Ozone Concentration Effects on the Dark Fade of Inkjet Photographic Prints

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Abstract

ANSI Standard IT9.9-1996 is commonly recommended for predicting dark storage print life for color photographic materials. This methodology focuses primarily on measurement of density changes that occur as a function of temperature at 50% ± 3% relative humidity (Arrhenius methodology). An additional factor in the dark stability of inkjet photographic prints is the presence of ozone. Current practical tests utilize a relatively high concentration (5 ppm) of ozone for short periods of time at ambient temperatures to predict what might occur for longer exposures at lower concentrations. However, ambient ozone levels are typically well under 0.1 ppm (100 ppb). The objective of this paper is to explore the effect of ozone concentration on inkjet photographic prints produced with commercially available desktop inkjet printers. The primary focus will be on current dye-based inks printed onto both porous and non-porous photo-quality papers. We will examine the reciprocity relationship between ozone concentration and the duration of exposure to ozone.

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. Recent reports have discussed various aspects of light fade[1] and humidity[2] keep of inkjet prints made with different types of inks and papers. 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.

In our preceding paper,[5] we discussed the problems associated with the estimation of dark fade at room temperature using the standard Arrhenius approach.[6] For certain combinations of porous receivers with cyan inks, the fade is rapid enough at temperatures near ambient that accelerated testing is not necessary. For swellable, non-porous receivers, the fade is slow even at 75°C. Arrhenius testing will likely take years to produce enough fade over a reasonable temperature range to be predictive. Although the mechanisms of dark fade for inkjet prints made on swellable receivers have not been reported, ozone-induced dark fade is one possible mechanism.

Another way to accelerate the rate of a reaction is to increase the concentration of one of the reactants, e.g., ozone. As with accelerate light fade, there needs to be a reciprocal relationship between ozone concentration, $[O_3]$, and time of exposure in order to use the results of accelerated tests at higher $[O_3]$ to predict how long it will take to produce the same amount of fade at lower $[O_3]$.

In contrast to the volumes of data available on the levels of ozone in the outside air, there has been very little reported with respect to the ambient levels of ozone inside homes and offices. Studies have shown that interior levels of ozone are generally lower than the corresponding exterior levels.[7] There also appears to be a significant diurnal dependence of ozone concentration, at least in outdoor air.[7] Based on the limited data available, it seems reasonable to assume that typical average indoor levels of ozone should be less than 100 parts per billion (ppb) by volume, and will most likely be under 50 ppb.

For the purposes of this study, we will compare the rates of ozone-induced dark fade of inkjet prints exposed to 100 and 1000 ppb (0.1 and 1.0 ppm). One objective of this study is to establish a direct link between the presence of ozone in the atmosphere and dye fade. Another objective is to establish whether a reciprocal relationship exists between the ozone concentration and the duration of ozone exposure.

Materials and Methods

Materials

Two different types of inkjet receivers combined with two different ink sets were studied. The receivers included a representative porous formulation from Epson (Premium Glossy Photo Paper, SO41286) and a representative non-porous (swellable) formulation from KODAK (Premium Picture Paper). Both receivers are coated on similar photo quality resin-coated base papers. The color ink sets were those provided with the Hewlett-Packard PhotoSmart P1000

series (#78 color cartridge) and the Epson Stylus Photo 780/870/875/890/1270/1280 series of inkjet printers (T008 color cartridge). The inkjet receivers and inks used in this study are representative of materials that were commercially available during mid-2000.[8]

Methods

The ozone treatment unit used for this study comprises an ozone generator (Dell #Z0151) plumbed to a custom-built Plexiglas enclosure. The output of the ozone generator was diluted to the desired level (either 0.1 or 1.0 ppm by volume) with dry nitrogen, and then humidified to 50% relative humidity by bubbling through water. The treatment enclosure is in the shape of a 45-cm cube with two inlets on opposite corners at the bottom. There is a baffle plate about 2.0-5.0 cm from the bottom to uniformly distribute the gas flow. The overall flow rate was 30 L/min. Ozone concentration was monitored at the outlet and was maintained to within ±10% of aim during the course of these studies. The temperature of the unit was monitored at 20°C ± 3°. The unit was kept in a darkened fume hood in order to minimize any light-induced fade.

The test targets used in this study were similar to those described previously.[1c] The test targets were subjected to either 0.1 or 1.0 ppm of ozone in the apparatus described above and were monitored at specified time intervals by status A densitometry (Gretag/Macbeth Spectro Scan T 3.273 spectrophotometer/colorimeter). An extra set of test targets was kept in the dark under ambient conditions and monitored for changes in density during the course of the study. Changes are reported as 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 was graphically interpolated to $D_o = 1.0$ above D_{min}.

Results and Discussion

Background

Previous studies have shown that the dark dye stability of inkjet prints is sensitive to both temperature and humidity under ambient atmospheric conditions.[2,5] At relative humidities greater than about 60% some density gain due to dye migration is observed for many combinations of dye-based inks and coated inkjet papers.[2] On the other hand, even at 24°C and 50% relative humidity, certain combinations of cyan dyes on porous inkjet papers display measurable fade, which can be accelerated by temperature and/or humidity.[2,5] In both studies, keeper prints kept in the dark out of direct air flow at 20—25ºC and 45–55% RH showed negligible dye fade or migration. Attempts to accelerate the dark fade using Arrhenius methodology gave mixed results. In these previous studies, no attempts were made to control the level of atmospheric ozone adjacent to the surface of the test samples.

In a separate study of reciprocity failure in accelerated light fade tests, it was shown that under an ozone-free atmosphere, the rate of observed fade at the lower intensity condition for the Epson 900 cyan and magenta inks was consistently lower when ozone was excluded from the air.[9] This effect was most noticeable on porous receivers, but was also observed to a much lesser degree for non-porous receivers as well.

It is against this background that this study was conceived. We chose to hold temperature and relative humidity constant at 25°C and 50%, and vary the concentration of ozone in the atmosphere adjacent to the samples. The lower concentration of 0.1 ppm was chosen as representative of a high level of indoor ozone. The higher level of ozone was chosen to be 10X the lower level, or 1.0 ppm.

Porous Receiver Results

The combination of Epson Premium Glossy Photo Paper with the Epson Stylus Photo 870 cyan ink was one of the first ink-receiver combinations to be flagged for ozone-induced dark fade.[3] Figure 1 is a plot of the cyan density loss as a function of *cumulative* ozone exposure (ozone concentration x duration of the exposure, in ppm-hr) for this ink-receiver combination exposed to 0.1 and 1.0 ppm ozone. Consistent with previous reports, the cyan dye fades rapidly at either level of ozone: 30% of the cyan density is already lost within the first 70 hr at 0.1 ppm ozone.

Figure 2 is a similar plot for the Epson 870 magenta ink on the Epson Premium Glossy Photo Paper. In this case, the rate of fade is not as rapid as with the cyan ink, and any deviation from reciprocity is minimal. The Epson yellow ink on the Epson porous receiver was even more stable, with only about a 5% density loss over the first 200 ppm-hr at either ozone concentration.

With the Hewlett-Packard ink set, both the cyan and magenta inks faded rapidly at both ozone concentrations, similar to the Epson 870 cyan ink on this receiver. The fade rate for the Hewlett-Packard yellow ink was similar to the Epson magenta ink and appeared to be slightly faster at 0.1 ppm than at 1.0 ppm.

Non-Porous Receiver Results

The combination of either ink set with the KODAK Premium Picture Paper, a non-porous, gelatin-based receiver, was much more stable to ozone. The Epson cyan ink was the most sensitive on this receiver (Fig. 3). Note that there appears to be significant reciprocity failure for the Epson cyan ink of the non-porous receiver. This was also observed for the Epson magenta ink on this receiver, which faded by about 13% after 200 ppm-hr of cumulative exposure at 1.0 ppm ozone concentration, but only about 7% at the same cumulative exposure at 0.1 ppm ozone.

In contrast, the Hewlett-Packard cyan and magenta inks on the Kodak paper did not show any significant deviation from reciprocity, with both inks at both ozone concentrations exhibiting about 10% dye fade after 200 ppm-hr. Neither yellow ink faded sufficiently at either ozone concentration to assess reciprocity on this paper.

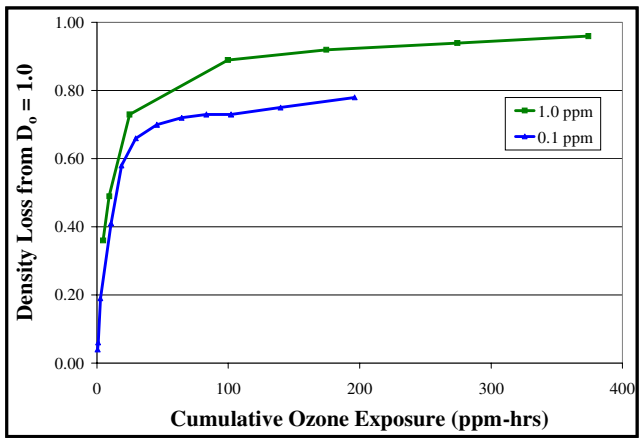

Figure 1. Density loss vs cumulative ozone exposure for the Epson 870 cyan ink on the Epson Premium Glossy Photo Paper.

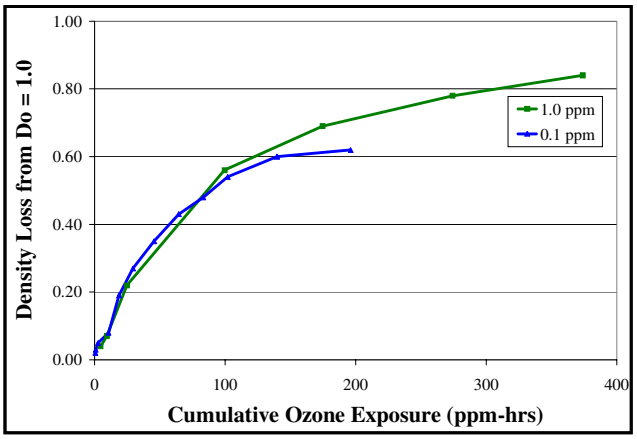

Figure 2. Density loss vs cumulative ozone exposure for the Epson 870 magenta ink on the Epson Premium Glossy Photo Paper.

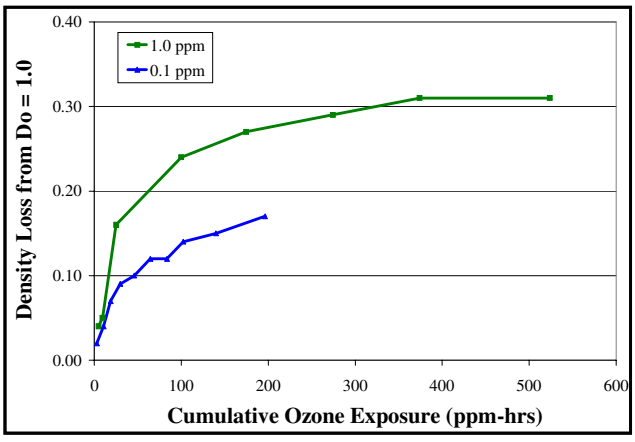

Figure 3. Density loss vs cumulative ozone exposure for the Epson 870 cyan ink on the KODAK Premium Picture Paper.

Discussion

The results of this study confirm previous reports of rapid, ozone-induced dark fade on the Epson Premium Glossy Photo Paper with the Epson 870 cyan ink. In addition, the Hewlett-Packard cyan and magenta inks are also prone to rapid fade on this receiver. Because of the high rate of fade at even 0.1 ppm ozone, there is little need to further accelerate the rate of fade by increasing the ozone concentration.

The Hewlett-Packard yellow and the Epson magenta inks faded more slowly on the Epson porous receiver. Comparison of the fade rates at the two ozone levels reveals nearly reciprocal behavior for both combinations.

If one assumes that the first color to experience a 30% loss of density represents and end-of-life condition then prints made on the Epson porous receiver with either ink set fail within about 10 ppm-hr of cumulative ozone exposure at 0.1 ppm ozone. This would translate to about 500 hr at an ambient level of 0.02 ppm of ozone assuming reciprocity exists between 0.1 and 0.02 ppm ozone concentrations.

The results for the non-porous Kodak receiver were quite different. Here the Epson cyan dye is more sensitive to ozone than the Hewlett-Packard cyan and magenta dyes. There is also significant deviation from reciprocity for the Epson cyan dye on the Kodak paper, with a lower rate of fade occurring at 0.1 ppm than would be predicted by the 1.0 ppm data. This suggests that it will be difficult to base predictions of ambient ozone-induced dark fade on accelerated tests that use much higher levels of ozone, at least for this example of a non-porous receiver.

The observed deviation from reciprocity can be explained if the rate of diffusion of ozone into the receiver is (a) slow relative to the rate of reaction of ozone with the dye and (b) dependent upon ozone concentration.

One general observation is that the rates for ozone-induced fade do not cleanly follow either first or second order kinetics, as was observed for the light fade rates of hundreds of ink-receiver combinations.[1c] In many cases, such as the one depicted in Figure 3, there appears to be a rapid initial rate of fade, followed by a much slower, long term fade rate. Such behavior might be expected if the dyes are partitioned between two local environments, one of which being more accessible and/or reactive to ozone than the other.

Summary

The effect of ozone concentration on the rate of fade of inkjet prints made with two sets of inks on two types of receivers was examined. For a porous receiver the rate of fade was rapid with both cyan dyes, and with one of the magenta dyes. The fade rate was so fast at even 0.1 ppm ozone that accelerated testing at higher ozone concentrations is not required. With this same receiver, slower rates were observed for the other dyes, and deviation from reciprocity was minimal.

For a non-porous receiver, the ozone-induced dark fade was much slower. The Epson cyan ink faded that fastest, but

displayed a measurably slower rate at the lower ozone concentration. For the Hewlett-Packard ink set on the non-porous receiver, the cyan and magenta inks exhibited similar rates of ozone-induced fade to each other, with both being noticeably slower than the Epson cyan ink. In these cases, the reciprocity was quite good. These results pose difficulties with the potential of using high ozone concentrations to generally predict the rate of fade at ambient ozone concentrations for the Epson ink set on this receiver.

Work is ongoing with a broader selection of both porous and non-porous inkjet receivers as well as with additional manufacturers' ink sets in order to understand how general these observations are.

Acknowledgments

The authors wish to acknowledge the assistance of Peter Artz and Dan Zaccour for their help in carrying out this study.

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. M. Oakland, D. E. Bugner, R. Levesque, and P. Artz, Proc. NIP17 (2001).
6. ANSI/NAPM IT9.9 (1996).
7. Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., M. Howe-Grant, ed. (John Wiley and sons, New York, 1996) vol. 17, pp. 953-994.
8. Epson has since replaced this formulation with one claimed to be more resistant to ozone: see The Hardcopy Supplies Journal, 7(1) 25 (2001).
9. D. E. Bugner, "Inkjet Media," presented at the Specialty Papers and Films 2001 Diamond Conference, Hilton Head Island, SC, February 25-27, 2001.

Biographies

Douglas Bugner received his BS in Chemistry from the Ohio State University in 1975, an MS 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 an MS 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, IA.