Arrhenius Testing under Controlled Atmospheres: Measurement of Dark Keeping Properties of Inkjet Photographic Prints

Michelle Oakland, Douglas E. Bugner, Rick Levesque, and Peter Artz
Imaging Materials and Media, Research & Development, Eastman Kodak Company
Rochester, New York

Abstract

ANSI Standard IT9.9-1996 is commonly recommended for predicting dark storage print life for color photographic materials. This standard is based on Arrhenius methodology and calls for measuring changes in print density that occur as a function of temperature at 50% ±3% relative humidity. The objective of this paper is to examine the dark keeping properties of inkjet photographic prints as a function of constant absolute humidity at various temperatures. The primary focus is on commercially available dye-based inks printed onto both porous and non-porous photo-quality papers.

Introduction

With the recent introduction of photographic quality inkjet printers from Hewlett-Packard, Epson, Canon, Lexmark, and Kodak targeted at owners of consumer digital cameras, attention has now focused on improving the image stability and physical durability of inkjet photographic output. In the past, inkjet prints have suffered from a number of image stability limitations, including light fade, waterfastness, dark storage, and image smear at high humidity. Recent reports have discussed various aspects of light fade[1] and humidity keep of inkjet prints made with different types of inks and papers.[2] The hypersensitivity of certain combinations of ink and paper to ozone has also been the subject of recent trade and technical publications.[3] Although the term "gas-fade" has been proposed for this phenomenon,[4] it might be more appropriately considered in the context of traditional dark fade studies.

For prints intended for indoor display in a home or office, there is a need to estimate print life with respect to different environmental factors. With respect to light fade, accelerated testing using either unfiltered or glass-filtered high-intensity fluorescent lamps has been used in accordance with ANSI Standard IT9.9 to provide an estimate of print life.[2] Also included in ANSI IT9.9 is a standard method for predicting print life with respect to thermally activated dark fade mechanisms. The latter is an adaptation of methodology first described by Arrhenius over a century ago.[5] This method is based on the relationship between the rate of a thermally activated process and temperature, as represented in the following equation:

$$\ln (k) = - (E_a/R) (1/T) + \ln (A) \qquad (1)$$

where k is the rate of the process, E_a is the activation energy of the process, R is the universal gas constant, T is the temperature in the Kelvin scale (K), and A is the pre-exponential factor.

For processes that are too slow to practically measure at ambient temperature, e.g., the dye fade in photographic prints, the rate can be increased to more practical time scales at elevated temperatures. Equation 1 can then be used to calculate the rate of dye fade at ambient temperatures, thus allowing the estimation of the time it will take to reach a given level of fade.

Although Arrhenius methodology works well for simple thermally activated phenomena, it can be difficult to interpret when either more than one rate constant is involved or when the system under study undergoes a phase transition. An example of the former could occur when a dye is partitioned among multiple environments, for example, between a bound and unbound state, or between an aggregated and de-aggregated state. An example of the latter might be found when a dye is absorbed in a polymer matrix, which has a glass transition temperature, T_g, not too far above ambient temperature. A further complication occurs when the T_g of the polymer matrix is found to be a sensitive function of absorbed moisture, such as might occur in response to changes in relative humidity. In practice, it is possible that all of the above conditions could be occurring at the same time in a single ink-receiver combination.

The purpose of this study is to survey the dark stability of a variety of ink-receiver combinations using Arrhenius methodology under constant absolute humidity (constant dew point). This condition was chosen to be equivalent to 50% RH at 25°C, where the corresponding dew point is 13°C.

Materials and Methods

Materials

A list of the different inkjet receivers used in this study is given in Table 1. All receivers comprise a resin-coated photo base coated with either a swellable or porous IRL as indicated in the table. The printers used for this study included the Hewlett-Packard DeskJet 970, the Epson Stylus Color 900, and the Epson Stylus Photo 870. All printers were equipped with the OEM-branded printheads and inks.

Table 1. Glossy inkjet receivers used in this study.

Brand	*Description*	**Type***
Kodak	Premium Picture Paper	S
HP	Prem. Plus Photo Paper C6831A	S
Epson	Premium Glossy Photo Paper	P
Konica	Photolike QP Glossy Med. Wt.	P

*S = swellable; P = porous

Methods

The test targets used in this study were generated as described previously.[1c] Test targets were incubated at 35, 45, 55, 65, and 75°C, at a constant dewpoint of 13°C, monitoring at specified time intervals by status A densitometry (Gretag/Macbeth Spectro Scan T 3.273 spectrophotometer/colorimeter). The samples were allowed to hang freely within the environmental chambers and were not sealed in foil bags. An extra set of test targets was kept in the dark under ambient conditions and monitored for any change in density during the course of the study. Changes are reported as percent density loss (%ΔD). An unprinted area (D_{min}) of the test target was also monitored, and %ΔD was corrected for D_{min}. At each time interval, plots of %ΔD vs initial density (D_o) were made for each primary color. From these plots, %ΔD for each color was interpolated to $D_o = 1.0$ above D_{min}.

Results and Discussion

Background on Humidity Effects

Previous studies[2] have reported that at ambient temperatures between 20–25°C, and at relative humidities below about 60%, most inkjet prints are quite stable in the absence of other environmental factors, such as light and air pollution. However, as relative humidities climb higher than about 60%, a combination of dye migration and dye fade can occur. The former leads to undesirable shifts in hue and/or loss of sharpness. The latter results in loss of density. Both can limit the useful life of an inkjet photograph.

It is hypothesized[6] that as humidity increases, the hydrophilic polymer matrix that comprises the ink-receptive layer (IRL) becomes plasticized by the absorption of moisture from the environment. This causes the T_g of the polymer matrix to be depressed. When the T_g falls below the ambient temperature, the dyes absorbed within the polymer matrix can diffuse more readily, leading to dye migration. In addition to dye diffusion, airborne pollutants such as ozone might also diffuse into the IRL more readily, increasing the rate of fade of any dyes that are sensitive to ozone-induced fade.

It is against this background that the results of this study will be discussed. Please note that as the temperature is increased while keeping RH constant (as recommended in ANSI IT9.9), the total amount of water in the atmosphere increases. This could depress the T_g of the IRL and lead to dye migration at lower temperatures. As the temperature increases at constant dew point, the total amount of water in the atmosphere should remain constant. It was felt that this condition offered the best chance of measuring dark fade independent from dye migration. Under either scenario, it is uncertain as to the impact on the concentration of water that is absorbed into the IRL, and thus, the effect on the T_g of the IRL at any given combination of temperature and humidity.

General Comments

The results for two representative receivers on two ink sets will sufficiently illustrate the general conclusions of this study. The two receivers are KODAK Premium Picture Paper, an example of “swellable” IRL technology, and Konica QP paper, an example of “porous” technology. Both receivers are high gloss, coated on resin-coated photo base, and are claimed to be compatible with most desktop inkjet printers.

The two representative ink sets are those provided with the Hewlett-Packard DeskJet 970 printers, which use a thermal inkjet printhead, and the Epson Stylus Color 900 printer, which uses a piezoelectric printhead. Both ink sets are water-based, and use full density cyan, magenta, and yellow dyes as colorants. They differ in the specific dyes used, as well as in the types and amounts of co-solvents and other additives that are included in the formulations. For the purposes of the following discussion, we will focus only on the results for the pure primary colors.

Dark Fade at Constant Dew Point

Figures 1–3 are representative plots of %ΔD vs time for the Epson 900 cyan, magenta, and yellow inks on the KODAK Premium Picture Paper at the five temperatures chosen for this study, all at a constant dewpoint of 13°C. Similar results were observed for both the Kodak and Hewlett-Packard swellable receivers with the Hewlett-Packard inks. As can be seen from the plots, there is very little, if any, fade occurring under these conditions. Note that the range of density change is only ±2-3% across all combinations of ink, temperature, and time. Clearly, if any dark fade is occurring under these conditions, it is not being accelerated sufficiently even at the 75°C condition to model by the Arrhenius method.

On the other hand, significant dark fade (15–30%) was observed for the porous receivers included in this study, especially with both manufacturers’ cyan inks. Figures 4 and 5 show the density loss for the Epson 900 and the Hewlett-Packard 970 cyan inks on Konica QP. Surprisingly, the fastest rates of fade appear to occur at both the highest and lowest temperatures in each case. Similar behavior was observed with Epson Premium Glossy Paper.

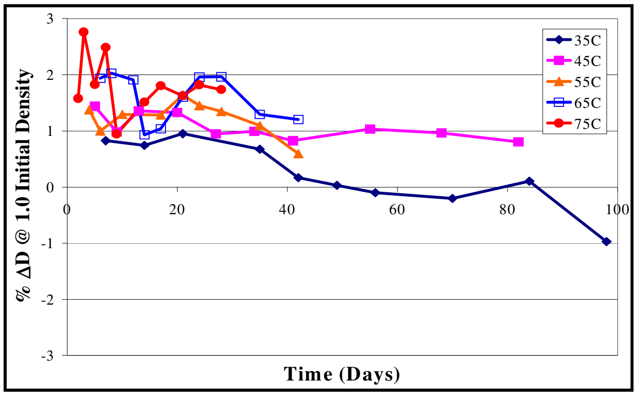

Figure 1. Percent change in density as a function of time for the Epson 900 cyan ink on KODAK Premium Picture Paper.

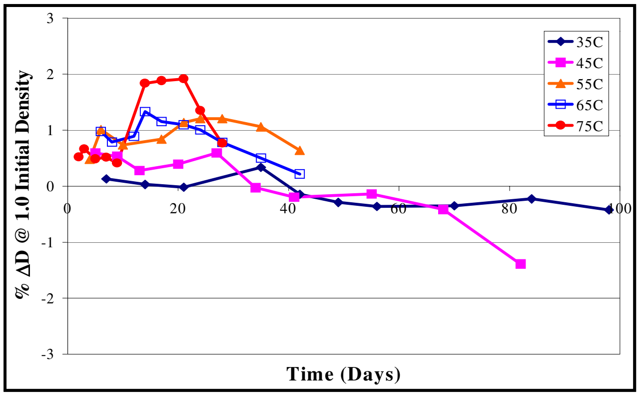

Figure 2. Percent change in density as a function of time for the Epson 900 magenta ink on KODAK Premium Picture Paper.

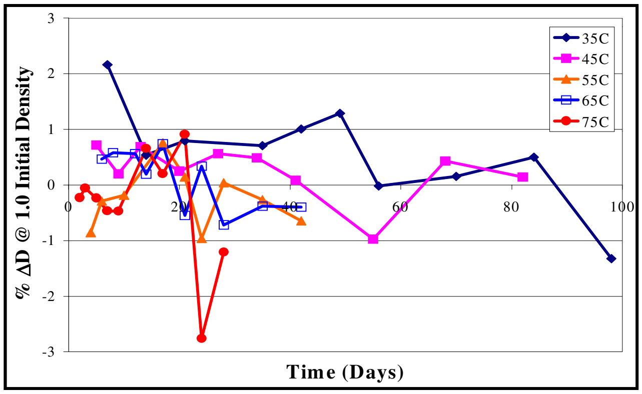

Figure 3. Percent change in density as a function of time for the Epson 900 yellow ink on KODAK Premium Picture Paper.

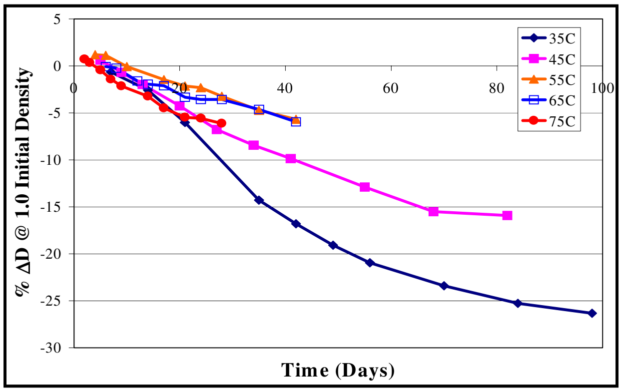

Figure 4. Percent change in density as a function of time for the Epson 900 cyan ink on Konica QP paper.

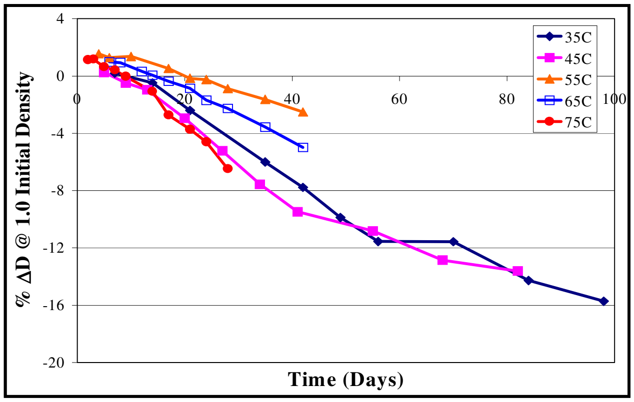

Figure 5. Percent change in density as a function of time for the Hewlett-Packard 970 cyan ink on Konica QP paper.

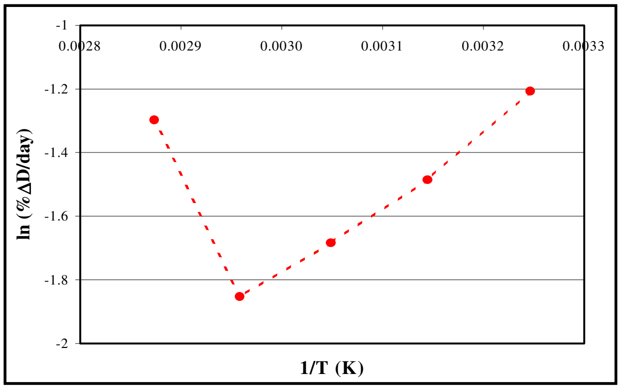

Figure 6. Arrhenius plot for the dark fade of the Epson 900 cyan ink on Konica QP paper.

Least-squares lines were fit through the data in Figures 4 and 5, with the slopes of the lines for each temperature taken as the apparent dark fade rate. Arrhenius plots were generated by plotting the natural log of the rates against 1/T (K). Figure 6 shows such a plot for the combination of Epson 900 cyan ink on Konica QP. This plot is typical of the dark fade behavior observed for all of the combinations of cyan inks and porous receivers included in this study. The highest rates of apparent dark fade occur at the lowest and highest temperatures, with the lowest apparent rates of fade observed at either the 55 or 65°C condition.

This unusual behavior can be rationalized as the result of at least two counterbalancing phenomena: dye migration and dye fade. As the temperature increases initially, the rate of dye migration, leading to density gain, more than offsets the increased rate of dark fade. As the temperature continues to increase, the rate of dark fade begins to overtake the rate of dye migration. Other explanations are possible.[7] Further work is needed in order to substantiate this hypothesis.

Regardless of the explanation, it is clear that the application of Arrhenius methodology to accelerate the dark fade rates of inkjet prints is not straightforward. Swellable inkjet receivers do not appear to fade at meaningful rates even at temperatures as high as 75°C. Porous receivers and cyan inks exhibit linear fade behavior at each of the temperatures studied, but the Arrhenius plots do not result in the expected straight line with negative slope.

It is interesting to note that the combinations of cyan ink on porous receivers also exhibited the largest apparent deviations from reciprocity in our light fade studies.[1c] Moreover, these same combinations have been reported to be particularly susceptible to ozone-induced fade.[3,8] Could it be that all three phenomena are related?

Summary

In this study we attempted to accelerate the rate of dark fade of inkjet prints using Arrhenius methodology. We chose to keep dew point (absolute humidity) constant in an attempt to isolate the effect of dye fade from dye migration. For non-porous, swellable inkjet receivers the apparent rates of fade were too slow, even at the higher temperatures, to construct an Arrhenius plot. For porous receivers, we were able to measure meaningful fade rates for the cyan inks at each temperature, but the Arrhenius plots did not yield the expected linear response. Although the specific reasons for the non-Arrhenius behavior are not known, it is clear that standard Arrhenius methodology is not amenable to the general determination of dark fade print-life estimates for inkjet prints made with representative combinations of commercially available inks and receivers.

Acknowledgments

The authors wish to acknowledge Pam Hill for laying the foundation for this work, and John Higgins and Gary Allen for insightful discussions along the way.

Notes and References

1. (a) E. Zinn, E. Nishimura, and J. Reilly, *Proc. NIP 15*, pp. 416-20 (1999); (b) S. Schuttel and R. Hofmann, *ibid.,* pp. 120-23 (1999); (c) D. E. Bugner and C. Suminski, *Proc. NIP 16*, pp. 90-94 (2000).
2. (a) P. Hill, K. Suitor, and P. Artz, *Proc. NIP 16,* pp. 70-73 (2000); (b) M. McCormick-Goodhart, *ibid.*, pp. 74-77 (2000).
3. M. David Stone, PC Magazine, pg. 52, January 16, 2001.
4. http://www.wilhelm-research.com.
5. S. A. Arrhenius, *Z. Phys. Chem.*, **4,** 226 (1889).
6. D. E. Bugner, *Handbook of Imaging Materials*, 2nd ed., A. Diamond and D. Weiss, eds. Marcel Dekker, New York, 2001, pp 603-627.
7. For a review of non-Arrhenius behavior see: J. R. Hulett, *Quart. Rev.,* **18,** 227 (1964).
8. (a) http://home.cox.rr.com/meyerfamily; (b) http://www.p-o-v-image.com.

Biography

Douglas Bugner received his B.S. in Chemistry from the Ohio State University in 1975, a M.S. in Organic Chemistry from UCLA in 1980, and a Ph.D. in Organic Chemistry from UCLA in 1982. In 1982, Dr. Bugner joined the Chemical Technology Laboratory in the Photomaterials Division of Eastman Kodak Company. In 1988, he accepted an assignment in the Photoconductor Technology Laboratory, and in 1991, he was appointed manager of the Chemical Technology Lab. In 1993, Dr. Bugner established a research effort in the area of inkjet materials, and the Inkjet Materials Technology Laboratory was formed in 1994, which he headed until 1999. Dr. Bugner is currently Senior Laboratory Head, Cut-Sheet Inkjet Commercialization Lab, Inkjet Printing Systems Division, Imaging Materials and Media Research and Development, Eastman Kodak Company.

In 1994, Dr. Bugner received the Distinguished Inventor Award, and in 1997, he was selected to participate in the Executive Development Program at the Tuck School of Business at Dartmouth. He currently holds over 50 U.S. Patents, and has authored over 20 scientific publications.

Michelle Oakland joined Eastman Kodak Company in 1997 following completion of a M.S. Degree in Paper Science and Technology from the Institute of Paper Science and Technology in Atlanta, GA. Her research includes support development for silver halide and inkjet products and measurement development for various media. Ms. Oakland had previously completed an undergraduate degree in Physics from Luther College in Decorah.