Ozone Concentration Effects on the Dark Fade of Ink jet Photographic Prints[1]

Douglas Bugner▲†, Richard Van Hanehem, Michelle Oakland, Peter Artz, Daniel Zaccour, and Rick Levesque
Research & Development Laboratories, Eastman Kodak Company, Rochester, New York, USA

Ambient levels of ozone have been reported to be a factor in the dark stability of ink jet photographic prints. Current practical tests utilize a relatively high concentration (5–10 ppmv) 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 ppmv (100 ppbv). In this article we describe a custom built ozone chamber with which we are able to explore the effects of chamber design, flow rate, relative humidity, and ozone concentration on the kinetics of fade for ink jet photographic prints.

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Introduction

With the proliferation of so-called photographic quality printers targeted at owners of consumer digital cameras, attention has now focused on improving the image stability and physical durability of digital photographic output. Recent reports have discussed the effects of light,[2–14] heat and humidity,[6,13,15–19] and air pollutants,[1,6,9–11,20–24] such as ozone, on ink jet photographic prints made with different types of inks and papers. The hypersensitivity of certain combinations of ink and paper to ozone has also been noted in the trade.[25]

Ozone, also known by the chemical symbol O_3, is a highly reactive form of oxygen that occurs naturally at relatively low levels in the stratosphere.[26] At ground level, ozone is primarily caused by the action of sunlight on automotive exhaust gases or other sources of hydrocarbons in the presence of oxides of nitrogen (NO_x).[26,27] Other potential sources of ozone in the home and workplace include photocopiers and electrostatic precipitators. Studies in Los Angeles[28,29] and elsewhere[30,31] in the 1970s established a clear link between indoor and outdoor levels of ozone. In the Los Angeles study, indoor ozone levels approaching 0.2 ppmv were reported in several office buildings and at least one home. One conclusion of these studies is that the most common source of indoor ozone is by infiltration of polluted outdoor air through doors, windows, and air conditioning intake vents. Because the half-life of ozone indoors is on the order of minutes, ambient levels of ozone typically drop below detection limits within about one hour when the supply of ozone is eliminated.[28] It should be mentioned, however, that the production and use of ozone as an air and water disinfectant is a common industrial practice[26] and has been recently promoted as a cure for indoor air pollution in homes.[32] To our knowledge, the generation of ozone for indoor air treatment is not widespread at this time.

Although ozone induced fade of photographic colorants is a relatively recent topic of discussion, the stability of textile dyes to airborne contaminants was first documented in the mid-1930s.[33] Thus, the term "gas-fading" was first coined to describe the sensitivity of certain fabric dyes to the by-products of combustion, identified as oxides of nitrogen, or NO_x.[34] Ozone as a factor in the stability of fabric dyes was discovered when dyes that had been patented[35] for their resistance to gas-fading by NO_x were found to fade rapidly in cities that were later found to have elevated concentrations of ozone.[36] Controlled experiments in the laboratory confirmed ozone as the causative agent.[36] The term "O-fading" was applied to this phenomenon to differentiate it from the effects of gas-fading caused by NO_x.

A more recent study on the effect of atmospheric pollutants on fabric dyes compared O_3, NO_x, and sulfur dioxide (SO_2) and concluded that O_3 and NO_2 were the most damaging, followed by SO_2 and NO in that order.[37] Several studies on the combined effects of ozone and humidity have noted that most fabric dyes fade faster as humidity is increased at constant ozone concentration.[38,39] Similar trends for ink jet dyes with respect to their relative sensitivity to the various pollutant gases[9,11,22] and the accelerating effect of humidity[20] have been recently reported.

Because of its high reactivity and relatively short half-life, ozone primarily affects photographic prints that are on display, as opposed to those that are being stored. One solution to fade caused by ozone or other indoor pollutants is to protect the print by displaying it behind glass, or by post-treating the surface of the print with a laminate or over-spray. However, this requires

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▲ IS&T Member

†Corresponding Author: D. Bugner, Douglas.bugner@kodak.com

additional steps and expense, and it is not appropriate for all situations. In fact, it has been found that the photostability of certain dyes is actually reduced when atmospheric oxygen is kept from the surface of a chromogenic photographic print.[40,41]

In the meantime, advances continue to be made in improving the ozone resistance of the inks and ink receptive coatings that comprise an ink jet photographic print.[18,42] Although some of the worst ink jet systems have been observed to fade within a matter of days or weeks when exposed to ambient levels of ozone, the ozone stability of the best ink jet systems is approaching that exhibited by other imaging technologies, such as thermal dye transfer (TDT), electrophotography (EP), and silver halide (AgX).[43,44] For these systems, some form of accelerated testing is required in order to obtain measurable levels of fade in a meaningful period of time.

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 environment. The latter approach is the basis of several current standard methods of assessing "dark" stability,[45] including the well-known Arrhenius method.[46] It has been shown that the application of these methods to ink jet prints, however, can be problematic.[17]

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 reliably to 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 ink jet prints exposed to 100 and 1000 ppbv (0.1 and 1.0 ppmv) in order to establish whether a reciprocal relationship exists between the ozone concentration and the duration of ozone exposure. In order to accomplish this objective, we first designed a test chamber, demonstrated its utility, and determined the experimental variability. We also investigated the sensitivity of the observed kinetics to the relative humidity and flow rate of a mixture of 1.0 ppmv ozone in nitrogen. 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 ink jet photographic prints.

Materials

Unless otherwise noted, the ink jet 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 Epson C80, the Canon S800, and the Hewlett-Packard DeskJet 990 ink jet printers. The cyan, magenta, and yellow colorants in these ink sets are all dye-based except the Epson C80, which uses pigments.

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. Pigmented inks, in general, are considered slow fading on any type of ink jet receiver. For the dye-based systems, the following glossy microporous ink jet 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 ink jet 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 manufacturers' ink sets.

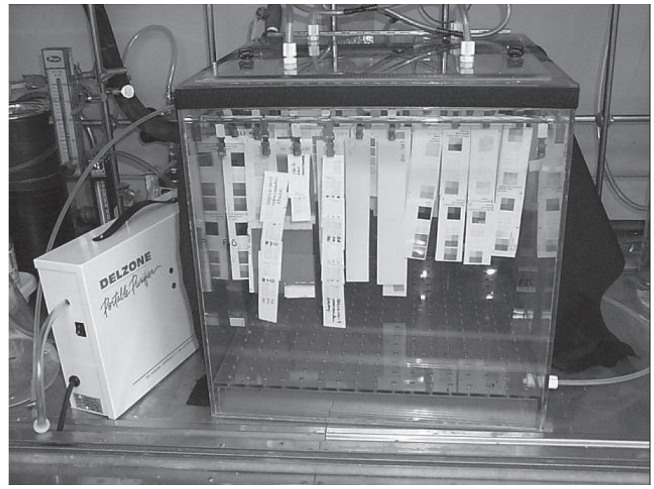

Figure 1. Photograph of an ozone chamber identical to those used for this study. The dark cloth that normally shrouds the entire chamber to prevent light-induced fade has been pulled back to provide a better view of the inside of the chamber.

Methods

The ozone treatment unit used for this study comprises an ozone generator (Dell #Z0151) plumbed to a custom built polycarbonate enclosure (see Fig. 1).[17] Ozone concentration was monitored at the outlet with a Dasibi model 1003-AH ozone analyzer and was maintained to within ±10% of target during the course of these studies. Temperature and humidity were monitored inside the chamber using a data logger ("NOMAD" OMEGA Engineering, Inc.). The unit was covered with a thick, dark cloth and kept in a darkened fume hood in order to minimize any light-induced fade.

Test targets used in this study were similar to those described previously.[4] The test targets 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). 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 versus initial density (D_o) were made for each primary color. From these plots, ΔD was interpolated to $D_o = 1.0$ above D_{min}.

An initial experiment was conducted to assess the variability of the test method as a function of sample packing density and location within the chamber (top versus bottom, back versus front, left side versus right side). For these experiments, Epson 890 magenta ink was printed onto strips of Epson receiver, code SO41141.[47] For these studies, a chamber packing configuration comprising 5 rows × 5 columns of 2 samples each, arranged back-to-back, was treated for 96 and 168 h at 1.0 ppmv ozone. Subsequent experiments were carried out with similar sample packing configurations.

A second preliminary experiment was designed to assess the influence of relative humidity on the observed rates of fade for cyan (DB 199) ink on two types of ink receptive layers: porous and swellable. This study was conducted at 20 ± 3°C, an ozone level of 5 ppmv, and a flow rate of 33 liters/min. Relative humidity was adjusted to 20, 50, and 80% by proportioning the amount of gas flow through the water column.

We also investigated the effect of flow rate of gas through the chamber. For this experiment we compared the fade kinetics of a subset of the samples at the standard 50 liters/min flow rate to a flow rate of 5 liters/min. The ozone level for this experiment was 1.0 ppmv, and the temperature and relative humidity were 24°C and 50%, respectively.

For the studies on reciprocity between ozone concentration and time of exposure, we used two identical chambers, with one set at an aim of 0.1 ppmv and the other set at 1.0 ppmv, both at 50 liters/min flow rates.

Results and Discussion

Background

Previous studies have shown that the dye stability of ink jet prints is sensitive to both temperature and humidity under ambient atmospheric conditions.[6,15–19] At relative humidities greater than 60% at room temperature, many combinations of dye-based inks and coated ink jet papers experience dye migration, as evidenced by density gain and/or loss of sharpness.[15] Conversely, even at 24°C and 50% relative humidity, certain dyes on porous ink jet papers display noticeable density loss, which can be accelerated by temperature and/or humidity.[17,43] These same ink–paper combinations have been reported to be prone to fade in the presence of low levels of ozone.[20,22,43]

In a separate study on the apparent light fade reciprocity for ink jet 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. A recommendation based on this study is to maintain an atmosphere within the light fade apparatus that is free from ozone or other pollutants. This would isolate the effects of light from ozone.

Although the impact of ozone on the fade of ink jet 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 susceptible to ozone induced fade, albeit at a much slower rate.[20,43] Nevertheless, over long periods of cumulative exposure to low levels of ambient ozone, it can be expected that ink jet prints made on these slower fading ink jet systems will fade to a noticeable, if not an intolerable, degree. Thus, there is a need for a standard test 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 much higher than ambient levels of ozone depends on a reciprocal relationship between ozone concentration and time of exposure, i.e., 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,[20] we flagged the possibility that deviations from reciprocity might be an issue for accelerated ozone testing at high concentrations. In this study, we have included a larger number of ink–media combinations, and we have increased the frequency at which we monitor the test samples during the initial stages of fade to more precisely quantify the extent of reciprocity failure.

Chamber Design and Uniformity

The ozone exposure chamber was a 45 cm cube (chamber volume approximately 95 L). The walls were 0.25 inch clear polycarbonate. One-eighth inch holes were drilled at equally spaced locations across a baffle plate, which was installed 5 cm above the chamber bottom and above the 2 gas inlets. The gas inlets were installed at opposite corners. This arrangement of inlets and baffle plate allowed the gas to enter the chamber in a relatively uniform fashion. One-eighth inch holes were also drilled in the hinged lid to allow the gas to exit the chamber evenly. Diluting compressed air with compressed nitrogen controlled the amount of oxygen input to the ozone generator. This combination of input gases was pre-dried by passing through a column of calcium sulfate. The ozone generator output was mixed with a make-up gas stream of humidified nitrogen. The humidity of the make-up gas stream was controlled by splitting its flow with one leg bubbled through distilled water. A valve in the other leg of the gas stream was adjusted to provide the target humidity. Thus, by controlling the distribution of overall flow through the two "legs" of the make-up gas flow stream, a degree of humidity control was achieved. Unless otherwise noted, however, relative humidity was held at 50 ± 5%. The relative volume ratio of make-up and ozone generator output streams was >100/1. By varying the flow rates and gas mixture going into the ozone generator, the ozone concentration in the chamber could be controlled, while maintaining total flow at a constant 50 liters/min.

Temperature was allowed to vary with ambient environment, which was controlled via the house HVAC system at 21 ± 3°C. Any drop in temperature caused by evaporation of the make-up gas as it is bubbled through the water column was relatively minor and constant. Immediately after refilling the water chamber used for controlling humidity of the make-up gas, the relative humidity does rise briefly; however, it is back in control within 3 hours. Changes in relative humidity also occur during sample introduction and removal. These changes are short-lived, typically no more than a few minutes.

Samples were suspended on dental film clips from bars mounted horizontally near the top of the chamber. This chamber contains 5 equally spaced bars. Ten samples that are between 1–1.5 inches wide and 8–9 inches long were mounted on each bar, with each dental clip holding two samples back-to-back. This arrangement provided good side-to-side spacing between samples.

Uniformity of the chamber system at 1.0 ppmv and 50% RH was determined by monitoring the fade of magenta flat field prints from an Epson 890 printer on Epson receiver, code SO41141. The nominal initial reflection density was 1.0. Readings were taken at timed intervals from marked spots on each strip near the top, middle, and bottom of the chamber. Mean fade was 0.22 ± 0.02 and 0.34 ± 0.02 density units for 4- and 7-day exposures, respectively. Thus, even for the more challenging fast fading systems, a chamber uniformity of < ± 10% of the measured density loss is demonstrated. It is expected that for the much slower fading systems, the effects of chamber non-uniformity will be dampened by the combination of sample rotation and the averaging out of any transient non-uniformity in the

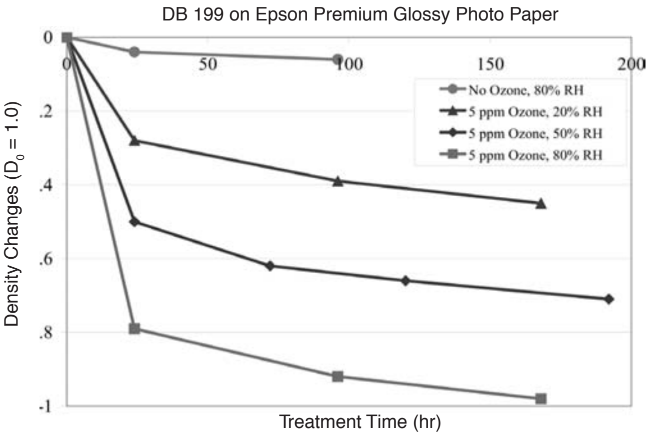

Figure 2. Effect of humidity on the ozone induced fade of a dye-based ink on a porous ink jet receiver.

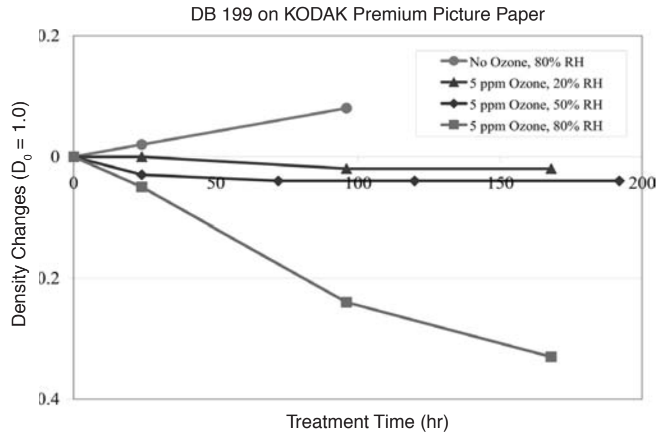

Figure 3. Effect of humidity on the ozone induced fade of dye-based ink on a swellable ink jet receiver.

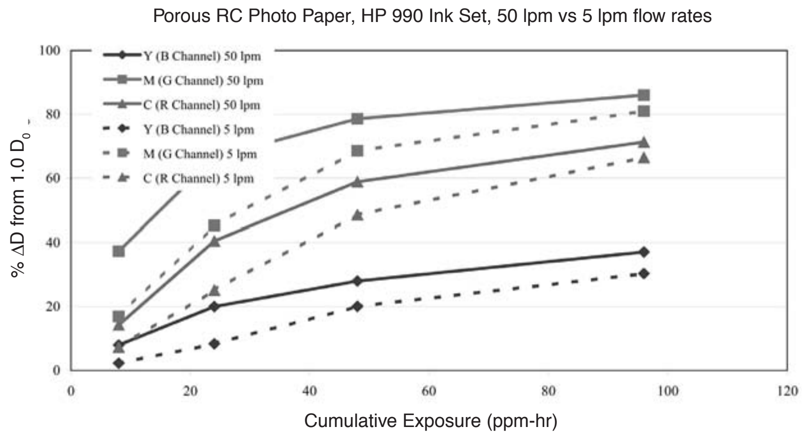

Figure 4. Effect of flow rate on the rate of fade of a porous, fast fading system.

ozone distribution within the chamber. Future chamber designs will explore the use of a small fan to more evenly distribute the atmosphere within the chamber.

Effect of Humidity

The effect of humidity on ozone induced fade was briefly examined. The results for the high humidity case are convoluted with a known, general tendency for dot spread to occur at high humidity conditions. Typically, this effect would result in density gain. In these experiments, the chamber relative humidity was 20, 50, or 80%, while the ozone concentration was kept constant at 5 ppmv. Figures 2 and 3 show the results for porous and swellable media examples, respectively.

Clearly, low humidity is beneficial, while high humidity is detrimental to dye stability at high ozone concentration. Given this humidity sensitivity, any standardized test method requires a specific and constant relative humidity in order to give reproducible results. We chose to use 50% relative humidity for the subsequent studies on flow rate and reciprocity.

Effect of Flow Rate

As it is currently constructed, the ozone gas in the chamber is constantly replenished at a nominal volume flow rate of about 50 liters/min (lpm). If the baffle plate works to distribute the flow upward evenly, it would take about two minutes to exchange the gas in the chamber once. This laminar flow rate (~1 ft/min) is believed to be comparable to that found in the typical home environment; however, attempts to quantify this assumption have not been successful using available instrumentation. Even at the higher 50 lpm flow rate, the sample strips are not observed to "flutter" or otherwise move in response to the movement of gas through the chamber.

To determine if the linear flow rate of gas across the print surface at this replenishment rate (50 lpm) artificially biased fade toward higher values compared to ambient condition fade, a comparison of fade rate for selected ink and media at two replenishment rates was made. Duplicate chambers were used in this experiment. In one, the replenishment rate was the norm, i.e., 50 lpm, while in the other, 90% of the input gas was diverted away from the chamber, so the nominal replenishment rate was 5 lpm in this chamber. Figures 4 and 5 compare the results for one porous media and one swellable media in combination with the two different dye-based ink sets. Note the difference in the abscissa and ordinate scales between these two graphs. Similar results were observed for the other ink–media combinations in this test.

In general, there was a consistently slower rate of fade observed for the 5 lpm flow rate condition, especially for the faster fading porous media. It should be noted, however, that at the 5 lpm flow rate there was a noticeable lag in recovery of the aim ozone concentration when the chamber is first loaded and each time samples were replaced into the chamber after densitometry measure-

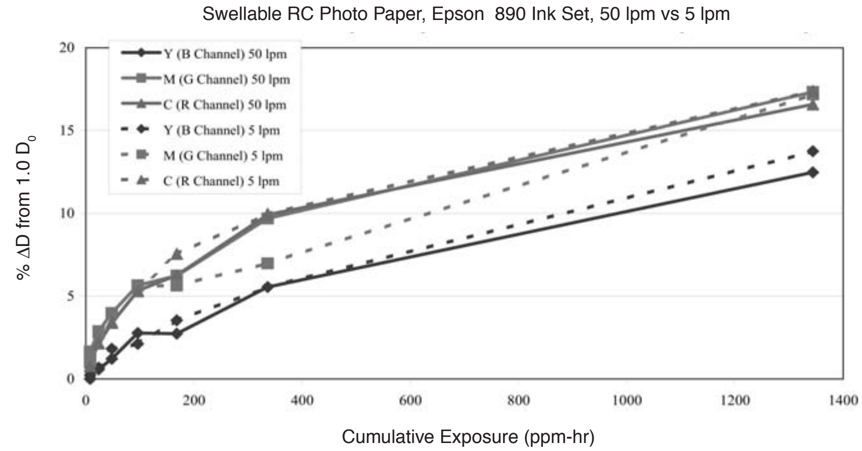

Figure 5. Effect of flow rate on the rate of fade of a swellable, slow fading system.

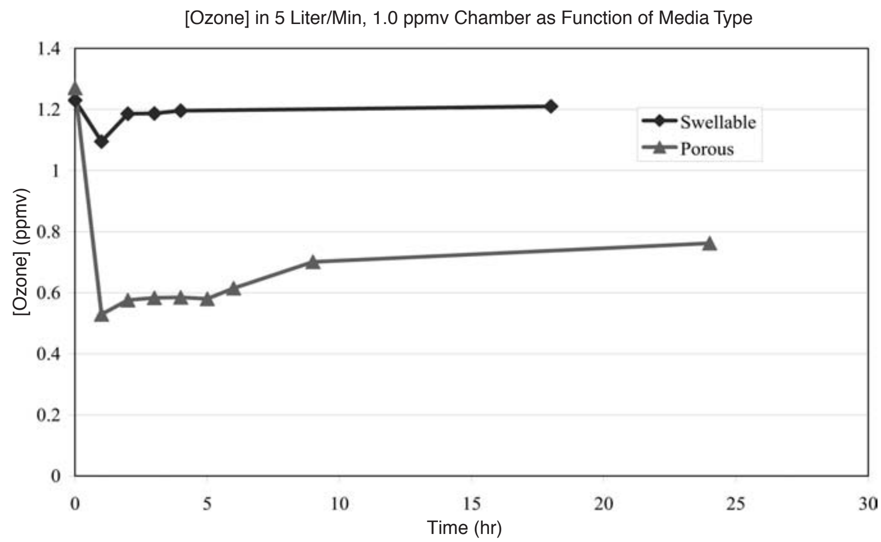

Figure 6. Aim versus measured ozone concentration after loading the chamber. Note that for this experiment, the target ozone concentration was 1.2 ppmv.

ments (see Fig. 6). It appears that the higher surface activity of the porous samples consumes the ozone at a rate faster than the replenishment rate. Over time (several days), the surface apparently becomes passivated and the ozone concentration recovers to the aim of 1.0 ppmv. When the ozone concentration is adjusted to compensate for this effect, the differences in fade rate between the two flow rate conditions are minimized. This strongly suggests that the ozone recovery effect is not simply due to the higher rate of dye fade for porous media samples.

The effect of flow rate was much less noticeable for the slower fading, swellable samples. The results of these experiments show that the effect of linear velocity across the print surface was not a significant factor and that a replenishment rate of 50 lpm is preferred for rapid recovery of the aim ozone concentration after samples are loaded into the chamber. For future studies that may require a much slower flow rate, it may be advisable to create a feedback loop to automatically adjust the ozone concentration in order to maintain a constant level at the chamber exit.

Effect of Ozone Concentration—Fast Fading Systems

Although the faster fading dye-porous ink jet systems do not actually require higher than ambient concentrations of ozone in order to exhibit objectionable levels of fade in just a few weeks or months,[44] it is of interest to understand whether reciprocity holds 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 slower fading dye-porous systems will need some level of acceleration in order to produce results in a meaningful time interval.

Figures 7 and 8 compare the rate of density loss at 0.1 and 1.0 ppmv of ozone for the Epson Stylus Photo 890 cyan, magenta, and yellow inks on two versions of Epson Premium Glossy Photo Paper. Figure 7 shows the result for the original version (2000) and Fig. 2 shows a more recent version (2001) that contains a sacrificial anti-ozonant additive (Fig. 8). 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

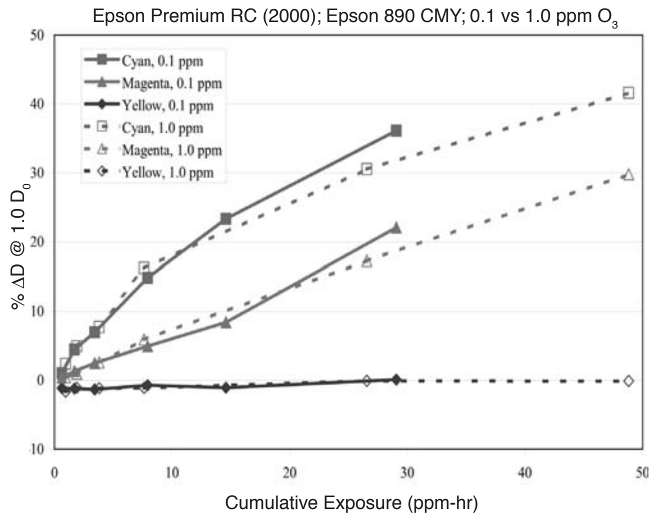

Figure 7. Comparison of the fade kinetics of the Epson 890 pure primary colors on the Epson Premium RC Photo Paper (2000) at 0.1 and 1.0 ppmv ozone.

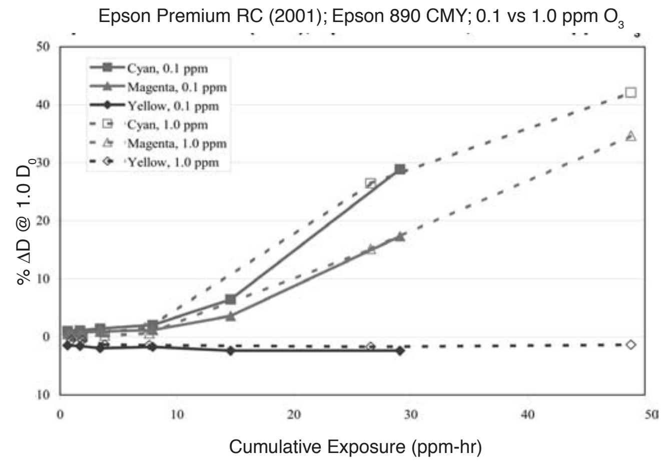

Figure 8. Comparison of the fade kinetics of the Epson 890 pure primary colors on the Epson Premium RC Photo Paper (2001) at 0.1 and 1.0 ppmv ozone.

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 9 shows the same ink–paper combination as Fig. 7, 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 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 to that shown in Figs. 7–9. However, there are several combinations of ink and photo paper 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 comprising the Canon S800 ink on the Office Depot Premium Glossy Photo Paper is illustrated in Fig. 10. This same photo paper also shows apparent reciprocity failure for HP 990 ink set but not for the Epson 890 inks. In fact, none of the fast fading porous receivers displays significant reciprocity failure with the Epson inks.

In each case in which significant deviation from reciprocity is observed, the extent of fade is greater for a given cumulative exposure at the 0.1 ppmv ozone level. This suggests that another fade mechanism may be occurring in addition to the ozone induced fade for these ink-receiver combinations. Because of the longer overall test duration at the 0.1 ppmv ozone level, an additional fade mechanism would contribute a proportionally greater amount to the overall observed fade than it would for the shorter duration 1.0 ppmv condition. If this is the case, it is unclear why only some ink-receiver combinations are affected and not others.

Effect of Ozone Concentration—Slow Fading Dye-Based Systems

Of the four slow fading, dye-based ink-media combinations, only one exhibits good reciprocity between 0.1 and

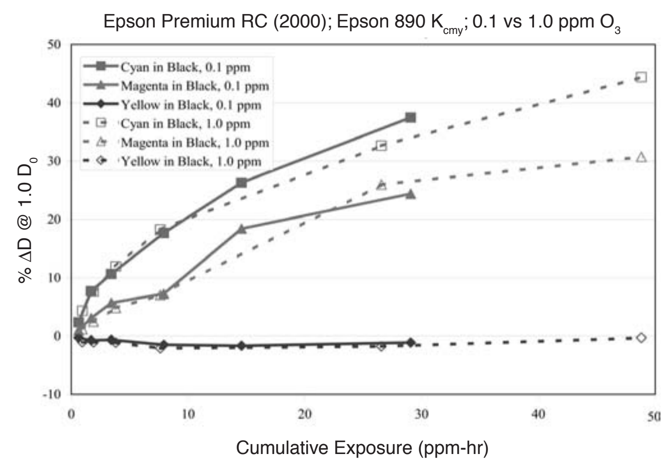

Figure 9. Comparison of the fade kinetics of the Epson 890 mixed primary colors on the Epson Premium RC Photo Paper (2000) at 0.1 and 1.0 ppmv ozone.

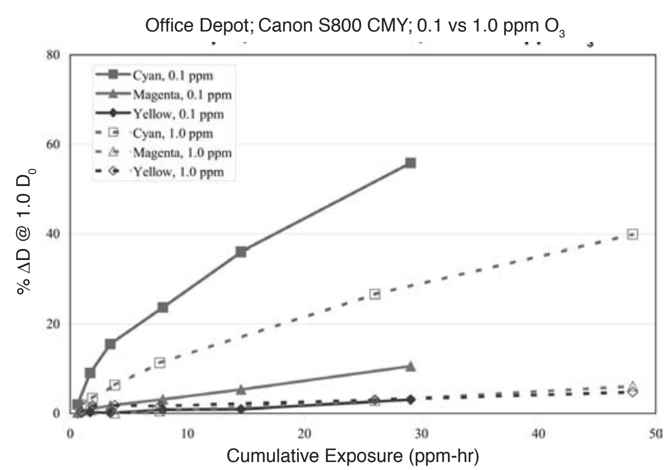

Figure 10. Comparison of the fade kinetics of the Canon S800 pure primary colors on the Office Depot Premium Photo Paper at 0.1 and 1.0 ppmv ozone.

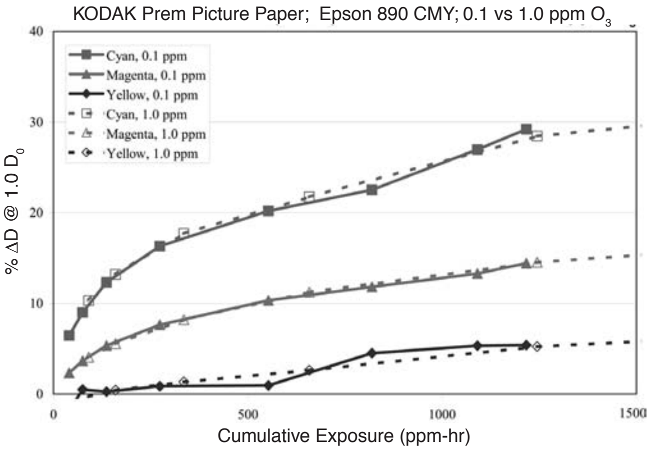

Figure 11. Comparison of the fade kinetics of the Epson 890 pure primary colors on the KODAK Premium Picture Paper at 0.1 and 1.0 ppmv ozone.

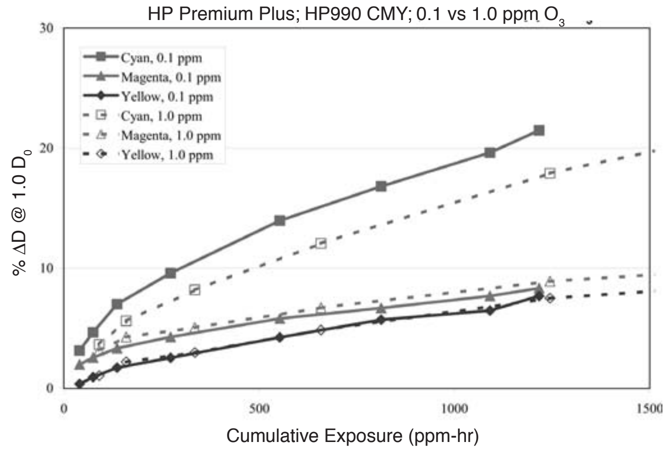

Figure 12. Comparison of the fade kinetics of the HP 990 pure primary colors on the HP Premium Plus Photo Paper at 0.1 and 1.0 ppmv ozone.

1.0 ppmv ozone (Fig. 11), although the others display apparent deviations from reciprocity, e.g., see Fig. 12. Figure 13 shows the same system as Fig. 11, illustrating the effect of ozone on the mixed primaries in a neutral patch. Note the change in both the abscissa and ordinate scales for these graphs, compared to Figs. 7–10.

As with the fast fading systems that exhibit apparent reciprocity failure, the amount of fade observed for the 0.1 ppmv ozone level is greater than those observed for the 1.0 ppmv level at equivalent cumulative exposures. Once again, it is unclear why only certain combinations of colorant and photo paper display this behavior.

In addition to the obvious differences in fade rates, another difference between the fast fading and slow fading systems included in this study is that, for the latter, the mixed primaries consistently fade more slowly than the pure primaries at either ozone level. One explanation for this observation is that with the higher overall ink load required to process a neutral color patch, the colorants are driven further into the swellable polymeric coating, which, in turn, offers further protection of the dyes from ozone at the surface of the print.

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, if not required. 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 ppmv ($\Delta D_{0.1\ \mathrm{ppmv}}$) to that observed at 1.0 ppmv ($\Delta D_{1.0\ \mathrm{ppmv}}$) at a given cumulative exposure:

$$R_f = [\Delta D_{0.1\ \mathrm{ppmv}} / \Delta D_{1.0\ \mathrm{ppmv}}] \tag{1}$$

Table I summarizes the calculated reciprocity factors for the pure cyan patches of three slow fading systems included in this study. Although a 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 Fig. 14). 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 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 are designed to better understand this phenomenon.

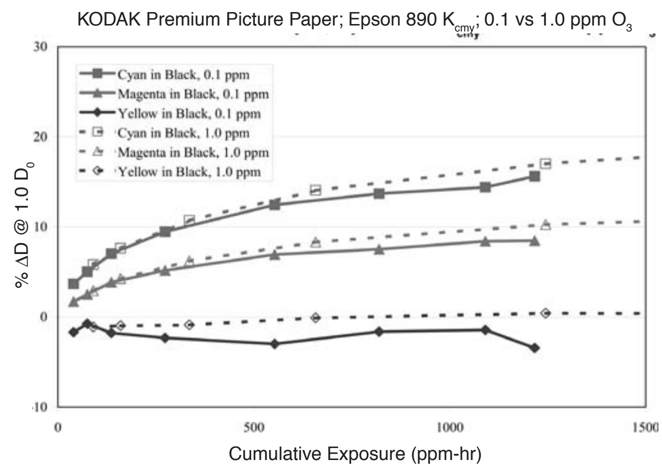

Figure 13. Comparison of the fade kinetics of the Epson 890 mixed primary colors on the KODAK Premium Picture Paper at 0.1 and 1.0 ppmv ozone.

TABLE I. Observed Reciprocity Factors for the Cyan Patches of the Slow Fading Systems Included in this Study at a Cumulative Exposure of 658 ppm hr.

	%Δ*D* at 0.1 ppmv	%Δ*D* at 1.0 ppmv	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

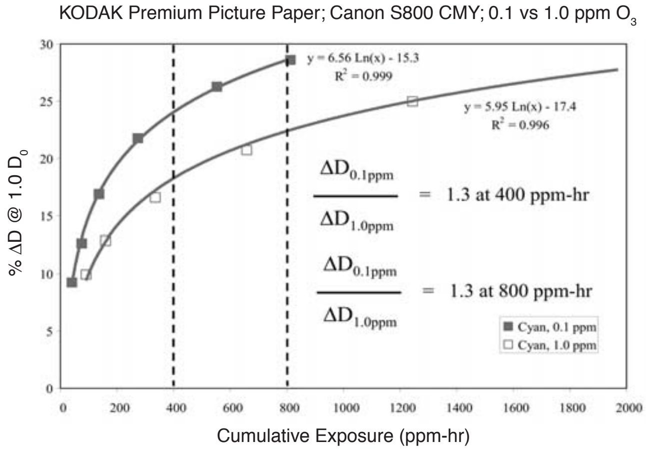

Figure 14. Comparison of the fade kinetics of the Canon S800 cyan ink patch on the KODAK Premium Picture Paper at 0.1 and 1.0 ppmv ozone illustrating the calculation of Rf.

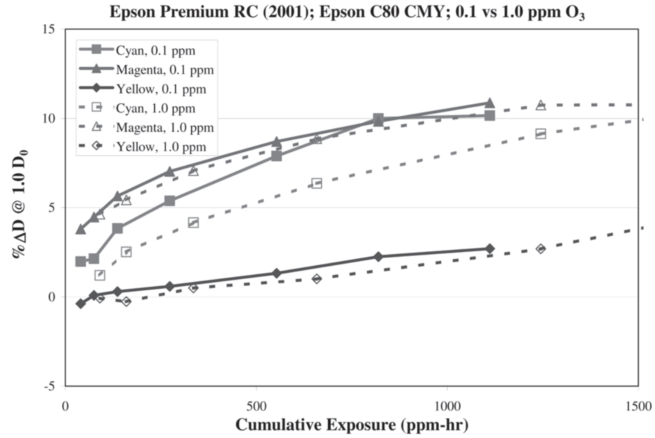

Figure 15. Comparison of the fade kinetics of the Epson C80 pure primary colors on the Epson Premium RC Photo Paper (2001) at 0.1 and 1.0 ppmv ozone.

Effect of Ozone Concentration—Pigment-Based Systems

Although it was originally thought that pigment-based ink jet systems were "ozone-proof," it has since been reported that ozone can, indeed, cause pigmented ink jet prints to fade. Figures 15–17 illustrate the effect of ozone concentration on the rate of fade for the Epson C80 inks on both porous and swellable receivers. It is interesting to note that some degree of deviation from reciprocity is observed, primarily with the cyan pigment. Furthermore, the direction and magnitude of the reciprocity failure is the same as that observed for several of the cyan dye-based systems.

Another interesting observation is that at either ozone concentration, the rate of fade for the pigmented inks on the swellable receiver is consistently less than that observed on the porous receivers. This is somewhat surprising given that for either type of receiver the pigments reside primarily on the surface of the receiver, unlike dye-based inks that are believed to be protected from ozone in swellable receivers because they diffuse into the coating (and are thus somewhat protected from the atmosphere). Further work is necessary to understand the generality of these results.

Summary

We have designed, fabricated, and characterized a simple test chamber for the controlled treatment of photographic test samples with elevated levels of ozone. The effects of chamber design, flow rate, relative humidity, and ozone concentration on the kinetics of fade of ink jet prints was examined. Sample-to-sample reproducibility within the chamber was found to be < ±10% of the measured density loss for the more challenging fast fading systems and even better for the slow fading systems.

The effect of relative humidity at a given temperature and ozone concentration is significant and appears to be a function of paper type (porous versus swellable). For the studies on flow rate and ozone concentration, a relative humidity of 50% at 23°C was targeted as a primary reference condition.

The effect of flow rate is seen primarily with the porous fast fading systems. At the lower flow rate of 5 lpm, an "ozone recovery" lag is observed after samples are loaded or reloaded into the chamber. A flow rate of 50

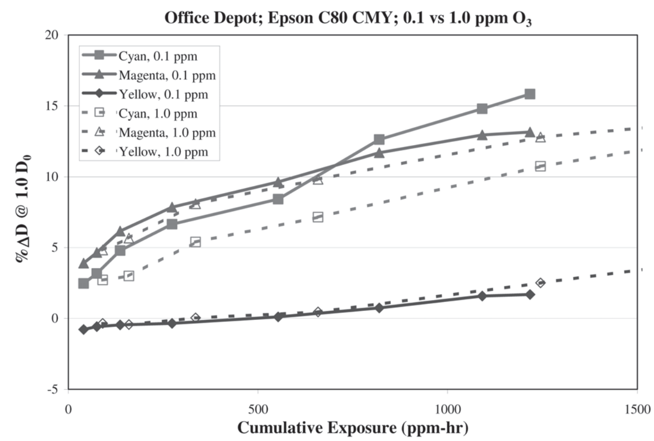

Figure 16. Comparison of the fade kinetics of the Epson C80 pure primary colors on the Office Depot Premium Photo Paper at 0.1 and 1.0 ppmv ozone.

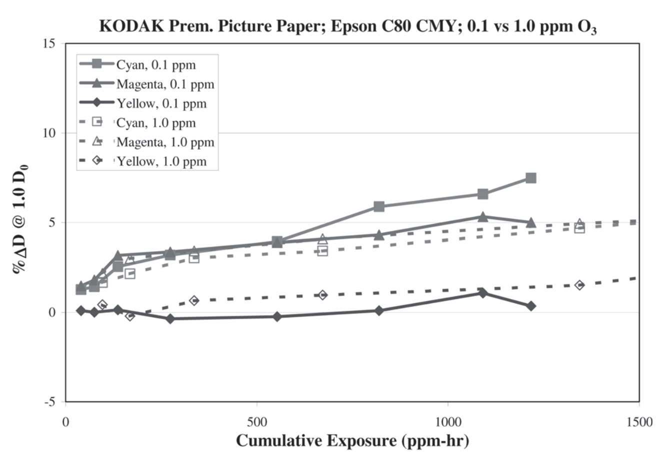

Figure 17. Comparison of the fade kinetics of the Epson C80 pure primary colors on the KODAK Premium Picture Paper at 0.1 and 1.0 ppmv ozone.

lpm minimizes this effect and does not appear to be unrealistically high relative to real world conditions. This flow rate was used for the studies on ozone concentration effects.

Based on these preliminary experiments, the rates of fade for 23 different ink–paper combinations were measured at both 0.1 and 1.0 ppmv ozone concentrations. The results can be divided into three groups: (a) "fast faders" that comprise papers with "porous" ink receptive coatings, (b) "slow faders" that comprise papers with "swellable" ink receptive coatings, and (c) "slow faders" that comprise pigmented inks on either type of coating. The fast faders, in combination with the Epson 890 ink set, exhibited good reciprocity within the variability of the test method. There were several cases for which a measurably faster rate was observed at the 0.1 ppmv ozone concentration. This was most noticeable for the HP and Canon cyan inks. However, the rate of fade is fast enough at even 0.1 ppmv that further acceleration with higher levels of ozone is not really necessary.

The reciprocity results for the slow fading combinations were similar. Very little deviation from reciprocity was observed for the Epson 890 ink set, but measurable deviations were observed for the HP and Canon inks, especially the cyan. In these cases, R_f was found to be approximately 1.3, i.e., the cyan patches faded 30% more for a given cumulative exposure at the 0.1 ppmv than at the 1.0 ppmv ozone concentration. The pigmented ink–media combinations also displayed a comparable level of reciprocity failure, again primarily with the cyan ink.

There were also noticeable differences among the dyes within an ink set, as well as among the various printer/ink manufacturers. In general, cyan and magenta inks appear to be the most sensitive to ozone compared to yellow inks. These same relative trends in dye stability are observed on both porous and swellable papers. In contrast to light-induced dye fade, there is little evidence of dye–dye interactions in secondary and neutral test patches in response to ozone. The pigmented inks were found to be of comparable sensitivity to ozone as the dye ink-swellable media combinations, but there was much less difference between porous and swellable media for these samples.

Further work is ongoing to better understand the observed deviations from reciprocity. In the meantime, it is recommended that accelerated ozone fade testing be conducted at more than one ozone concentration to assess potential deviations from reciprocity.

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