High-Temperature Component Interactions in Pigment-Based Thermal Ink Jet Printing Inks

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Abstract

Thermal ink jet printing presents some unique challenges to pigment-based inks. The process of superheating and vaporizing an ink at an elevated temperature can severely foul the heater and surrounding surfaces. Understanding the component interactions under these conditions can be beneficial to the design of stable and effective inks. Thermal ink jet devices configured for open pool operation are an especially useful tool to study the physical and chemical processes that occur during the vapor generation phase of the ejection cycle. These devices not only can be used for fundamental ink examination, but also as a predictor of ink performance in full ejectors.

Introduction

Thermal ink jet technology can provide high-quality prints at low cost. However, these advantages are only achieved when ink is properly formulated to avoid excessive buildup of solids on ejector surfaces during normal operating conditions. This is particularly challenging for pigment-based inks because of their inherent colloidal instability under conditions necessary to eject a droplet from a thermal print head.

The process of forming an ink droplet in a thermal ink jet ejection device can be broken down into three sequential stages: prenucleation heating, vapor generation, and refill. Several interesting theoretical and experimental studies have been done on the topic over the past 2 decades [1−5]. Each stage places the ink under significantly different stress conditions that can lead to undesirable interactions between ink components, compromising ink stability and ultimate ejector performance. However, when an ink is formulated appropriately, the conditions of each stage can also lead to desirable interactions between ink components and actually improve ejector performance and life.

Thermal ink jet vapor generation is accomplished under film boiling conditions such that the vapor phase is homogeneously nucleated from a super-heated boundary layer. This elevated transient temperature under hydrated conditions offers an entirely different set of conditions than the subsequent vapor generation stage that subjects the ink to a heterogeneous dehydration event. The refill stage offers the ink an opportunity to rehydrate any components that have been deposited onto the heater surface. Unless the ink is properly formulated, each of these individual process stages has the potential to severely foul the ejector microheaters. This paper examines the second stage of vapor generation utilizing the open pool configuration of a thermal ink jet ejection device.

Open pool devices are intermediate structures in the microelectromechanical systems (MEMS) fabrication of thermal ink jet heads. All of the logical and electrical components are in place, but the chamber, nozzle plate, and ink feed channels are absent. Vapor bubbles formed on the heater in open pool do not detach and leave the surface. Rather, they pulsate on the surface through the stages of nucleation, growth, and collapse. An open pool configuration is useful for studying the vapor-generating properties of an ink as well as conveniently allowing access of the heater surface for further analysis. The buildup of solids on heater chamber surfaces is termed kogation. These deposits on a flat open pool substrate unobstructed by an ejector dome can be analyzed by any number of common spectroscopic methods including optical microscopy, micro infrared, SEM, AFM, STEM, EDS, SIMS, and others.

Open pool devices are useful for studying short-term kogation and vapor bubble dynamics, but cannot typically be used for long-term heater life tests because of the destructive nature of the bubble collapse. As vapor bubble collapse tends to be concentrated toward a single point on the heater surface, premature heater failure from cavitation usually occurs well before the resistive element would normally fail. This effect is largely eliminated in chambered devices due to refill from a direction more parallel to the heater plane. A secondary reason for limiting open pool studies to short operation is that the ink is constantly being circulated and repeatedly heated. At some point, the ink in the pool is loaded with boiling debris and is no longer the starting ink of interest. All of the open pool experiments carried out here were of a short duration, usually not more than 10 million electrical actuations.

Experimental

Bubbles on open pool microheaters were visualized with a microscope and illuminated with an infrared LED strobe similar to others in the field [6−8]. The LED pulse was synchronized with the end of the applied heater waveform. The waveform was a simple square wave pulse of 0.6 μs duration at a voltage appropriate for the heater sheet resistance and geometry. The heaters consisted of two counterdirectional elements connected in series. Typical firing frequencies were from 10 to 20 kHz.

Images were captured by a high-speed monochrome video camera and recorded digitally to an IBM PC via a commercial video card. The LED delay could be tuned to capture the vapor bubble growth from nucleation to collapse. An example sequence of still images extracted from a video is shown in Figure 1. From these images, bubble dimensions were measured with digital calipers and calibrated to scale with the known design dimensions of the device. The clarity of the images is somewhat fuzzy because of a combination of video resolution limitations under low illumination, the composition of each video frame from multiple bubble pulses, and the refractive effects of viewing through a moving fluid with thermal gradients. A vapor bubble growth curve is plotted in Figure 2. The locations of the accompanying vapor bubbles in Figure 1 are designated by the letters A−F.

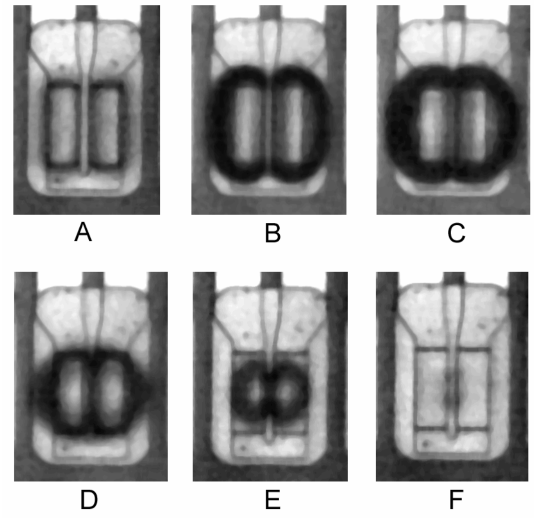

Figure 1. *Captured video images with various strobe delays*

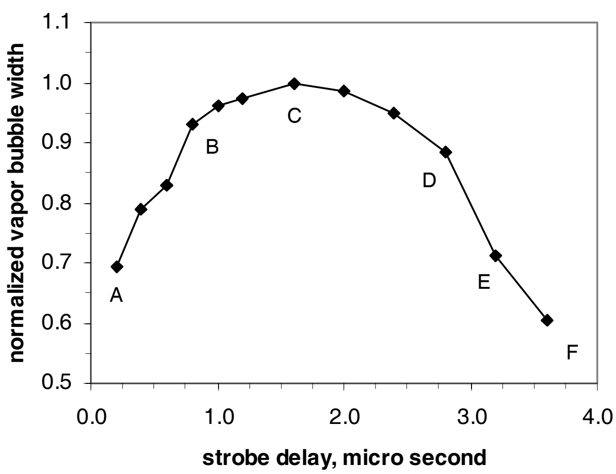

Figure 2. *Vapor bubble size as a function of strobe delay*

The experiments utilizing ejectors with completed domes were carried out using an automated optical laser drop detection fixture. Leading drop velocity and a metric related to ejected volume were among the droplet characteristics measured.

Unless explicitly stated otherwise, all open pool vapor bubble dimensions were measured at the strobe delay with the maximum size (point C in Figure 2). All heater kogation micrographs reproduced here were made on a separate microscope after removing the testing fluid. In general, the kogation for a pigmented ink is the same color hue as the pigment in the ink. For publication purposes, all micrographs in this paper were converted to black-and-white Adobe Photoshop 6.0.

Results and Discussion

The kogation of pigmented inks is very often in the form of small concentrated domains. These domains contain pigment and other nonvolatile ink components. In a video sequence, the domains are observed to be dynamic in nature—forming, detaching, and reforming in an apparently stochastic process. The video image of vapor bubbles undergoing this dynamic process is manifested as an apparent bubble "shimmer." In a static analysis, this process can be represented with a series of microscope images taken of a single heater element at various times. For convenience and clarity, the ink was removed between samplings. The sequence of images in Figure 3 clearly shows the dynamic nature of the kogation by the movement of the individual domains. Of course, there is always the possibility of permanent koga (both visible and transparent) underneath or around these individual deposits.

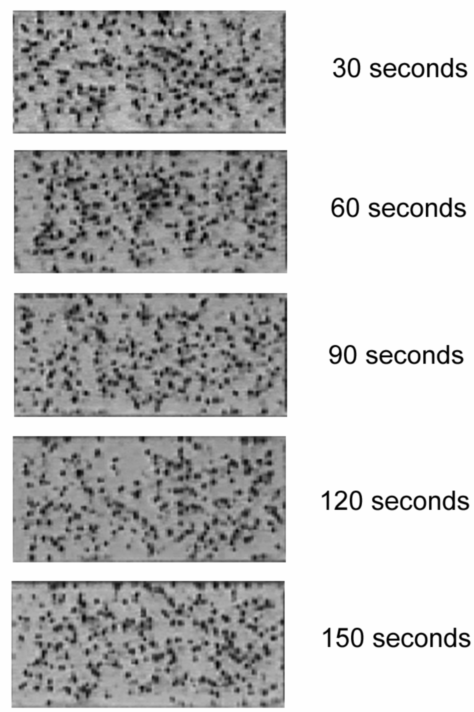

Figure 3. *Koga domains changing in time on a single heater*

The relationship of open pool vapor dynamics to ejection of ink in fully chambered devices is not fully understood. The pressure associated with vapor bubble formation in a confined chamber is the force that accelerates the ink out of the chamber and nozzle bore. Several studies have anticipated that vapor bubble size should be correlated to ejected droplet velocity [9, 10]. Here, an example of this is illustrated with an interesting ink that displayed an unusual vapor bubble response to the applied heater voltage. Above nucleation, this ink exhibited a local minimum vapor bubble size at moderate overvoltage. An ideal curve of this type would stabilize to a constant vapor bubble size above the threshold voltage.

The maximum open pool vapor bubble width is indicated by point C in Figure 2. The maximum bubble width was measured at several overvoltage ratios and compared to the identical operation of a full ejector device. This vapor bubble size correlated reasonably well to the ink droplet velocity in the corresponding chambered device. This is shown in Figure 4, where both vapor bubble width and velocity have been normalized at an overvoltage ratio of 1.025. Despite good agreement at lower overvoltage ratios, there are discrepancies at higher ratios. The reason for this probably stems from the ejected droplet redistributing mass from the main droplet into the satellite(s) and ligament at higher voltage. Because the drop velocity in this case was measured from the transit time of the main drop, perhaps better agreement would have occurred had we calculated the velocity using the center of mass.

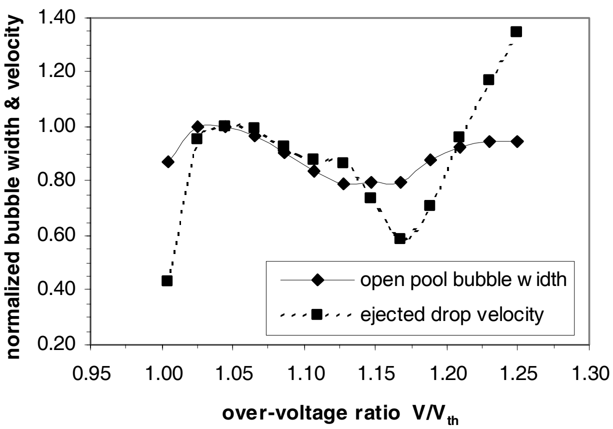

Figure 4. Comparison of open pool and ejector results

The various regimes in the voltage response curve can be understood in terms of the level of kogation present. In this case, several different heaters were operated at a series of voltages for a predetermined period of time. It is clear from the micrographs of Figure 5 that there is an elevated level of dynamic kogation in the region of depressed vapor formation. This higher level of surface deposition would act as a resistance to efficient heat transfer, resulting in a smaller effective vapor bubble size and more heat shunted into the device. In addition to the reduced bubble size, the vapor bubble also becomes unstable in this region.

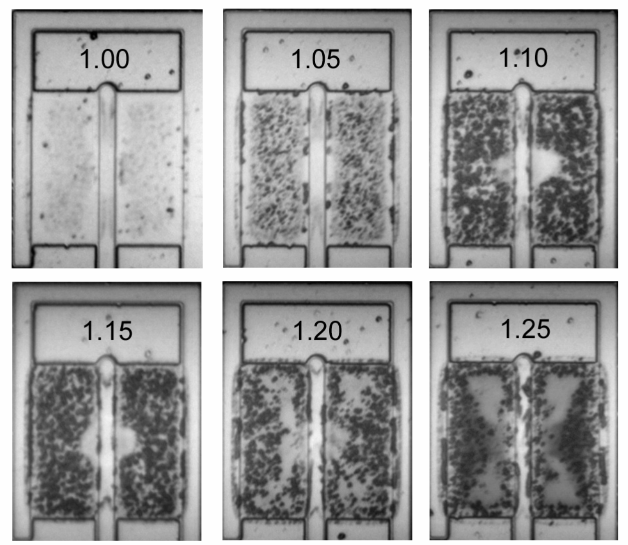

Figure 5. Heater koga at various overvoltage ratios

Several researchers have studied the effects of surface topology and wetting characteristics on vapor bubble nucleation [11, 12]. The effect here seems to be temperature dependent, with gross kogation failure at intermediate heater temperatures. The clear area in the center of the split heaters is the location of vapor bubble collapse. The signature "X" at 1.25 overvoltage ratio is an interesting artifact.

The interactions between ink components play a key role in the effectiveness of a pigmented ink. A practical example of this was encountered when an ink-containing pigment, humectant, binder, and surfactant were incubated in both glass and high-density polyethylene (HDPE) bottles for 4 weeks at 60 ^{o}C. The sample incubated in glass demonstrated heavy kogation and a vapor bubble that quickly disappeared in open pool. The sample incubated in HDPE had a large and stable vapor bubble comparable to the fresh control. Micrographs of the heaters are shown in Figure 6.

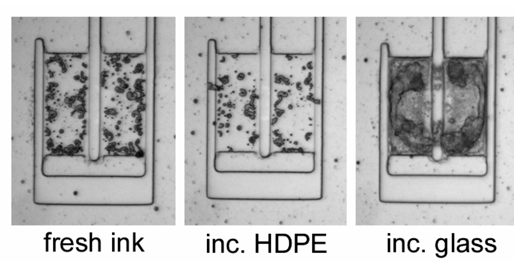

Figure 6. Heater koga from incubated pigmented ink

A metals analysis was conducted on both the fresh and glass incubated samples. An abridged summary of the inductively coupled plasma mass spectrometry (ICP-MS) results is shown in Table 1. Several metal ion levels increased during incubation in glass, the most prominent being calcium.

Table 1. ICP-MS of fresh and incubated ink samples

element	fresh ink	incubated ink
Ca	3.9	26
Fe	0.8	0.8
K	2600	2600
Mg	0.6	3.9
Na	34	75
Zn	1.2	1.3

To diagnose the undesirable interaction between the ink and glass, a series of inks containing one- and two-part combinations was designed and incubated in glass. The results are summarized in Table 2, where it is evident that all samples containing Trudot IJ-4655 binder (manufactured by MeadWestvaco Corporation) fouled the open pool heaters after incubation. The interaction was proposed to be ionic bridging between multivalent metal ions and the acid-solubilizing groups on the polymeric binder. The metal ions presumably leached into the ink or ion-exchanged with cationic species already present. A further example of the heater fouling observed in this experiment is shown in Figure 7. This ink contained no pigment and was designated as ink number 6 in Table 2.

Table 2 Ink component interactions table

ink	pigment	IJ-4655	humectants	surfactant	fouling
1	X	X	X	X	yes
2	X			X	no
3		X		X	yes
4			X	X	no
5	X	X		X	yes
6		X	X	X	yes
7	X		X	X	no

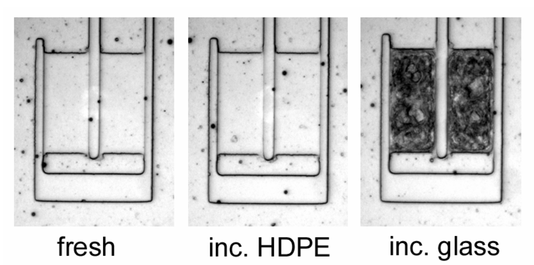

***Figure 7**. Heater koga from incubated pigment-less ink*

To study if there was a threshold for this effect, we formulated a series of fresh inks that were doped with calcium ion. Calcium nitrate was used as the doping species with concentrations as mass parts per million of calcium ion. The open pool kogation micrographs for some of the doped levels are shown in Figure 8.

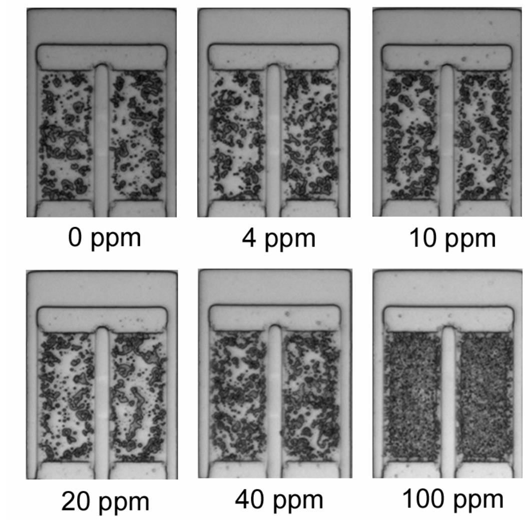

***Figure 8**. Open pool kogation for inks doped with calcium*

A visible difference was noted at 40 parts per million and higher. The micrographs were evaluated for mean blue code value within Adobe Photoshop. Blue code values were chosen because the ink and koga were yellow. For inks containing circa 1% Trudot IJ-4655 polymeric binder, it is clear that the content of calcium ion would need to be maintained below about 20 ppm.

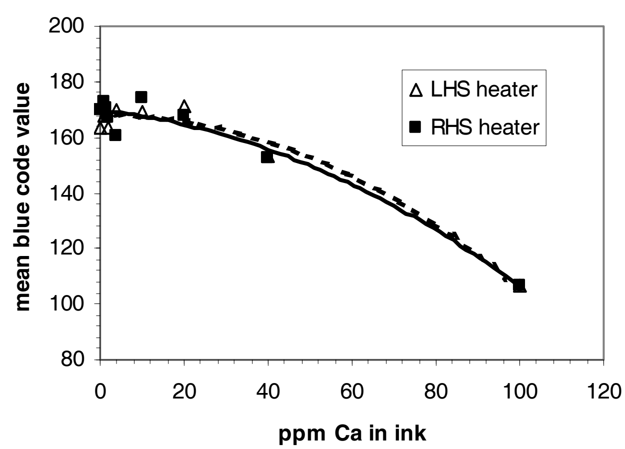

***Figure 9**. Micrograph code value vs. level of doped calcium*

The critical concentration for other multivalent metal ions may be higher or lower than those for calcium depending on their pKsp with the polymeric-bound anion. It is also likely that the combined levels of multivalent species are important. For this reason, many commercial inks contain metal-sequestering agents such as EDTA [13–16].

Conclusions

The process of superheating and then vaporizing an ink on an ink jet microheater places some unique challenges on the design of pigmented inks. The ink components can interact in sometimes predictable and sometimes unpredictable ways. Open pool intermediate devices have been shown to be a useful and effective means to study some of these component interactions. In addition, these devices can be predictive of ink performance in fully functional ink jet printing heads.

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Author Biography

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