

Kogation: A New Mechanism and Solution

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Introduction

Thermal ink jet relies on superheating ink to form a bubble which then ejects a drop of ink. In order to form a bubble, ink at the resistor surface is exposed to temperatures over 300°C, albeit for very short times. For a resistor which is operated with a pulse width of a few microseconds, the temperature excursion over 300°C lasts for a period less than the pulse width. Even though such temperature excursions are very short for chemical reactions to occur, repeated firing of a resistor in some cases results in deposition of residues on the resistor surface. The term kogation has been used to describe this phenomena. It is commonly believed that these deposits result from thermal decomposition of ink components because of the high temperature. It has been reported that azo dyes decompose at temperatures of 250-300°C and kogation from inks containing azo dyes results in insoluble deposits that are primarily carbon.¹ Another report which focused on thermal decomposition of glycols and glycol ethers concluded that diethylene glycol thermally decomposes in ink jet devices and results in the formation of kogation.² Even though such reports have contributed to the understanding of kogation, the chemical mechanisms which occur are still not well understood.

This paper provides new insight into the mechanisms of kogation by presenting data on the elemental composition of kogation and identifying a class of ink additives which effectively prevent kogation. In addition, experimental evidence is presented which suggests that the type of kogation observed here is not the formation of insoluble carbon residues. Although the results may not be conclusive, they do provide new insight into a difficult and lingering thermal ink jet problem.

Experimental

The pens used in this study were Hewlett-Packard black DeskJet print cartridges. They were filled with inks consisting of 2 to 6% dye, 5 to 10% of either diethylene glycol or 2-pyrrolidone, and the balance of deionized water. The dyes were anionic azo dyes. Inorganic salts were added to these inks in order to investigate their effect on kogation.

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Drop weights were measured with a Mettler analytical balance. The pen and carriage from a DeskJet printer were mounted over the balance pan and the ink was collected in an aluminum dish. The pen was operated with a standard pulse width using discrete energies which act on four distinct subsets of resistors. Measurements were taken by firing 20,000 drops from each nozzle in a nozzle subset, weighing the total and calculating the average drop weight for a single nozzle. This process was repeated for all four nozzle subsets. These measurements were alternated with stress firings which emulate actual printer conditions. Kogation was analyzed by Auger Electron Spectroscopy (AES) in pens from this test and also from pens printed in a DeskJet printer.

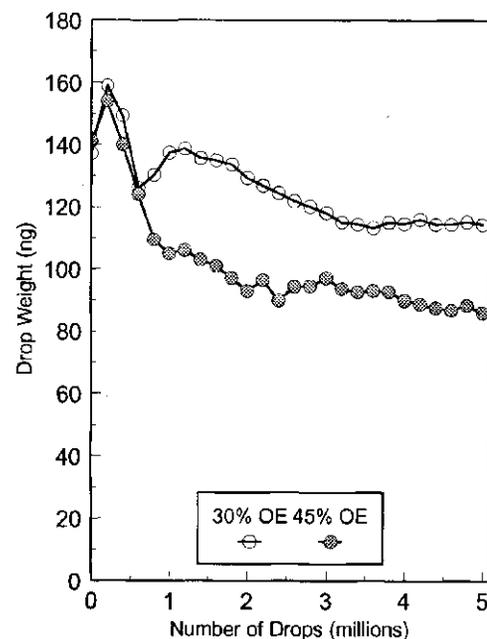


Figure 1. Drop weights for a kogating ink

Results and Discussion

The build-up of residue on the resistor surface will affect bubble formation and subsequent drop ejection. Therefore, one method of monitoring kogation in a pen is to measure drop weights as a function of the number of drops ejected. A typical example of kogation monitored by this test method is shown in Figure 1. In this example, subsets of resistors in a pen were operated at

two different energies over the minimum for drop ejection (OE), 30% and 45%. In general, the formation of kogation will result in a decrease in drop weight. In the case of extreme kogation, drop weights will decrease rapidly to zero, i.e. no drops are ejected.

It can be verified that the decrease in drop weight was due to a residue formed on the resistor at the end of the test by removing the orifice plate and examining the resistors with an optical microscope. Scanning Electron Microscopy (SEM) has been used to further characterize these residues. Figure 2 is a photomicrograph of a single resistor operated at 30% OE. A heavy residue with an uneven texture is evident.

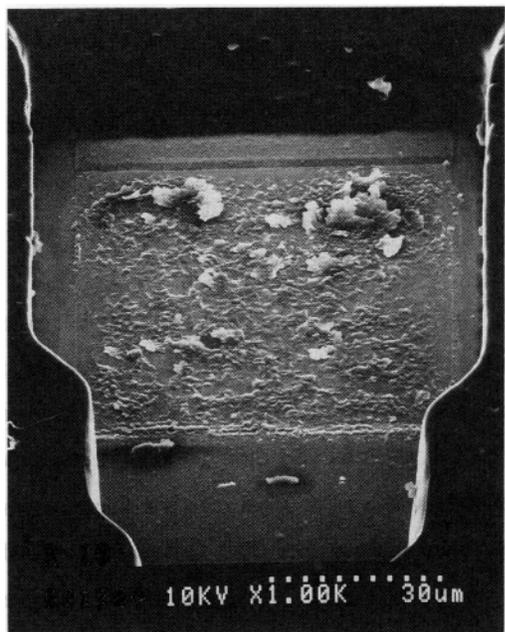


Figure 2. Photomicrograph of kogation on a resistor

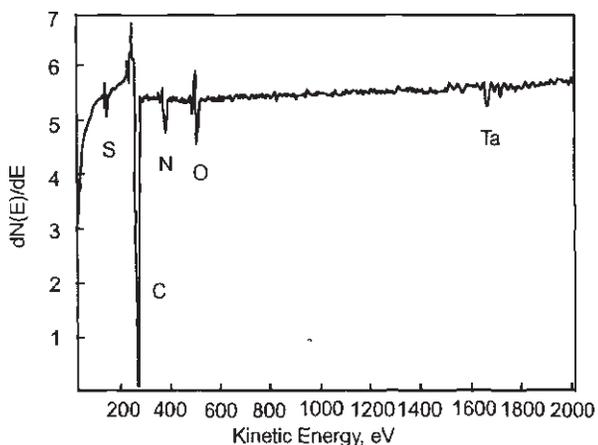


Figure 3. Auger Spectrum of kogation on a resistor

The elemental composition of the residue can be determined by Auger Electron Spectroscopy (AES). Resistor residues from inks made with each of the dyes all

consisted of carbon, oxygen, nitrogen and sulfur. Figure 3 shows a typical AES survey of the residue. Although carbon is the most abundant (70-90 atomic %), the residues always contained oxygen, nitrogen and sulfur, each in the range of 1 to 10 atomic %. This composition suggests that these residues are organic compounds rather than just a carbon residue. The vehicles consisted of either diethylene glycol or 2-pyrrolidone and water. These compounds do not contain sulfur and therefore can not be the source of this element in the residue. Further, no kogation was observed when the vehicle was tested. The most likely source of carbon, oxygen, nitrogen and sulfur are the dyes. The dyes are all sulfonated azo dyes and contain all four elements. The dyes were also analyzed by AES and Figure 4 shows a comparison of the elemental composition of a dye and kogation that was formed with an ink containing the same dye. The concentrations of these elements are very similar and further support the conclusion that the kogation observed here is not just carbon but may be intact or only slightly decomposed dye.

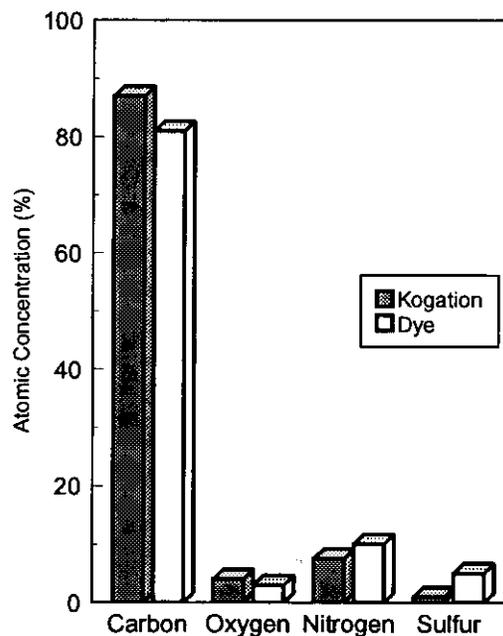


Figure 4. Elemental composition of kogation and dye determined by AES

Certain additives can be used to prevent kogation and it is known that oxo anions are effective at preventing kogation.³ Phosphate is a particularly good anion which prevents the formation of kogation and results in very stable drop weights (see Figure 5) when added to an ink which does kogate (compare to Figure 1). Phosphate is effective at stabilizing drop weights and preventing kogation even at very low concentrations (parts per million). Resistors examined by optical microscopy, after firing ten million drops with this phosphate containing ink, showed no visible residue on the resistors.

Analysis of resistors by AES exhibited only a very thin layer of carbon containing material as shown in the depth profiles (Figure 6). This should be compared to the relatively thick organic layer shown in Figure 7 for the same ink without phosphate. The depth of the residue (Figure 7) can be estimated from the sputter rate and appears to be approximately 2,000 Å. There does not appear to be a sharp interface between the thick organic residue and the tantalum resistor surface. However, this may not be the case since the residue appears to be rough and uneven. If the spot being analyzed by the AES electron beam includes both a thick residue (high carbon and no tantalum) and a very thin residue which would be rapidly penetrated by the electron beam into the tantalum resistor overcoat, then it would appear as if the organic layer and tantalum were intermixed rather than two distinct layers with a sharp interface.

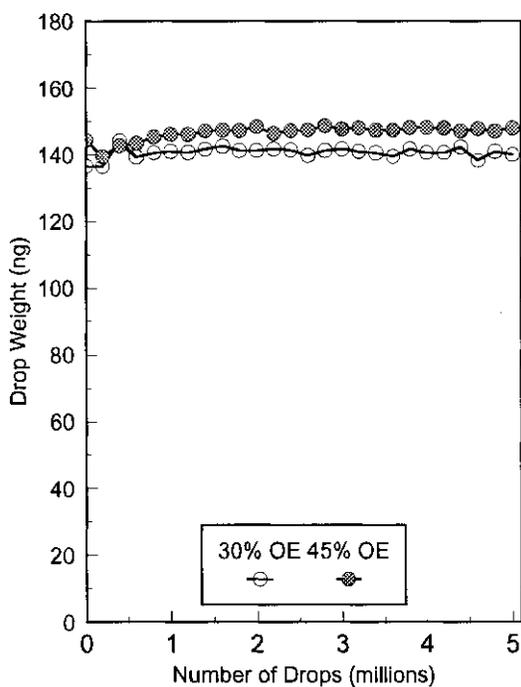


Figure 5. Drop weights for an ink that does not kogate

Conclusions

Analysis of kogation by AES indicates the presence of elements other than carbon which is in contrast to previous reports. The dyes used in this study contain all the elements found in the kogation residues and are the most likely source of the residue, although this can not be conclusively determined from elemental composition alone. Kogation can be effectively prevented with the addition of oxo anions, with phosphate being particularly effective. The fact that certain anions can prevent kogation suggests a mechanism other than thermal decomposition. If ink components were decomposed to insoluble carbon, then it does not seem likely that the mere addition of anions would prevent this process. The kogation observed in this study is thought to be intact,

or only partially decomposed, dye adsorbed on the resistor surface. In light of these results, viewing kogation as only thermal decomposition of ink components to form insoluble species which adhere tenaciously to a resistor surface is an over simplification of the process. Kogation should not always be assumed to be thermal decomposition which results in insoluble products. Further experimental work is still needed to fully understand kogation mechanisms.

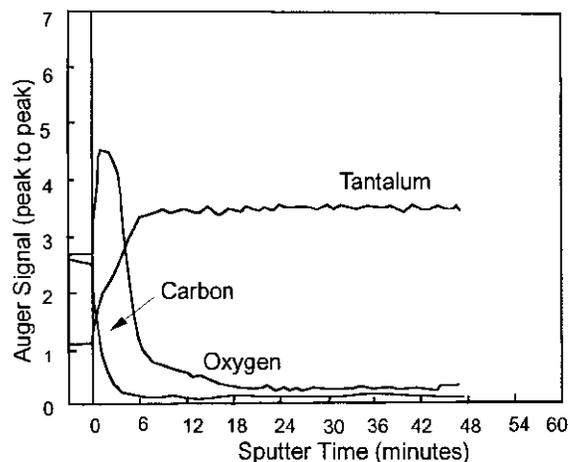


Figure 6. AES depth profile of a resistor without kogation after 10 million drops

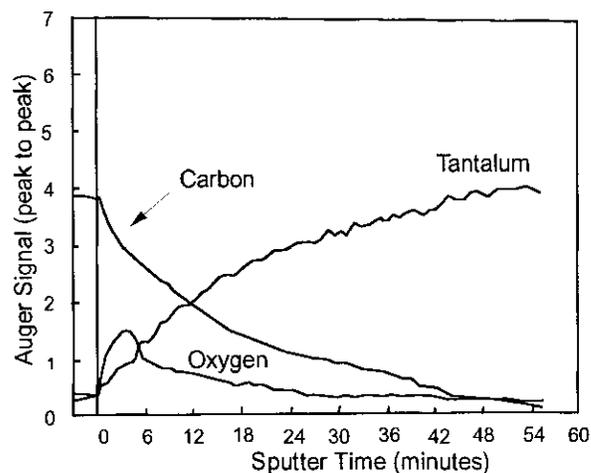


Figure 7. AES depth profile of a resistor with kogation after 5 million drops

References

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2. P. L. Gendler, and A. H. Sporer, "Thermal Decomposition (Kogation) of Ethylene Glycol and Diethylene Glycol in Thermal Ink Jet Inks", *IS&T's Eighth International Congress on Advances in Non-Impact Printing Technologies*, pp. 308-310, October 25-30, 1992.
3. D. J. Halko, US Patent 5,062,892 (1991).