Evidence for Thermally Induced Fade and Yellow Stain Formation in Inkjet Photographic Prints

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Abstract

In our previous papers, we have shown how light, ozone, and humidity can affect the image stability of inkjet photographic prints. Previous attempts to measure the thermal dark fade of inkjet prints by the Arrhenius method have been confounded by dye migration. When tests are carried out at a constant, absolute humidity equivalent to 50% RH at 24°C (constant 13°C dew point), temperatures as high as 75°C can be utilized for many ink-media combinations without encountering significant dye migration. In this paper, we provide evidence for thermally induced changes to inkjet photographic prints, including fade, hue shift, and/or yellowing. Results will be discussed in the context of the Arrhenius relationship.

Introduction

In previous reports, we have discussed various aspects of light fade and humidity keep of inkjet prints made with different types of inks and papers.[1–4] The high sensitivity of certain combinations of ink and paper to ozone has also been reported.[5–7] For prints intended for indoor display in a home or office, there is a need to estimate useful print life with respect to all relevant environmental factors, including light, heat, humidity, and air pollutants such as ozone. With respect to the effects of heat on image stability, accelerated testing using an adaptation of methodology first described by Arrhenius[8] over a century ago has been used for traditional silver halide photographic materials.[9,10] 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 a pre-exponential factor.

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

Although the 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 the system being studied undergoes a phase transition.[11] An example of the latter might be found when a dye is absorbed in a polymer matrix that has a glass transition temperature, T_g, not far above ambient temperature. A further complication occurs when the T_g of the polymer matrix is also found to be a sensitive function of absorbed moisture, which might occur in response to changes in atmospheric humidity. In a previous study of thermal fade of inkjet prints, we found that by testing under constant absolute humidity (constant dew point) conditions, temperatures as high as 75°C could be employed without evidence of significant dye migration.[12]

One complication with the previous study was that low levels of ambient ozone confounded the results. We have since installed activated carbon filters in the HVAC system for the image stability testing area of the building, and we continually monitor for ambient ozone to ensure it remains below our detection limit of about 1.0 ppbv. In this present study, we have reinvestigated the thermal image stability of a broad variety of ink and media combinations using the free-hanging Arrhenius methodology under the conditions of constant dew point and in an ozone-free environment.

Materials and Methods

A list of the different inkjet media included in this study is given in Table 1. The printers/inks used for this study are listed in Table 2. All printers were equipped with current generation (late 2003) OEM-branded print heads and inks. The test targets and methods used in this study have been described previously.[1,12] One key difference between the present and previous studies is that we have installed ozone abatement filters and monitors to ensure that the Arrhenius studies are carried out in an ozone-free environment. The temperatures used for this study were 35, 45, 55, 65, and 75°C. The dew point was held at 13°C at each of these dry-bulb temperatures. In addition, a separate set of samples were kept in a dark, ozone-free chamber at 24°C, 50% RH (dew point: 13°C).

Table 1. Glossy inkjet media used in this study.

Brand	Description	Type*
HP	Premium Plus (Q1785A)	S
Epson	Premium Glossy (SO41667)	P
Canon	Photo Paper Pro (PR-101)	P
Hammermill	Jet Print Pro (10830-0)	P
Ilford	Printasia (199 9488)	S
Ilford	Gallerie (197 9293)	P
Kodak	Ultima Picture Paper (811 0579)	S

*S = swellable; P = porous

Table 2. Printers and inks used in this study.

Model	Ink Cartridge	Type
HP 7550	HP57/HP58	Dye
HP 3820	HP58	Dye
Epson 825	T008201	Dye
Epson 960	T033x20	Dye
Canon i550	BCI-3e	Dye
Canon i950	BCI-6	Dye
Lexmark Z65	#83 (18L0042) or #88 (18L0000)	Dye

Results and Discussion

General Observations

Consistent with our previous Arrhenius study at constant dew point,[11] we saw no evidence of humidity-induced dye migration over the temperature range covered in this study. We also verified that the test results were free of interference from ozone-induced fade. In addition to monitoring for ambient ozone with a recording ozone detector, we confirmed the absence of ozone-induced fade by checking the fade of known ozone-sensitive ink-media combinations, especially the Epson and Canon cyan dye-based inks and the HP magenta dye-based ink on any of the porous media. Figure 1 shows an example of the observed density change for a known ozone-sensitive ink-media combination over the complete range of temperatures employed for this study. It can be seen that there is very little, if any, loss of density for this dye under these conditions. Similar results were observed for the other known ozone-sensitive combinations. Lastly, for those ink-media combinations for which thermal fade was observed (see below), we crosschecked and found that these same combinations did not exhibit comparable ozone-induced fade under controlled ozone testing. Based on these observations, we have concluded that ozone interference was not an issue for the current study.

One concern that was raised when we first proposed a constant dew point-Arrhenius study is the possibility that the image-bearing layers may lose moisture as temperature is increased at constant dew point. Although we did not characterize the moisture isotherms for each of the different media included in this study, even at constant 50% RH there are differences in absorbed moisture as one traverses the 35–75°C range covered in this study. This is clearly evidenced by the inability to go higher than 50°C at 50% RH before significant dye migration is observed for many ink-media combinations. Nevertheless, as we discuss the results of this study, we will address the possible effects of sample desiccation on the observed densitometric changes.

Evidence for Thermal Dark Fade

Figures 2 and 3 are representative plots of %ΔD vs time for the pure yellow and yellow component of a neutral for one combination of ink and media that exhibits dye fade as a function of temperature. This combination represents a dye-based ink on the OEM-branded porous media. Similar results are observed for the yellow component of the red and green secondary color patches. Although the overall fade under the worst condition (75°C) is only about 10% at this point in the study, the initial fade rates can be determined from the slopes of the least-squares lines drawn through each temperature series, as shown in the Figures 2 and 3.

It should be noted that the cyan ink (Figure 1), as well as the magenta ink (not shown) from the same ink set, do not exhibit any significant fade under these same conditions. Therefore, the effect of thermal fade is more noticeable, visually, in the neutral and secondary colors than in the pure yellow. The other dye-based ink set (printer "C") from the same printer manufacturer gave very similar results. Yellow fade was observed to varying degrees for all of the porous media in this study. Several of the swellable media also exhibited some initial yellow fade with these same inks that have since leveled off, with no apparent temperature dependence.

Figure 4 is the Arrhenius plot of the natural log of the rate vs the reciprocal of temperature for the data contained in Figure 2. It can be seen that the data fit a good straight line, indicating that the observed loss of density is consistent with a thermally driven process. Using the least-squares equation for the data plotted in Figure 4, we can estimate that it should take approximately 7 years to reach a 30% loss of pure yellow from a 1.0 initial density at 24°C.

Figures 5 and 6 show two more examples of different ink-media combinations that exhibit apparent Arrhenius behavior. This is evidence that the issue of thermal dark fade for inkjet prints is not limited to just one manufacturer's inks, or to just one dye class. Again, to varying degrees, this behavior is observed only for the porous media included in this study.

Evidence for Heat-Induced Yellow Stain Formation

Evidence for heat-induced yellow stain formation in the background or D-min areas of inkjet papers has been previously reported,[13] but a broader study of glossy photo quality papers has not yet been published. Figure 7 is an Arrhenius plot of blue density increase (yellow stain) to D-min for one of the worst-case porous papers included in this study. The effect is clearly reproducible and independent of

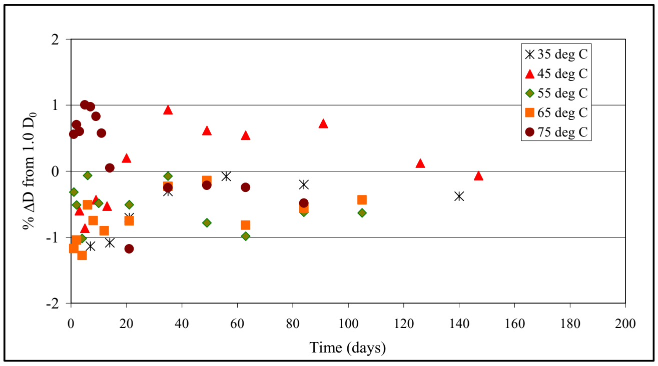

Figure 1. Percent change in density as a function of time for the combination of inkjet media "B" with the pure cyan ink from printer "D" across the range of temperatures used for this study.

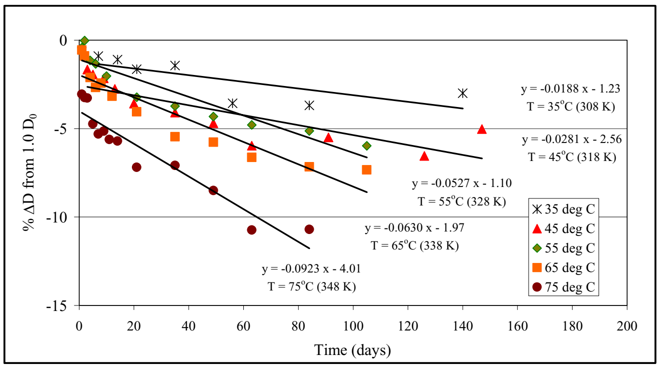

Figure 2. Percent change in density as a function of time for the combination of inkjet media "B" with the pure yellow ink from printer "D" across the range of temperatures used for this study.

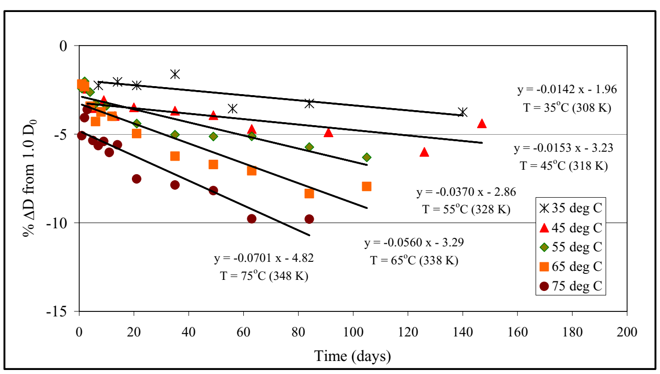

Figure 3. Percent change in density as a function of time for the combination of inkjet media "B" with the yellow component of a 1.0 neutral from printer "D".

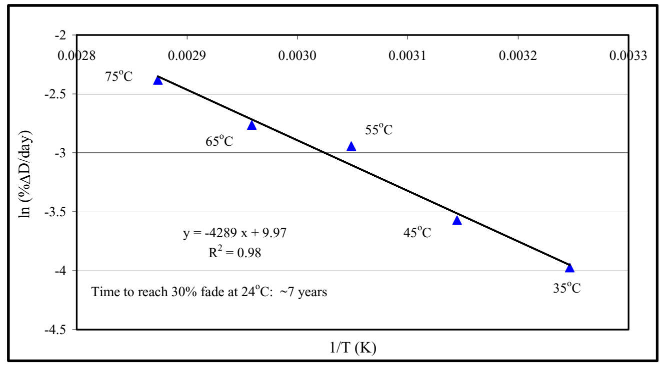

Figure 4. Arrhenius plot for the combination of inkjet media "B" with the pure yellow ink from printer "D".

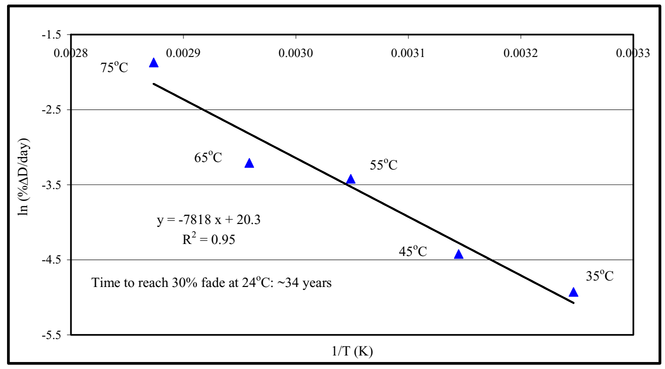

Figure 5. Arrhenius plot for the combination of inkjet media "C" with the pure magenta ink from printer "A".

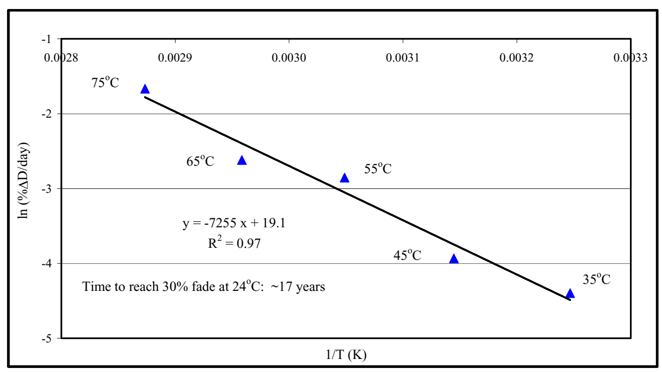

Figure 6. Arrhenius plot for the combination of inkjet media "D" with the pure cyan ink from printer "G".

ink set. All of the porous media exhibit heat-induced yellow stain formation to varying degrees. In several cases, the Arrhenius plots predict that a 0.10 blue density increase will be exceeded in less than 10 years. In fact, some of the samples kept at 24°C are already exhibiting noticeable levels of yellow stain that fall in line with the Arrhenius projection.

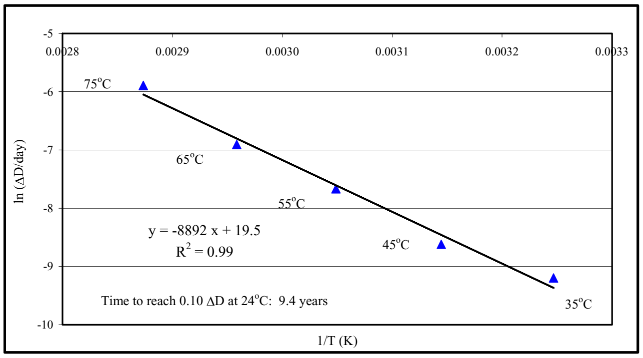

Figure 7. Arrhenius plot for the increase in D-min blue density (yellow stain formation) for media "F".

Evidence for Heat-Induced Hue Shift

Hue shifts can also occur as a result of heat-activated processes such as dye de-aggregation, dye migration, pigment polymorphism, thermochromism, etc. For phenomena such as these, Status A density changes may or may not be significant even though the colorimetric effect can be quite noticeable. For the dye-based printers included in this study, we see no clear evidence of heat-induced hue shift other than that caused by simple dye fade and/or D-min stain as discussed above. However, in a second round of Arrhenius testing currently underway, there is early evidence of a hue shift for at least one manufacturer's pigment-based yellow ink, which appears to follow Arrhenius kinetics. We will report on these interesting results separately.

Conclusions

The high degree of linearity of the Arrhenius plots shown in Figures 4–7 is a strong indication that variable moisture content within the image-bearing layer for these samples is not likely to be a significant cofactor. Conversely, there are several ink-media combinations for which somewhat erratic fade behavior is observed. It is uncertain whether this behavior is related to the variable moisture content or to more complex heat-induced phenomena specific to those ink-media combinations. Work is ongoing to better understand the significance of these results.

To our knowledge, this is the first time that the effect of heat on the image stability of inkjet photographic materials has been cleanly isolated from the other known environmental factors: light, humidity, and air pollutants, such as ozone. This is significant because some have claimed that if inkjet prints are framed behind glass (and thereby protected from the effects of air pollution and humidity), then one need only to be concerned the effect of light on long-term image stability.[14] Based on the results of the present study, it appears that the long-term effects of heat cannot be summarily dismissed as insignificant. Given the clear influence of both the ink and media on this phenomenon, it is imperative that any testing intended to produce a realistic print-life claim must be include some form of Arrhenius or other thermal fade testing in order to substantiate that heat is or is not a significant environmental factor.

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Biography

Douglas Bugner received a B.S. in Chemistry from The Ohio State University in 1975, an M.S. in Organic Chemistry from UCLA in 1980, and a Ph.D. in Organic Chemistry from UCLA in 1982. Dr. Bugner spent the first 10 years of his career at Eastman Kodak Company researching toners and photoconductors for electro-photographic applications. 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 Commercialization Lab, Inkjet Systems Division and Director of Product Delivery, Inkjet Media, Digital and Film Imaging Systems.