Update on Reciprocity Effects for Accelerated Ozone Fade Testing of Inkjet Photographic Prints

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Abstract

Inkjet photographic prints, especially those printed with dye-based inks on porous media, are subject to rapid dye fading when exposed to ambient levels of ozone. The rate of fade is much slower with dye-based inks on swellable media and, in general, with pigment-based inks. As part of an ongoing effort to establish a standardized test method to accelerate the rate of ozone-induced fade, we have been exploring the use of high concentrations of ozone under controlled conditions. A key assumption, necessary to estimate the corresponding rate of fade at much lower, ambient levels of ozone, is that there is a reciprocal relationship between ozone concentration and time of exposure. In this presentation, we will provide an update on our previous report[1] of various ink-media combinations with respect to ozone reciprocity effects.

Introduction

With the recent introduction of photographic quality inkjet printers 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 the effects of light,[2-12] heat and humidity,[6,13-16] and air pollutants,[1,6,9-11,17,18] such as ozone, on inkjet photographic 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 publications.[19-20]

Two common ways of accelerating a chemical reaction, such as the oxidation of a dye by ozone are to: (a) increase the concentration of one or more of the reactants, and/or (b) to increase the temperature of the reactants. The latter approach is the basis of several current standard methods of assessing "dark" stability,[21] including the well-known Arrhenius method.[22] It has been shown that the application of these methods to inkjet prints, however, can be problematic.[15]

An alternate approach to accelerating the ozone-induced dark fade of a print is to increase the concentration of ozone in the atmosphere adjacent to the print surface. As with accelerated light fade testing where elevated light levels are used to accelerate the rate of fade, there needs to be a reasonable degree of reciprocity between ozone concentration, [O_3], and time of exposure. Otherwise, the results of accelerated tests at higher [O_3] cannot be used to reliably predict the extent of fade over longer periods of exposure at lower [O_3].

The primary objective of this study is to compare the kinetics of ozone-induced dark fade of inkjet prints exposed to 100 and 1000 ppb (0.1 and 1.0 ppm) in order to establish whether a reciprocal relationship exists between the ozone concentration and the duration of ozone exposure. In this report, we describe the results of these experiments and discuss the applicability of this test method to the accelerated testing of ozone-induced dark fade of inkjet photographic prints.

Materials and Methods

Materials

Unless otherwise noted, the inkjet receivers and inks used in this study are representative of materials that were commercially available during the second half of 2001. The inks used in this study were those provided by the printer manufacturers for the Epson Stylus Photo 890, the Canon S800, and the Hewlett-Packard DeskJet 990 inkjet printers. The cyan, magenta, and yellow colorants in these ink sets are all dyes.

The various ink-receiver combinations included in this study are classified as either being "fast fading" or "slow fading," based on the nature of the ink-receiving formulation. The following glossy microporous inkjet receivers are considered fast fading: Office Depot Premium Photo Paper, NCR Deluxe Photo Paper, Epson Premium RC Photo Paper (2000 and 2001 versions), Konica QP Professional Photo Paper, and Canon Photo Paper Pro. The following swellable inkjet receivers are considered slow fading: KODAK Premium Picture Paper and Hewlett-Packard Premium Plus Photo Paper. The OEM-branded receivers were only tested in combination with their respective ink sets. All other receivers were tested against all three ink sets.

Methods

The ozone treatment unit has been described previously.[1] The temperature of the unit was maintained at 21°C ± 3º, the relative humidity was held at 50 ± 5%, and the flow rate was 50 L/min. Two identical treatment units were used for this study; one was maintained at $[O_3] = 0.1$ ppm and the other at $[O_3] = 1.0$ ppm. The units were covered with a thick, dark cloth and kept in a darkened fume hood in order to avoid any light-induced fade.

Test targets used in this study were similar to those described previously.[1] Replicate test targets for each ink-receiver combination were subjected to ozone as outlined above and were monitored at specified time intervals by status A densitometry (Gretag/Macbeth Spectro Scan T 3.273 spectrophotometer/colorimeter). Results for the replicate samples were averaged, and changes are reported as density loss (ΔD) from a 1.0 initial density. Data analysis was carried out as previously described.[1]

Results and Discussion

Background

Previous studies have shown that the dye stability of inkjet prints is sensitive to both temperature and humidity under ambient atmospheric conditions.[6,13-16] At relative humidities greater than 60% at room temperature, many combinations of dye-based inks and coated inkjet papers experience dye migration as evidenced by density gain and/or loss of sharpness.[13] On the other hand, even at 24°C and 50% relative humidity, certain dyes on porous inkjet papers display noticeable density loss, which can be accelerated by temperature and/or humidity.[15,23] These same ink-paper combinations have been reported to be prone to fade in the presence of low levels of ozone.[1,18,23]

In a separate study on the apparent light fade reciprocity for inkjet prints, it has been shown that the primary cause of observed reciprocity deviations is most likely due to ozone-induced dark fade.[12] This effect was most noticeable on porous ink-receptive layers but was also observed to a lesser degree for swellable receivers as well. A recommendation based on this study is to maintain an atmosphere within the light-fade apparatus that is free from ozone or other pollutants, isolating the effects of light from ozone.

Although the impact of ozone on the fade of inkjet prints is most noticeable for certain combinations of dye-based inks on porous media, recent studies have shown that dye-based inks on swellable media, as well as pigment-based inks, are also susceptible to ozone-induced fade, albeit at a much slower rate. Nevertheless, over long periods of cumulative exposure to low levels of ambient ozone, it can be expected that inkjet prints made on these slower fading inkjet systems will fade to a noticeable, if not an intolerable, degree. Thus, there is a need for a method to accelerate the rate of ozone-induced fade that can be used to project the long-term effects of low levels of ambient ozone.

The usefulness of an accelerated test method that depends on higher than ambient levels of ozone relies on the existence of a reciprocal relationship between ozone concentration and time of exposure. Stated another way, the extent of fade should be directly related to the cumulative exposure as measured by the product of ozone concentration, times the duration of exposure, independent of the ozone concentration.

In our previous study,[1] we had flagged the possibility that deviations from reciprocity might be an issue for accelerated ozone testing at high ozone concentrations. In this study, we have included a larger number of ink-media combinations, and we have also increased the frequency at which we monitor the test samples during the initial stages of fade to better quantify the extent of reciprocity failure.

Fast Fading Systems

Although the faster fading dye-porous inkjet systems do not require higher than ambient concentrations of ozone in order to exhibit objectionable levels of fade in just a few weeks or months,[18] it is of interest to understand whether reciprocity over the range of concentrations explored for this study. This is in anticipation that more ozone-resistant dyes will be invented in the future and that, in the future, slower fading dye-porous systems will need some level of acceleration in order to produce results in a meaningful time interval.

Figures 1 and 2 compare the rate of density loss at 0.1 and 1.0 ppm of ozone for the Epson Stylus Photo 890 cyan, magenta, and yellow inks on two versions of Epson Premium Glossy Photo Paper. Figure 1 shows the result for the original version (2000) and Figure 2 shows a more recent version (2001) that contains a sacrificial anti-ozonant additive (Figure 2). With respect to reciprocity, it can be seen that both systems are reasonably well behaved. It is interesting to note that the paper with the sacrificial anti-ozonant displays a delayed onset of fade but, at longer cumulative exposures, both papers display comparable levels of density loss. Note also that the yellow ink in both cases is essentially insensitive to ozone-induced fade.

Figure 3 shows the same ink-paper combination as Figure 1 but, in this case, the fade of each of the primaries combined in a neutral patch is plotted. It can be seen that reciprocity is again quite reasonable, and the fade rates of the mixed primaries are quite similar to those of the pure primaries. This suggests that there is little dye-dye interaction in which one colorant might protect and/or destabilize another colorant in the mixture. It further suggests that ozone is not a limiting reagent at either concentration.

The results for many of the other fast fading systems included in this study are, for the most part, similar. However, there are several systems for which there appears to be a significant deviation from reciprocity, especially with the cyan ink, and, to a lesser extent, the magenta ink. One such system is illustrated in Figure 4. This same photo paper also displays similar reciprocity failure for the HP 990 ink set but not for the Epson 890 inks.

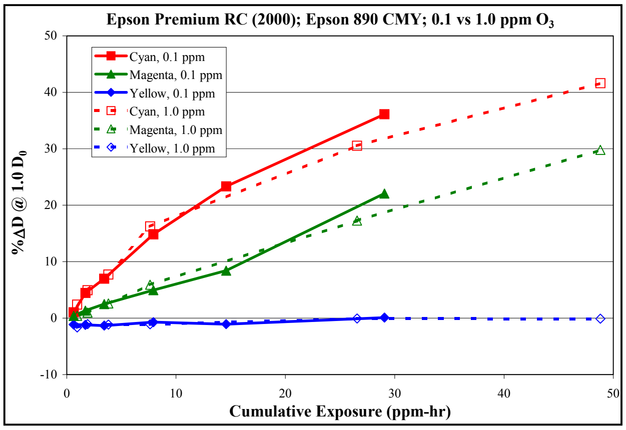

Figure 1. Comparison of the fade kinetics of the Epson 890 pure primary colors on the Epson Premium RC Photo Paper (2000) at 0.1 and 1.0 ppm ozone.

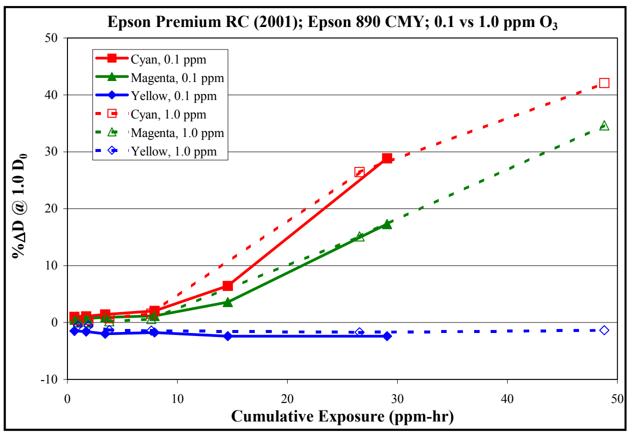

Figure 2. Comparison of the fade kinetics of the Epson 890 pure primary colors on the Epson Premium RC Photo Paper (2001) at 0.1 and 1.0 ppm ozone.

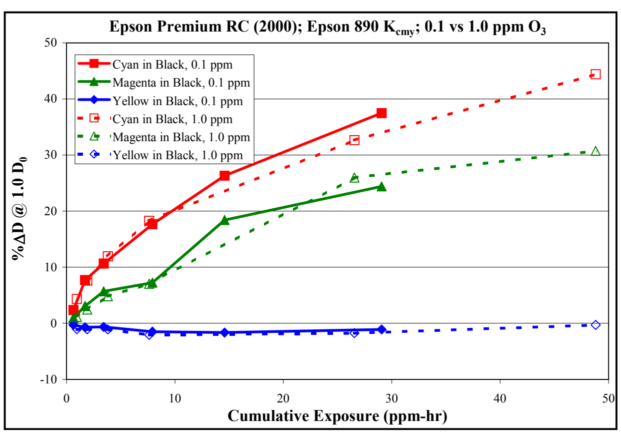

Figure 3. Comparison of the fade kinetics of the Epson 890 mixed primary colors on the Epson Premium RC Photo Paper (2000) at 0.1 and 1.0 ppm ozone.

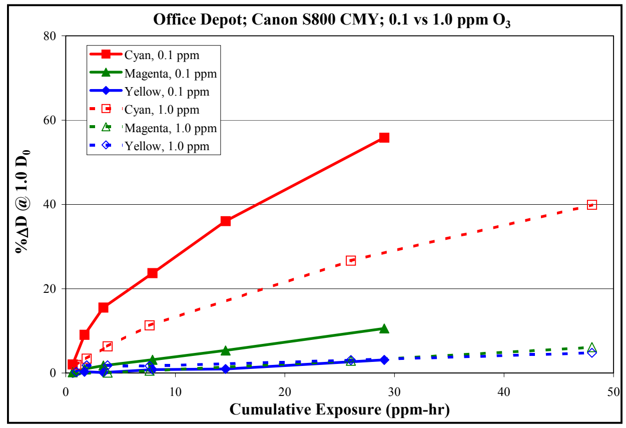

Figure 4. Comparison of the fade kinetics of the Canon S800 pure primary colors on the Office Depot Premium Photo Paper at 0.1 and 1.0 ppm ozone.

Slow Fading Systems

Of the four slow fading ink-media combinations, only one exhibits good reciprocity between 0.1 and 1.0 ppm ozone (Figure 5), while the others display apparent deviations from reciprocity (for example, see Figure 6). Figure 7 shows the same system as Figure 5, illustrating the effect of ozone on the mixed primaries in a neutral patch. Note the change in the x-axis scale for these graphs compared to Figures 1-4.

As with the fast fading systems, in those cases for which apparent reciprocity failure is present, the amount of fade observed for the 0.1 ppm ozone level is greater than those observed for the 1.0 ppm level at equivalent cumulative exposures. One difference between the fast fading and slow fading systems included in this study is that, for the latter, the mixed primaries consistently fade slower than the pure primaries.

Discussion

At this time, we have no good explanation as to why apparent reciprocity failure is observed for some systems, such as those shown in Figures 4 and 6. However, in each case where deviations from reciprocity have been observed, the results for the 0.1 ppm level of ozone display greater degrees of fade than the 1.0 ppm level at equivalent cumulative exposures. For these systems, this suggests that there may be another environmental factor that is causing the inks to fade, in addition to ozone. The longer duration required for the 0.1 ppm test to reach the same cumulative exposure as the 1.0 ppm condition would result in a greater contribution to the overall observed fade by this unidentified fade factor.

From a practical perspective, the issue of reciprocity with respect to [O_3] and time is of greater concern for slow fading systems for which some form of accelerated test is desired. This is especially true if long-term print life projections are the goal. One way of assessing the degree of apparent reciprocity failure is to calculate the reciprocity factor, R_f, defined as the ratio of the change observed at 0.1

ppm ($\Delta D_{0.1\ ppm}$) to that observed at 1.0 ppm ($\Delta D_{1.0\ ppm}$) at a given cumulative exposure:

$$R_f = [\Delta D_{0.1\ ppm} / \Delta D_{1.0\ ppm}]$$

Table 1 compares the calculated reciprocity factors for the pure cyan patches on a common swellable inkjet receiver. Although cumulative exposure of 658 ppm-hr was chosen for this calculation, R_f was found to be essentially constant for cumulative exposures between 400 and 800 ppm-hr (see Figure 8). It can be seen that with the exception of the combination of KODAK Premium Picture Paper and Epson Stylus Photo 890 inks, the degree of reciprocity failure is in the 20-30% range. It is interesting to note that the Epson 890 inks also showed very little deviation from reciprocity for the fast fading systems, suggesting that there may be something unique about the Epson cyan ink formulation with respect to ozone reciprocity. Although the cause of this apparent reciprocity failure is not clear at this time, further experiments are underway that we hope will help us better understand this phenomenon.

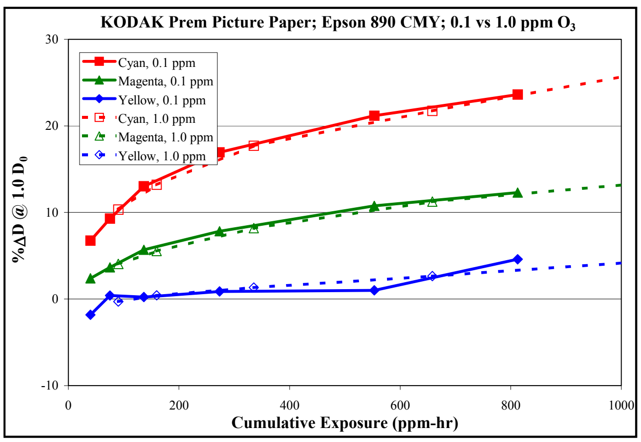

Figure 5. Comparison of the fade kinetics of the Epson 890 pure primary colors on the KODAK Premium Picture Paper at 0.1 and 1.0 ppm ozone.

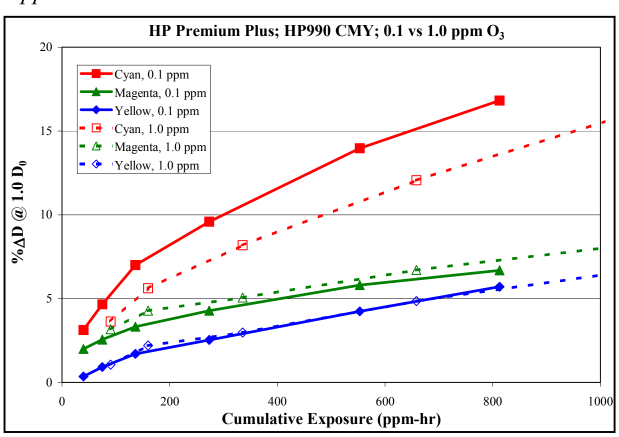

Figure 6. Comparison of the fade kinetics of the HP 990 pure primary colors on the HP Premium Plus Photo Paper at 0.1 and 1.0 ppm ozone.

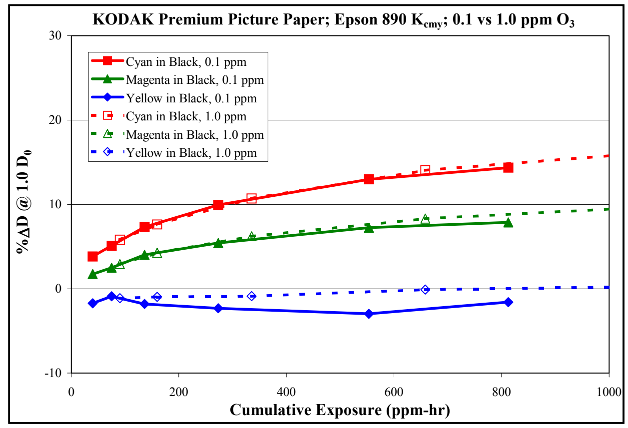

Figure 7. Comparison of the fade kinetics of the Epson 890 mixed primary colors on the KODAK Premium Picture Paper at 0.1 and 1.0 ppm ozone.

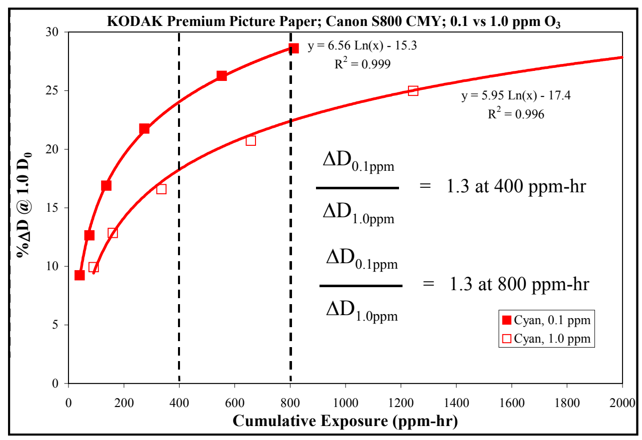

Figure 8. Comparison of the fade kinetics of the Canon S800 cyan ink patch on the KODAK Premium Picture Paper at 0.1 and 1.0 ppm ozone illustrating the calculation of R_f.

Table 1. Observed reciprocity factors for the cyan patches on a common swellable receiver at a cumulative exposure of 658 ppm-hr.

	%ΔD at 0.1 ppm	%ΔD at 1.0 ppm	R_f
KODAK Premium Picture Paper Epson 890	22	22	1.0
KODAK Premium Picture Paper Canon S900	27	21	1.3
KODAK Premium Picture Paper HP 990	20	15	1.3

Summary

The effect of ozone concentration on the rate of fade of inkjet prints was examined. Although the rate of fade for the porous receivers included in this study is so fast at even 0.1 ppm ozone that accelerated testing at higher ozone concentrations is not required, we did see some evidence of apparent reciprocity failure for some of these fast fading systems.

For nonporous receivers, the ozone-induced dark fade is much slower. For the Epson inks, good reciprocity was observed. For the HP and Canon inks, the samples treated at 0.1 ppm ozone faded approximately 20-30% more at equivalent cumulative exposures than replicate samples treated at 1.0 ppm.

The cause of this observed reciprocity failure is unknown at this time. Until this phenomenon is better understood, it is critical that comparative testing be done at more than one ozone concentration, with the lower level as close as possible to ambient as is practical. Ongoing studies include the longer term fading at lower levels of ozone, as well as an investigation of reciprocity effects on pigmented ink systems.

Acknowledgments

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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 is currently Senior Laboratory Head, Desktop Commercialization Laboratory, Inkjet Materials and Printing Systems Division, Research and Development, and Director of Product Development, Digital Consumables, Digital and Applied Imaging, Eastman Kodak Company.

In 1994, Dr. Bugner received the Distinguished Inventor Award, and in 1997, he completed the Executive Development Program at the Tuck School of Business at Dartmouth. He currently holds 58 U.S. Patents, and has authored over 30 scientific publications. He is a member of the American Chemical Society, the Society for Imaging Science and Technology, and the Project Management Institute.