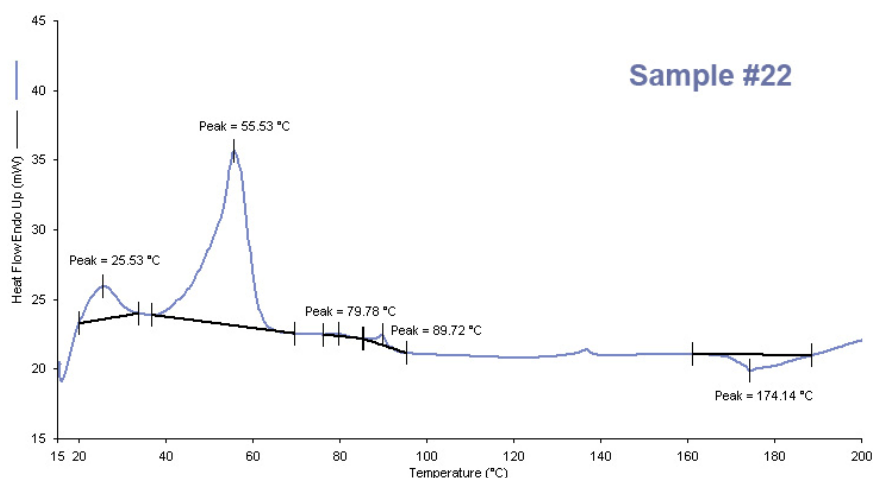


Figure 3: Thermal Analysis of Ink Sample #22

From the DSC analysis, we can distinguish the melting points of the ink components and the decomposition point of the blowing agent. The hot melt ink formula has a melting temperature well segregated from the decomposition point of the blowing agent. Also, it was found that the peak for the polyamide resin, which should decompose at 127°C, was not present in the graph. We presume that polyamide resin might react with one of the ink components, most likely with low molecular alcohol II, and form some other substances. Apparently, there is a peak showing melting point at 25°C. This peak doesn't correspond to any of the chemicals used in the formula. From additional experiments that were carried out, we realized that the presence of the low molecular weight alcohol II

is responsible for observance of the unusual peak and most likely also causing fuming at low temperatures.

Although the final ink performed better than the previous one, the final properties were still not as good in quality as expected, e.g. , flake appearance, fuming, viscosity of 24 cPs at 130°C. The additional modifications were made to reach desired properties of the ink. The final formulation does not include the alcohol and accordingly exhibits enhanced overall performance (**Table 5**).

Table 5: Formula #4 (Sample #23) Pbw- parts per weigh, [%]- weight percent of material in the formulation

S.No.	Component	Function	pbw	%
1	Carnauba wax	Ink vehicle	5.0	5.0
2	Polyamide resin	Imparts adhesion	17.0	17.0
3	Low molecular alcohol I	Lower viscosity	50.0	50.0
4	Hydrogenated rosin ester	Tackifier	25.0	25.0
5	Blowing agent	Gas release	3.0	3.0
	Total		100.0	100.0

Figure 4 illustrates a differential scanning calorimeter trace of the ink. All the corresponding melting temperatures of the ink components are listed in the **Table 4**.

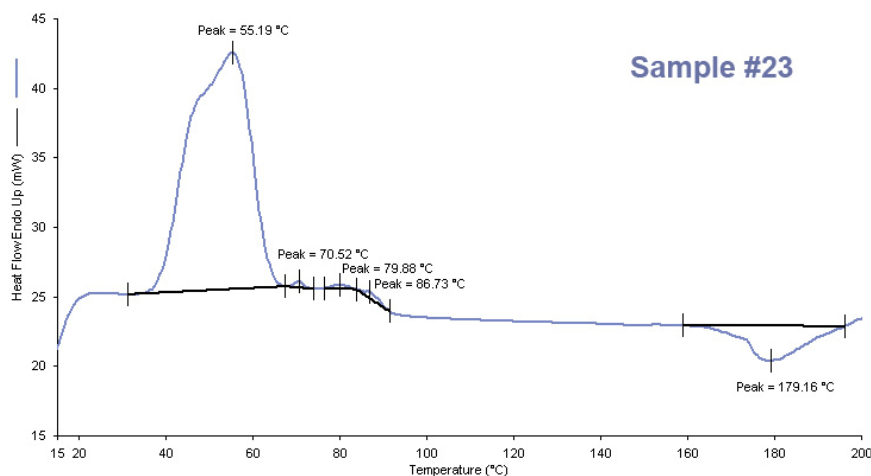


Figure 4: Thermal Analysis of Ink Sample #23

As seen, the resulting hot melt ink formula has a melting temperature and the decomposition of the blowing agent separated with temperature gap of 90°C. The components of the ink show sharp peak when melting (~ 55°C) followed by additional peaks in the temperature range from 70–87°C. Note that the blowing

agent decomposition is exothermic at temperature of approximately 179°C. Viscosity of the final hot melt ink was found to be 19 cPs at 130°C and ink had good adhesion to the substrates.

Fta32 Video 2.0 software was used to capture images of two final inks (**Figure 5 and 6**). The simulated droplets were created by deposition of molten inks on the substrates using the micropipettes. Fta32 Video 2.0 also provided the printability analysis in terms of height, contact angle, base area, etc (**Table 5**).

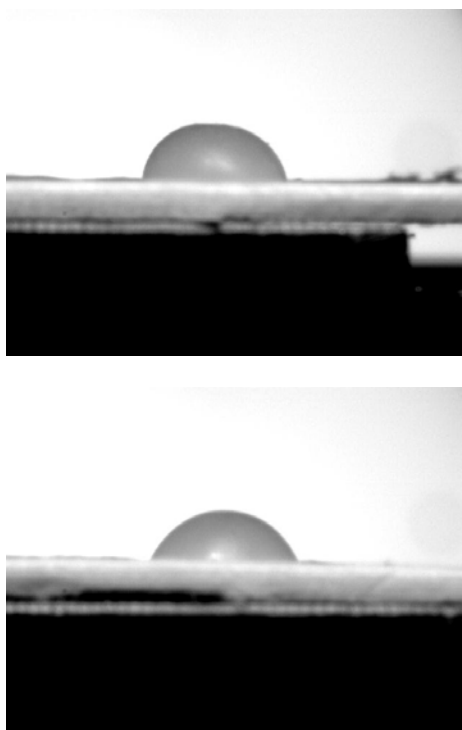


Figure 5: Sample #22 (top) and Figure 6: Sample #23(bottom)

Table 5: Formula #4 (Sample #23)

Component	Sample #22	Sample #23
Contact Angle (deg)	30.16	37.97
Base (mm)	3.54	3.21
Base Area (mm ²)	9.84	8.11
Height (mm)	0.477	0.553

Conclusions

The formulation of hot melt inks with addition of blowing agent was carried out. It was found that the linear alcohols lower melt viscosity. However, they probably react with other ink components and cause fuming of the inks. Therefore, in further work, inks with altered low molecular linear alcohols were formulated. These inks showed better heat stability and sufficiently low viscosity (19cPs at 130°C). Differential scanning calorimetry was found useful in evaluation of thermal behavior of novel phase change inks.

Future Work

The final ink, which is suitable for the hot melt printer, will need further adjustments. We would like to extend the research to the paper/substrate area. There has already been some work done on barrier coating that can be employed in this project. The surface tension of the ink needs to be modified in order to achieve proper ink/substrate interaction.

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