Comparison of Different Methods for Estimating the Sensitivity of Inkjet Images to Gas Fading

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Abstract

This study compares the fading of inkjet prints tested in environmental chambers using either an electrostatic discharge or ultraviolet radiation to produce ozone. Our results indicate that over the range of 0.1 to 5.0 ppm ozone in air, very similar fading characteristics are obtained at 50% RH with the microporous and swellable polymer based inkjet papers tested, whether ozone is produced with an electric discharge or with a UV radiation source. Reciprocity between ozone concentration and time is observed for the fading of dye-based inkjet images printed on microporous papers. In addition, results from the accelerated ozone fading tests are compared with fading under "real world" ambient indoor air conditions.

Introduction

Over the last few years, there have been significant improvements in the stability of inkjet images to light exposure. However, certain inkjet prints, especially those made with dye-based inks and microporous media, can exhibit significant fading in the presence of atmospheric pollutants even in the absence of light. The cause of this "gas fading" has been attributed to the presence of oxidizing airborne compounds, especially ozone, in the air.[1,2] In addition, ozone has been shown to confound the interpretation of both light and dark fading studies of digital prints.[3,4,5,6] Therefore it is important to study and model the effect of ozone on printed media in controlled environments.

Currently, there is no standard method for testing a print's sensitivity to ozone. Often the literature does not explicitly detail the mechanism of ozone generation. Some have studied fading with ozone generated by electric discharge,[7,8] either from a high voltage electric spark in air or a continuous corona discharge, and other studies have generated ozone with a UV radiation source.[1,9] The UV method has been said to be the "cleanest" method of ozone production, because the UV energy is specifically absorbed by the oxygen molecule, which then splits into oxygen atoms. Oxygen atoms (O) then react with oxygen molecules (O_2) to create ozone (O_3). Since an electrostatic discharge is less specific in introducing energy into a gas, other chemically active species such as oxides of nitrogen (from molecular nitrogen) and hydroxyl radicals (from water vapor) in addition to oxygen atoms and ozone may be produced.

The focus of this study is to characterize the dark fading of images in the presence of ozone produced by electrostatic and UV methods and to determine whether comparable results are obtained. In this report, we compare data from our studies and from appropriate literature sources. We also describe those variables that can affect the ozone sensitivity of printed images. Over the years, the textile, rubber, and plastics industries developed standard testing protocols for ozone testing, specifying important variables and how they must be controlled in order to achieve reproducible results. The imaging industry is currently developing a standard method for testing ozone fading of digital prints; therefore characterizing the significant variables in the testing method is essential.

Experimental

Ozone Test Equipment

A commercial ozone testing chamber, Model OTC-1, produced by INUSA, of Needham, Massachusetts, USA, was used for testing with ozone produced with a corona discharge. This chamber is specified to operate in the range of 0.1 to 6 ppm ozone at ambient humidity and temperatures. The ozone, produced from room air, is controlled to within +/- 5% or 0.05 ppm. The OTC-1 interior sample space is approximately 2 cubic feet, and the samples are attached to a rotating carousel inside the chamber. The testing chamber is refreshed approximately 1.5 times per minute with fresh air and ozone. Ozone is removed with a chemical filter before exiting the chamber. The OTC-1 has been designed to satisfy the requirements for testing textiles according to the AATCC (American Association of Textile Chemists and Colorists) Test Method 109-2002 "Colorfastness to Ozone in the Atmosphere under Low Humidity".

Another commercial ozone testing chamber, Model 903, produced by Hampden Test Equipment, of Northamptonshire, UK, was used for testing with ozone produced with UV light. This chamber can operate in the range of 0.01 – 5 ppm ozone and has the ability to control both the temperature and RH. Samples in this chamber are also attached to a rotating carousel, in a 5 cubic foot volume. The air and ozone are refreshed 3 times per minute and re-circulated in this equipment.

Samples were also tested in ambient air in a home environment. A "forced air flow" configuration described by Wight[1] was employed. With this configuration, the samples were kept in a dark ventilated cardboard box approximately 1 cubic foot in volume and ambient air was drawn over the samples at about 0.2 ft/sec with a fan. The temperature varied from 60-80 F and the relative humidity varied from 55–70% RH during the test. (Boston, Massachusetts, USA, during May and June 2003). Draeger tubes indicated that the ambient ozone concentration in the home varied between 0 and 0.03 ppm during the ambient test period.

Sample Print Preparation

For this study, one swellable-polymer and three microporous inkjet receivers were printed with dye based inks. The printed test targets have been described previously.[3] The Canon S900 printer and recommended manufacturer's inks (6-ink BCI-6 series) were used with the Canon Photo Paper Pro PR-101 (microporous, lot 2D21-2NX). The Epson Stylus Photo 960 printer and recommended manufacturer's inks (6-ink T0331-336 series) were used with the Epson Premium Glossy Photo Paper (microporous v2000 – Lot # B0IJ43010 and v2001- Lot # I2KA52231) and the Epson ColorLife Photo Paper (swellable-polymer). After printing, the samples were equilibrated at standard room conditions in the dark to "dry down" for a period of from 8 to 25 days. It has been found that some dye based inkjet prints require a dry down period to allow for the solvents in the inks to equilibrate in or to evaporate from the paper and that the testing of some freshly printed inkjet images before appropriate equilibration can lead to errors in stability assessments.[10] Table 1 summarizes the different prints used for the tests.

Table 1. Inkjet Printer and Media

Designation	Printer	Paper	Type
A	Canon S900	Photo Paper Pro PR-101	Microporous
B	Epson SP 960	Premium Glossy Photo (v2001)	Microporous
C	Epson SP 960	ColorLife Photo	Swellable Polymer
D	Epson SP 960	Premium Glossy Photo (v2000)	Microporous

Methods and Measurements

Table 2 provides the details of the tests undertaken in this study. A GretagMacbeth SpectroScan and Spectrolino were used to obtain Status A densitometry and L*a*b* measurements for the neutral and pure color CMY patches. The analysis in this paper is based on neutral patches with initial densities of 1.0, 0.6 and 0.35. Table 2 summarizes the different test conditions for the prints.

Table 2 Summary of Test Conditions

Ozone	Cumulative Exposure	Prints Tested in OTC-1	OTC-1 Humidity Level	Prints Tested in Hampden 903
ppm	ppm-hours		%RH (Range)	(at 40°C 50%RH)
0.2	1.6	A.B	45 - 55	
0.2	4.8	A,B	48 - 53	
0.2	24	A,B	48 - 56	
1.0	5	A,B,C,D	54 - 57	A.B
1.0	24	A,B,C,D	54 - 57	A.B
1.0	72.7	A,B,C	54 - 56	A.B
1.0	5	A,B	66 - 72	
1.0	24	A,B	66 - 72	
1.0	72	A,B	68 - 71	
2.0	24	A,B,C	45 - 55	
5.0	10	A.B	52 - 57	
5.0	40	A.B	52 - 57	
ambient		A,B,C	55 - 70	

Results and Discussion

It has been previously noted that the susceptibility to ozone of different inkjet prints depends both on the inks and the media.[8,9,11,12] In general, pigmented inks have been found to be more stable to ozone than dye based inks, and certain cyan and magenta dye based inks are more prone to fading than most yellow dye based inks. Previous work indicates that media based on microporous chemistry are considerably more vulnerable to ozone attack than are swellable polymer based media. The results obtained in this study with the OTC-1 ozone chamber are consistent with the observations reported by others who have used UV generated ozone, and most importantly with real world observations.

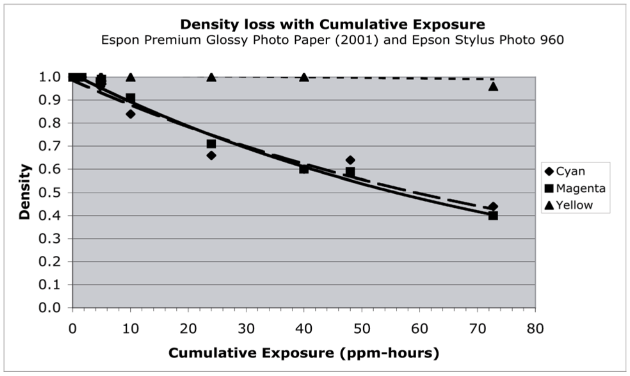

Figure 1. Density Loss with Cumulative Exposure of Ozone for Epson Premium Glossy Photo Paper (2001)

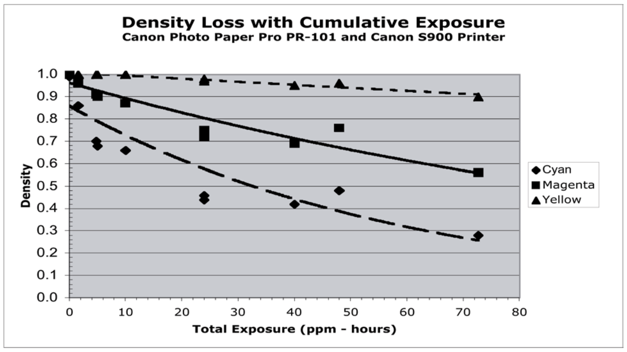

Figure 2. Density Loss with Cumulative Exposure of Ozone for Canon Photo Paper Pro PR-101.

Figures 1 and 2 show the different fading characteristics of the Epson and Canon microporous systems out to 72 ppm-hours cumulative exposure. The results for the Epson ColorLife Photo Paper are not graphed since this swellable polymer paper showed very little loss in any of the dyes out to the 72 ppm-hour exposures.

The relative loss of cyan and magenta densities with the two microporous receivers that we tested are characteristic of the specific dyes and receiver in these systems, as individual cyan and magenta dyes have different susceptibility to ozone fading. The fading at 24 ppm-hours cumulative exposure for the Epson system shows slightly more loss of cyan than magenta, with little yellow fade, while the Canon system shows a cyan loss about twice that of magenta with measurable yellow dye degradation. These results are consistent with those of Bugner[9] in a test of Epson Premium Glossy paper (v2000 and v2001) printed with the Epson SP890 and exposed to UV generated ozone and to those of Oki et al[13] as shown in Table 3. Reported temperature studies by Oki et al indicate an increase in fading by ozone of this system by about 30% by increasing the temperature from 23 to 40°C and would bring our UV generated ozone (UV) studies conducted at 40C into good agreement with the corona discharge (ED) studies conducted at 23°C.

While there is generally good agreement between different fading studies of the Epson system using ozone generated with electric discharge or UV light, our tests with the Canon system show that the correlation between UV and ED generated ozone may not be as not as straightforward. Table 4 shows that a similar degree of fading occurs at 5 hours in the Hampden ozone chamber (UV, at 40°C) that requires 24 hours of exposure with the OTC-1 chamber (ED, at 23°C). Also, a 24-hour test with the Hampden chamber exhibits more fading than does 72 hours in the OTC-1 chamber.

However, the relative fading of the different dyes are quite similar with the two different chambers. It possible that the effect of temperature on ozone fading is more pronounced with the Canon system than with the Epson system. These results indicate that care must be made in making real world fading predictions due to ozone. The temperature sensitivity to ozone fading of specific ink and paper combinations must be characterized and ambient temperatures must be considered in predicting fading by ozone.

Table 3. Comparison of Density Loss for Exposure at 24 Hours at 1 ppm Ozone

Source	Paper Type	Ozone Type	Temp C	%RH	C %loss	M %loss	Y %loss
This study	2001	ED	23	55	34	29	0
This study	2000	ED	23	55	32	23	0
This study	2001	UV	40	50	42	36	5
Bugner (9)	2001	UV	24	50	28	15	2
Bugner (9)	2000	UV	24	50	28	19	1
Oki (13)	N/A	ED	24	60	35	28	-2

Epson Premium Glossy Photo Paper with Epson SP890 and SP960 6-ink photo printers.

Table 4. Comparison of Density Loss for Exposure 1 ppm Ozone for UV and ED Tests

Hours	Ozone	Temp C	%RH	C %loss	M % loss	Y % loss
24	ED	23	55	44	20	3
72	ED	23	55	73	45	10
5	UV	40	50	44	20	1
24	UV	40	50	78	60	17

Canon Photo Paper Pro PR-101 with Canon S900 printer.

Kinetics of Ozone Fading

While a majority of the data presented in this study had initial densities of 1.0, very similar fading kinetics were found for 0.60 and 0.35 initial densities. Figure 3 tests a 1st order or pseudo 1st order decay for the Canon system (Cyan). The decay rate constants are largely independent of the initial density. This behavior was observed for both the cyan and magenta dyes. However, overall the observed agreement with pseudo 1st order kinetics is only fair, in agreement with a previous study[6] that noted the complexity of ozone degradation kinetics.

Reciprocity

For the microporous papers tested there does appear to be good agreement with published results. Figures 4 and 5 plot the cyan density for the Epson system and the Canon system tested as a function of cumulative exposure. Beyond the first few initial ppm-hours, a smooth fit can encompass the different ozone concentrations, indicating for these dyes and media that reciprocity is obeyed. Comparable reciprocity behavior was also observed for initial densities of 0.60 and 0.35.

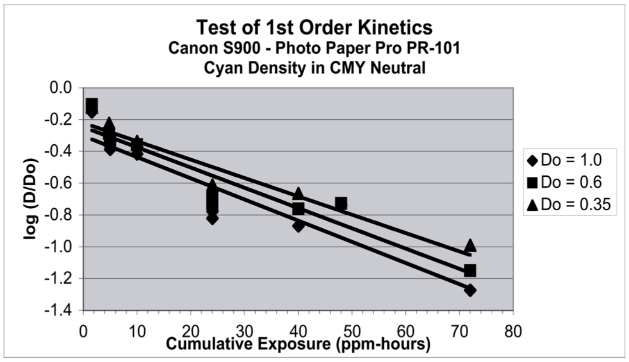

Figure 3. Test of 1st order kinetics with Canon System.

Cyan

Do	R2	Equation
1.00	0.8539	y=-0.0133x-.30
0.60	0.8861	y=-0.0128x-.25
0.35	0.9191	y=-0.0116x-.22

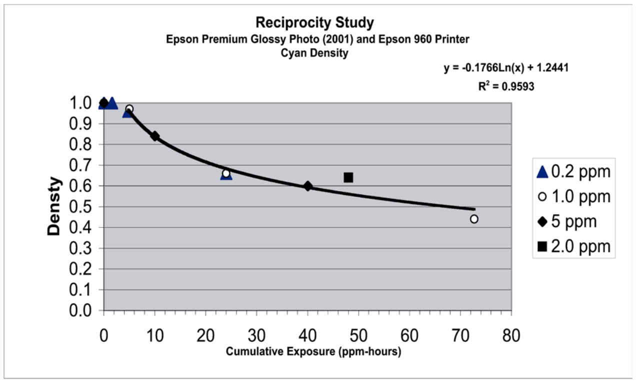

Figure 4. Reciprocity for the Epson system.

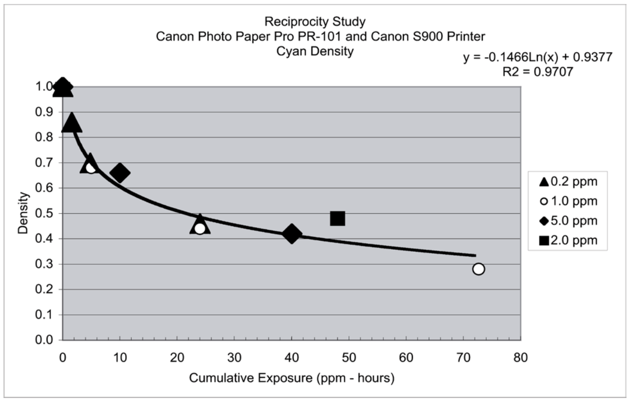

Figure 5. Reciprocity for the Canon system.

The Effect of Relative Humidity

Previous studies have indicated that the relative humidity can affect ozone fading.[7,10,13] Since the OTC-1 chamber does not control the relative humidity, RH in the test chamber was adjusted to within plus or minus 5% RH by controlling the relative humidity of the room in which the chamber was located. Tests were conducted nominally at 55% RH and 70% RH at 1 ppm ozone. Our experiments show that the effect of RH on ozone fading is dependent on the media system. Over the range of cumulative exposures tested, the Canon system showed a greater cyan and magenta density loss at 70% RH than at 55% RH by almost 15–25% RH. The Epson system was less sensitive, only showing a 10% increase in degradation of both cyan and magenta going from 55% RH to 70% RH. Oki et al.[13] reported a 20% increase in degradation in going from 55 to 70% RH for a similar Epson system. Shibahara et al.[7] reported a strong increase (40%) in the rate of cyan dye loss when the humidity was increased over a range similar to the range in this study, for an unspecified inkjet system using ozone produced with an electric discharge.

At this time it is not clear by what mechanism relative humidity impacts ozone fading of images. The effect of relative humidity requires more study for several reasons. For example, it is possible that ozone generated with an electric discharge may generate different chemical species at high humidity because water molecules in the electric discharge may participate in a variety of gas phase reactions to produce chemically reactive species different from those that exist at low humidity or with UV generated ozone. It is known that the efficiency of the corona discharge to produce ozone decreases significantly at very high humidity. Thus comparison of fading by ozone generated with an electric or corona discharge and by ozone generated with UV must be conducted at higher humidity levels. Second, the reactivity of the print itself with ozone may be affected by relative humidity. Possible effects of higher humidity include increasing the diffusivity of ozone into the media, increasing the solubility of the absorbed dye and hence its reactivity, and complex reactions that involve water, ozone and the microporous interstitial surface chemistry.

In order to be able to compare inter-laboratory data, it will be important to specify standard RH conditions for testing. The AATCC standard test method 109 for evaluating textile fading in ozone specifies 65 +/-2% RH. Also, to determine chemical mechanisms for ozone fading or to predict a useful lifetime before failure, the role of humidity in ozone generation and image degradation by ozone must be studied further. However, it appears that in the range of 50 – 55% RH, there is good agreement between fading studies using UV or electric discharge generated ozone.

Comparison of Accelerated Ozone Testing with Ambient (Actual) Conditions

The ambient air-flow test apparatus was run for a total of 20 days during which the ozone concentration varied from 0 to 0.03 ppm. If reciprocity is observed, our ambient fading results are consistent with a cumulative exposure of ~ 3.0 ppm-hours in the OTC-1 chamber. Our estimated average ambient ozone concentration of 0.007 ppm is below the estimated indoor yearly average ozone concentration[1,7] of 0.010 – 0.015 ppm. Table 5 compares observed ambient fading and predicted fading if reciprocity were obeyed. While the density losses involved in this experiment are quite small, there is generally good agreement between the observed and predicted fading. The large uncertainty in this test arises from the lack of accurate measurement of ambient ozone levels.

Table 5. Results of Ambient Forced Air Tests

System		C % loss	M % loss	Ratio of C/M loss
Canon	Actual	15	3	4.8
Canon	Predicted	19	6	3.2
Epson	Actual	7	3.5	2
Epson	Predicted	5	2.5	2

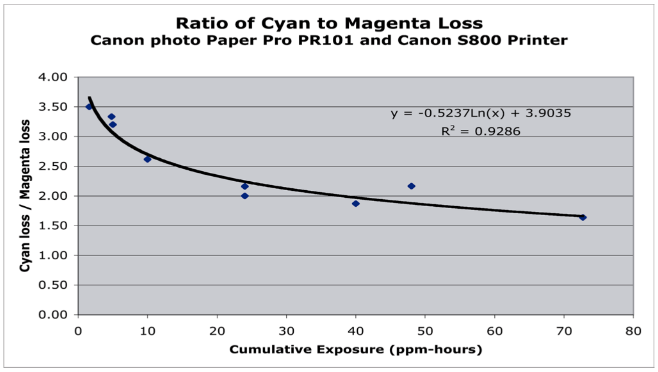

Figure 6. Ratio of Cyan/Magenta Fade - Canon system.

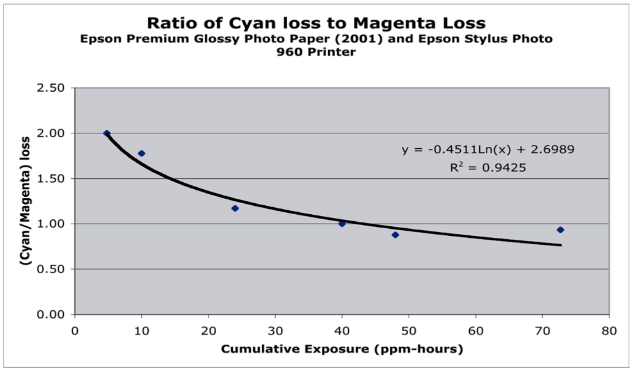

Figure 7. Ratio of Cyan/Magenta Fade - Epson system

The ratio of cyan/magenta loss can indicate the extent of fading for initial 1.0 density patches because the ratio incorporates the different rates of decay of the cyan and magenta dyes as well as cumulative exposure. Figures 6 and 7 show the ratio changes with cumulative exposure for the Canon system for initial density of 1.0. If one quantifies the fading for each dye it is possible to predict loss ratios for different cumulative exposures.

In summary, our ambient forced airflow studies indicate that the characteristics of "real world" gas fading is predictable for some (microporous) systems based on accelerated testing with ozone. Further testing with several other systems under a variety of conditions will indicate the precision of such predictions.

Conclusions

There is good agreement between fading tests using ozone produced with electric (corona) discharge and ozone produced with UV over the range 0.2–5.0 ppm ozone. Reciprocity is observed between ozone concentration and exposure time for the microporous media tested. More research is required to quantify the effects of temperature, relative humidity and airflow in order to understand degradation mechanisms and to be able to predict useful image lifetimes over a range of real world conditions. Additional studies should be undertaken to enable standardization of testing protocols for ozone fading – such as dry down time before testing is initiated and possible interactive effects of concurrent light exposure in the presence of ozone.

Acknowledgements

The authors would like to acknowledge the assistance of Oleg Baburin, Jack Robertson, Dima Shklyarov, and Barbara Stahl of Wilhelm Imaging Research in conducting the experiments with the INUSA OTC-1 chamber.

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Biography

Dr. Berger received his Ph.D. in Physical Chemistry from Harvard University and spent several years as a Senior Technical Manager with Polaroid Corporation. Dr. Berger has investigated the stability of various imaging media to light exposure and to atmospheric chemicals. He has authored over 15 technical papers and articles on several aspects of photochemistry, atmospheric chemistry, and digital imaging, and he has nine patents. Dr. Berger is currently working with Wilhelm Imaging Research on the characterization of gas fading of digital images by atmospheric pollutants.