Air Fade and Ozone Fade on Porous Media

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Abstract

The air fade of inkjet images on porous media is attributed to chromophore destruction by atmospheric pollutants and/or their byproducts. Many studies suggest a strong correlation between air fade and accelerated ozone exposure. Most investigators regard other pollutants as minor contributors to chromophore destruction relative to ozone. Despite the growing popularity of ozone testing, there are few reports that directly compare ozone data with real-time air fade experiments. In this report we assess air fade pollutant effects, single pollutant gas fade, and the correlation between ozone fade and air fade. We also make a comparison of literature and industry estimates of ambient ozone levels.

Introduction

The permanence of inkjet printed photos is receiving increasing media attention. Articles reviewing protected (framed) photo permanence compare the number of display years a consumer can expect before noticeable light fading occurs.[1,2] The display permanence of unprotected inkjet prints remains largely undocumented because microporous photo media suffer from an additional air pollutant fading mechanism. Internal HP tests corroborate other studies[3] demonstrating minimal pollutant sensitivity on swellable photo media such as HP Premium Photo Paper, Glossy. The scope of this paper is limited to air and ozone fade occurring on unprotected microporous photo media.

The high porosity and surface area of porous media facilitate air pollutant penetration and subsequent chromophore degradation. Previous studies show both dye and pigment chromophores can be susceptible to pollutant attack on porous media.[3,4] Pollutant induced fading is responsible for photo lifetime overestimation by traditional accelerated light fade tests (reciprocity failure). Since photographs are routinely displayed in unprotected environments, it is imperative that an understanding of uncovered permanence be further developed.

Wight outlined two methods for evaluating pollutant fading on porous media: "forced air flow" (air fade) and "controlled ozone exposure" (ozone fade).[5] Air fade experiments are lengthy and variable because air consists of a low concentration "cocktail" of pollutants whose constituents are location and time dependent. Ozone fade experiments focus on the pollutant that is reported to be most degrading to inkjet prints.[6] Unlike air fade, ozone exposures are conducted in closed loop chambers that can precisely control ozone concentration, temperature, humidity, and air flow.

While ozone fade is often used to approximate real time air fade, there are surprisingly few studies that actually compare air fade with ozone concentration or controlled ozone exposure.[4] We address this deficiency by monitoring pollutant concentration during air fade, evaluating single pollutant gas fade, and comparing lifetimes obtained in air fade and ozone fade experiments. Finally, we compare the industry estimates of ambient ozone with literature studies of residential ozone concentration.

Experimental

Air Fade

The experimental chamber consisted of a dark stainless steel cabinet containing 11 shelves (24" × 53") with alternating cutouts allowing air flow. Two fans located at the bottom of the chamber pull air (300-400 ft/min) through a top chamber opening and across each shelf in alternating directions. Each shelf holds a centered sample tray (16" × 22") that is rotated daily. A humidity and temperature-controlled lab (58 ± 4% RH, 20 ± 2°C) houses the chamber. Gas analyzers for O_3, NO_x, and SO_2 measured lab pollutant concentrations at five-minute intervals (see below).

Gas Fade

All single pollutant gas fade studies used either a custom built multiple gas exposure chamber or a commercial ozone exposure chamber. The multiple gas exposure chamber was constructed from a modified environmental chamber with temperature (30 ± 1°C) and humidity (50 ± 1% RH) control. A mixture of 80:20 N_2:O_2 gas carried all pollutants into the chamber at a flow rate of 2 LPM. O_3 is generated by an API Photoelectric Ozone Calibrator (Model 401). All other pollutants are introduced with certified permeation devices used as received from VICI Metronics, Inc. A VICI Metronics Dynacalibrator (Model 190) produced known generation rates (ng/min). Gas analyzers for O_3, NO_x, and SO_2 measured chamber exhaust at five-minute intervals (see below). We conducted NO_2 (7.0 ppm), NO (0.78 ppm), SO_2 (6.2 ppm) and O_3 (0.024 ppm and 0.72 ppm, assuming 20% O_3 decomposition between the chamber and analyzer) exposures in this chamber. We conducted all other O_3 exposures in a

Hampden Ozone Test Cabinet (Model 903) equipped with temperature (30 ± 1°C) and humidity (50 ± 1% RH) control.

Gas Analyzers

The following gas analyzers from Monitor Labs measured pollutants in the air fade chamber and the multiple gas exposure chamber: ML 9810B (O_3), ML 9841B (NO_x), ML 9850B (SO_2). The lower detection limits are 0.5 – 1 ppb with 1 ppb resolution.

Sample Measurement

Test specimens consisted of 10-step ramps of increasing print density from which an initial optical density of 0.5 is interpolated. All samples dried at least 24 hours prior to color measurement with a Gretag Spectrolino spectrophotometer (D65 illuminant, 2° observer). The following optical density loss criteria determined ink failure times: cyan 30%, magenta 25%, yellow 35%, black 25%.

Results and Discussion

Air Fade

We conducted a three month air fade experiment to determine the relationship between pollutant concentration and air fade. Air exposures occurred from September 11 to December 18 of 2002 during which time the climate and pollutants were representative of summer, fall, and winter seasons. Gas analyzers measured indoor pollutants (O_3, NO, NO_2, SO_2) while several dye-based ink and porous media combinations were exposed to a dark air flow. After a week of exposure, samples were removed, measured for color change, and replaced with new identical samples. Figure 1 illustrates a representative example of weekly dye fade versus total pollutant exposure. Sulfur dioxide (SO_2) concentrations were lower than the analyzer detection limit and are omitted for clarity.

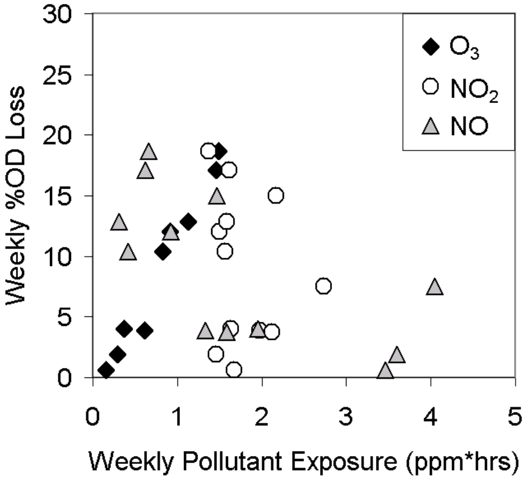

Figure 1. Weekly %OD loss vs weekly pollutant exposure. Two weeks of ozone exposure were not measured.

Dye optical density loss exhibits a linear dependence on weekly ozone exposure ($R^2 = 0.95$). The average weekly ozone exposure varies between 0.16 and 1.5 ppm×hrs corresponding to weekly concentrations of 1 to 9 ppb. Weekly nitrogen dioxide (NO_2) exposures show no correlation with dye fade and range between 1.4 and 2.7 ppm×hrs corresponding to weekly concentrations between 8 and 16 ppb. Average nitric oxide (NO) exposures exhibit a weak inverse correlation with optical density loss and varied between 0.3 and 4.0 ppm×hrs corresponding to 1.5 and 24 ppb. We attribute this inverse relationship to the rapid reaction between ozone and nitric oxide to yield oxygen and nitrogen dioxide. When nitric oxide is in excess, ozone efficiently converts to oxygen thus reducing the rate of dye fade.

Gas Fade

While air exposes samples to an assortment of pollutants, the following gas fade experiments focus on controlled single pollutant exposures for 34 dye/media combinations (2 media, 17 dyes). Figure 2 illustrates the fade of a fugitive dye to several common air pollutants. The dye was unaffected by nitric oxide while sulfur dioxide exposure produced an initial 10% optical density loss suggestive of multiple dye/media environments varying in reactivity and/or accessibility. Both nitrogen dioxide and ozone exposure result in extensive dye fade, however, dye reactivity with ozone is far greater.

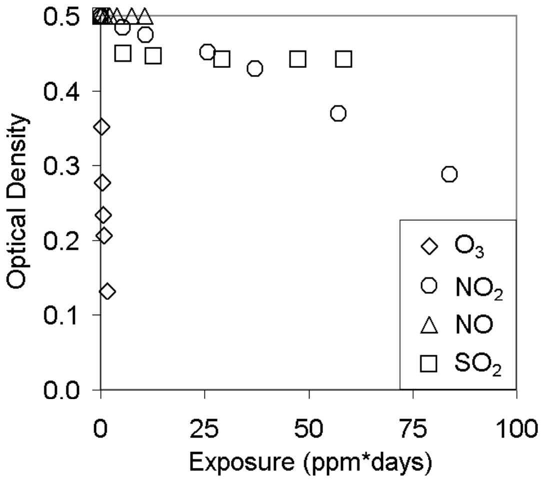

Figure 2. Fugitive dye on porous media exposed to various pollutants.

Figure 3 illustrates a dye-based ink with gas fade behavior representative of most airfast dyes. For these less fugitive dyes, only ozone exposure produced significant fade. In fact, for all 34 dye/media combinations tested, ozone fade rates far exceeded the combined fade rates of the other three pollutants.

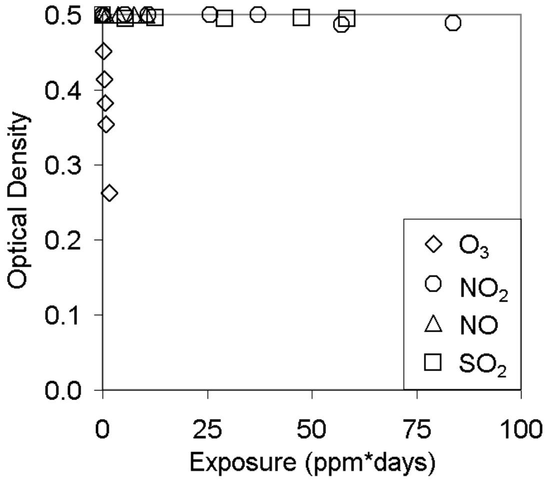

Figure 3. Moderately airfast dye on porous media exposed to various pollutants.

Ozone Fade

Extrapolations of high concentration ozone exposures to ambient concentrations require a reciprocal relationship between concentration and exposure duration. Several earlier studies support the existence of a reciprocal relationship for certain dye-based inks on porous media.[7,8] Precisely controlled environmental conditions are essential since high humidity is known to accelerate the fade of some dyes.[8]

Figure 4 illustrates an example of dye fade versus ozone exposure at multiple concentrations (30°C, 50% RH). All four ozone concentrations exhibit a similar optical density loss at equivalent ozone exposures (ppm×hrs). All other inks tested exhibited a similar reciprocal relationship between ozone concentration and exposure duration. However, in separate studies we have noted deviations from reciprocity for media containing ozone scavengers.

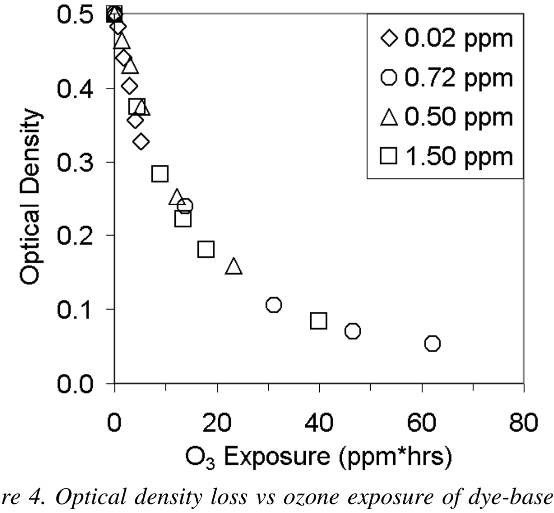

Figure 4. Optical density loss vs ozone exposure of dye-based ink on porous media.

Ozone Fade vs. Air Fade

Ozone exposure at high concentrations has become an increasingly popular method for estimating long-term exposure at ambient concentrations. However, few investigators have directly compared ozone exposures with air fade experiments.[4] In this section we compare failure times from two long-term air fade studies with the corresponding ozone exposures required to reach failure.

We evaluated over 50 dye/media combinations (CMYK inks, 3 porous media types) in 252 day (2/22/02 – 11/22/02) and 158 day (5/28/02 – 11/19/02) air fade experiments. We exposed identical samples to 0.5 ppm ozone (50% RH, 30°C) and determined ozone failure exposures (ppm×hrs). Failure times and exposures for samples not reaching failure are estimated by extrapolation. Only samples achieving >5% OD loss in both air fade and ozone fade experiments were considered. Figures 5 and 6 plot ozone fade failure exposures versus air fade lifetimes. Data points beyond the dashed lines indicate extrapolated values. Both plots exhibit a linear correlation between ozone failure exposures and air fade failure times. Major sources of error include lab air pollutant fluctuation, failure time and exposure extrapolations, non-ozone pollutant fade, and different temperature/humidity test conditions. Calculated slopes approximate ambient ozone concentrations (0.0065 & 0.0076 ppm) assuming no reciprocity failure. These estimates are well within the range (1-9 ppb) previously described for ozone in our air fade chamber (Figure 1).

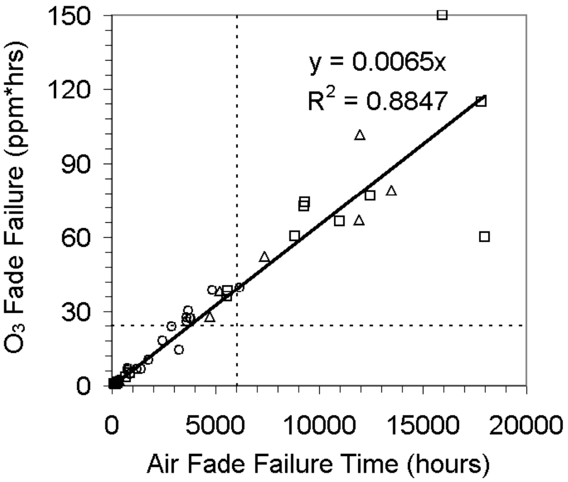

Figure 5. O_3 failure dosage vs air fade failure time (252 days). Data point shape represents porous media type.

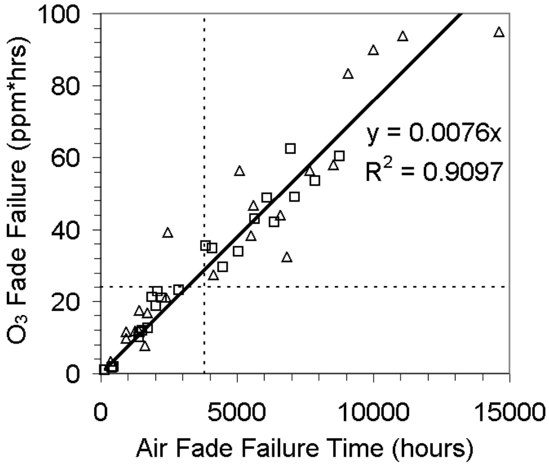

Figure 6. O_3 failure dosage vs air fade failure time (158 days). Data point shape represents porous media type.

Ozone Fade as an Accelerated Test

High concentration ozone exposures are sometimes used to predict ink/media lifetimes at ambient ozone levels. These extrapolations assume no reciprocity failure and are calculated by dividing the ozone fade exposure at failure (ppm×hours) by the ambient ozone concentration (ppm). Industry researchers use a variety of ozone concentrations (IPI = 25 ppb[4,9], Kodak = 20 ppb[7], Fuji = 10 ppb[8]) for lifetime prediction. The dependence of these predictions on ambient concentrations is reminiscent of the illumination assumption (450 lux per 12 hour day) used in some accelerated light fade testing.[10]

We conducted a survey of the literature to gain more insight into indoor ambient ozone concentrations. The survey was limited to residential studies encompassing more than five homes. Table 1 summarizes eight residential studies and compares outdoor and indoor ozone means and standard deviations.

Table 1. Residential Ozone Concentrations (ppb)

Ref	Location	# Of Homes	Year	Indoor Ozone	Outdoor Ozone
11	Houston	12	1981	1.3 ± 5.9	22 ± 25
12	Toronto	40	1992	1.6 ± 4.1	15 ± 6
13	Boston	9	1993	4.2 ± 6.6	16 ± 7
			1993	6.7 ± 9.7	26 ± 12
14	Mexico City	145	1994	7 ± 5	37 ± 12
			1993-94	5 ± 4	27 ± 10
15	Sou. CA	126	1994	13 ± 12	37 ± 19
16	France	110	1995-96	16 ± 9	33 ± 14
17	Sou. CA	119	1996	15 ± 13	56 ± 22
18	Hong Kong	10	1997	2.7 ± 1.9	6.8 ± 4.1
	Average			7	27

Both indoor and outdoor ozone concentrations vary significantly across all eight studies. In general, indoor ozone concentrations are much lower than outdoor concentrations. This suggests that lifetimes calculated from outdoor ozone concentrations may not accurately reflect actual indoor lifetimes. Indoor ozone is a function of outdoor ozone, air exchange rates, air treatment (heating, cooling, filtration), and indoor environment composition. Carpet, paint, and other common indoor materials are known to serve as indoor ozone sinks. Electrostatic air cleaners, photocopiers, and laser printers are potential indoor sources of ozone. In all eight studies, indoor/outdoor (I/O) ratios less than 1 implicate outdoor ozone as the leading source of indoor ozone. Substantial house-to-house variability reflected by large indoor standard deviations could account for the variable air fade rates observed by consumers printing with the same printer/media combination. Coincidentally, the average indoor ozone concentration (7 ppb) is approximately equal to the ambient ozone concentrations (6.5 and 7.6 ppb) estimated in Figures 5 and 6. Based on these studies, we recommend a standard indoor ozone concentration between 1 and 15 ppb for ozone fade extrapolations to ambient conditions.

Conclusion

Controlled ozone exposure has become a common accelerated method for approximating real time air fade. However, few studies have compared air fade with ozone concentration or controlled ozone exposure.

In this study we found air fade on porous photo media to be directly proportional to ambient ozone concentrations. Single pollutant exposures show ozone to be far more damaging to chromophores than other common air pollutants (NO, NO_2, SO_2). Ozone exposures at multiple concentrations illustrate the reciprocal relationship between concentration and exposure duration that is necessary for lifetime extrapolation to ambient conditions. Finally, a linear correlation between air fade and ozone fade shows how ozone exposures can provide an accelerated and accurate assessment of air fade. However, industry differences in test conditions and ambient ozone estimates illustrate the need for a standardized ozone fade test.

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Biographies

Matthew Thornberry[*] received a B.S. degree in Chemistry from James Madison University in Harrisonburg, VA in 1997 and a Ph.D. in Chemistry from Virginia Tech in Blacksburg, VA in 2001. His academic work involved the synthesis, characterization, and application of homogenous organometallic catalysts. In 2001, he began working at the Hewlett-Packard Company in Corvallis, OR where his efforts have primarily focused on the image permanence of inkjet prints.

Steve Looman received a B.S. degree in Chemistry from Hope College in Holland, MI in 1990 and a Ph.D. in Chemistry from the University of Utah in Salt Lake City, UT in 1995. His academic work involved the synthesis and characterization of organometallic compounds for carbon-halogen bond activation. In 1995, he began working at the Hewlett-Packard Company in Corvallis, OR where his efforts have included ink development, system reliability testing, writing systems, and image permanence of inkjet prints.

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