Evaluating the Ozone Resistance of Inkjet Prints: Comparisons Between Two Types of Accelerated Ozone Tests and Ambient Air Exposure in a Home

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Abstract

This paper addresses the questions of whether there are significant differences in the observed accelerated fading of inkjet prints when they are exposed to ozone generated either with electrical corona discharge or ultraviolet radiation, and how these accelerated tests compare with exposure to ambient indoor air containing commonly encountered levels of ozone. These questions must be answered before an accelerated ozone resistance test method is adopted. While previous ozone fading experiments have shown general agreement between the accelerated test methods, prints from only a limited number of inkjet technologies were studied, and some differences were noted. The study presented here includes a larger variety of inkjet inks, including pigmented inksets, a variety of media, and a post-treatment protective spray. The results indicate that for a wide range of inks and inkjet media, ozone induced fading is independent of the method of ozone generation. In general, these accelerated ozone tests correlated well with "real world" gas fading experienced in a non-air conditioned home located in a suburb of Boston, Massachusetts during the summer months of 2004.

Introduction

As reported previously, the authors found a comparable amount of fading of dye-based inks printed on microporous papers when these prints were exposed to ozone generated either by electrical corona discharge or by UV radiation.[1] However, there has been limited quantitative data available for the many different ink/media combinations that have substantially greater resistance to ozone fading. Bugner et al[2] reported that some of the more ozone-resistant papers based on swellable polymer technology had substantially slower fading overall but showed about 20 to 30% more fading than expected at low ozone concentrations; that is, they exhibited reciprocity failures. Kitamura et al[3] showed that there was a good correlation in observed fading between an accelerated ozone fade test with a total ozone exposure of 40 ppm-hours (total ozone exposure equal to parts per million ozone times the number of hours of exposure) at 60% RH, 24°C and ambient conditions averaged over a year for Epson inks and porous and microporous media. Thornberry and Looman[4] correlated "real world" conditions and accelerated ozone fading for a large number of porous media and dye-based ink combinations and concluded that reciprocity was observed to a large degree. Moreover, they presented data showing that the yearly average residential ozone concentration was about 7 ppb (parts per billion). They concluded that "industry differences in test conditions and ambient ozone estimates illustrate the need for a standardized ozone fade test."

To help define the significant parameters for a standardized ozone fade test, this paper compares the results from two different types of ozone chambers to fading under ambient indoor home conditions for a broad range of ink and media combinations of interest to the fine art and professional photographer as well as to the home photo enthusiast.

Experimental

Ozone Test Equipment

The commercial ozone testing units have been described before.[1] The IN USA Model OTC-1, manufactured by IN USA, Inc. (Needham, Massachusetts), was used for testing with ozone produced by a corona electrical discharge (ED). The Hampden Model 903, produced by Hampden Test Equipment (Northamptonshire, UK), was used for testing with ozone produced by UV radiation from a UV lamp (UV).

Samples were also tested in ambient air in a home environment. A "forced air-flow" configuration described by Paul Wight[5] was used and the authors have described this type of unit in a previous article.[1] For the experiments reported here, the forced air-flow chamber was constructed entirely of plastic materials in order to reduce the destruction of ambient ozone by the unit itself. It was placed in the living room of a Boston suburban home about eight feet from the windows (the windows were usually open during July 2004, when most of the ambient tests were conducted). The temperature, relative humidity, and ozone concentration were recorded every 15 minutes with the HOBO U12 Data logger obtained from Onset Computer (Pocasset, Massachusetts). Figure 1 shows that the daily pattern of temperature maxima and percent RH minima (in late afternoons) correlates with the daily ozone maxima.

The data logger records the temperature and relative humidity (± 0.6°F and ± 2.5 % RH) as well as records input voltages from the ozone monitor, Model C-30ZX, manufactured by EcoSensor (Santa Fe, New Mexico). The ozone monitor is pre-calibrated by the manufacturer using NIST traceable calibration devices. This monitor is linear in the range of 0.10 to 0.14 ppm ozone with an accuracy of ± 10 %. The device employs a heated metal oxide semiconductor as the sensor. The device is not recommended for outdoor use, since the monitor will also respond to oxides of Nitrogen which may be present in the outdoor environment of urban areas due to significant vehicular traffic and could lead to incorrect measurements of ambient ozone levels in the test environment. Thus the ozone levels can be overstated in heavily polluted air. The best estimate of the actual average ozone concentration during the July 2004 period is 40 ppb, which corresponds to a total ozone exposure over the 29 days equal to 28 ± 4 ppm-hours.

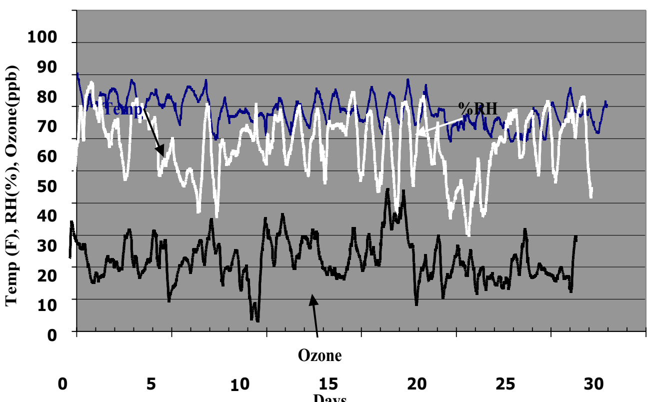

Figure 1. Temperature, relative humidity, and ozone concentrations for an ambient indoor home condition in Boston, July 2004.

Sample Print Preparation

Print test samples were prepared with a variety of commercially available inkjet systems; the manufacturers' recommended ink sets were used. Desktop printers using dye-based inks included the Canon S900, the Epson Stylus Photo 960, the HP Photosmart 7960 with HP 57/58/59 ink cartridges, and the Epson R300 photo printer which was introduced in late 2003 and uses a new inkset which is more ozone resistant than previous Epson dye-based inksets. Printers using pigmented inks included the Epson Stylus Pro 4000 (Epson UltraChrome inks) and the Epson Stylus Photo 2000P (Epson Archival inks). A variety of media was tested and included glossy microporous inkjet papers, such Canon's Photo Paper Pro PR-101 and Epson's Premium Glossy Photo Paper, and papers based on swellable polymer technology, such as Epson ColorLife, Kodak Ultima Picture Paper High Gloss ColorLast (2003), and HP Premium Plus Glossy Photo Paper. The test prints were allowed to "dry down"[6] in the dark for two weeks at 60% RH and 24°C before initiating the tests. The prints used in the Hampden chamber were dried down for about four weeks before the tests were initiated. The printed test targets have been previously described.[7] A Canon Photo Paper Pro PR-101 test sample was sprayed with a protective coating of Lumijet™ ImageShield™ following the procedures by the manufacturer, Luminos Photo, Yonkers, New York. The spray contains UV absorbers and was developed to "seal the surface" of the print; its use as an ozone retardant is evaluated in this paper.

Methods and Measurements

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. While the color patches were examined for corroborative data, the analysis in this paper focuses on neutral patches with initial densities of 0.6 and 1.0. The effect on the fading rate of mixed versus pure dyes is important to the understanding of image fade caused by ozone, but is beyond the scope of this paper.

Summary of Test Conditions

The samples were exposed in the OTC-1 and Hampden 903 ozone chambers at a range of concentrations and times selected to insure that reciprocity could be thoroughly evaluated. See Table 1 for test conditions used in the OTC-1 ozone chamber. For comparative data, testing in the Hampden 903 ozone chamber was conducted at 25 hours at 1 ppm ozone. Both ozone chambers were operated at 60% RH and 24°C.

Results and Discussion

Characteristics of Fading

Figure 2 shows two typical examples of fading due to ozone exposure experienced in this study. In general the dye-based inks printed on microporous or matte porous inkjet receiver systems show an exponential decay in density with

Table 1. IN USA OTC-1 Test Conditions (ppm-hours)

	Ozone Concentration		
	5 ppm	1 ppm	0.2 ppm
Hours			
2	10		
5	25		
10	50	10	
25	125	25	
50	250	50	10
100	500		
125		125	25
250		250	50
625			125

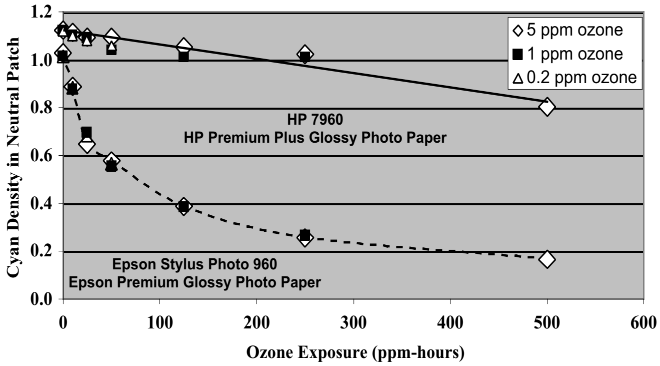

Figure 2. Dye-based cyan ink ozone fading characteristics of Epson (microporous) and Hewlett-Packard (swellable) glossy photo paper combinations at three different ED ozone concentrations.

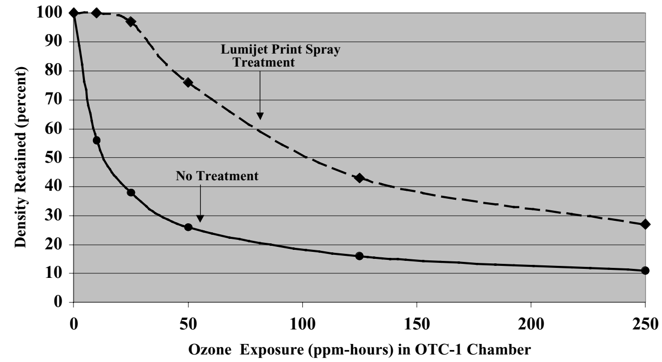

Figure 3. Effect of Lumijet protective spray on ozone fading of prints made with a Canon S900 photo printer and Canon Photo Paper Pro PR-101.

increased exposure to ozone as demonstrated by Epson Premium Glossy Photo Paper printed with the Epson Stylus Photo 960. The more ozone resistant swellable polymer receivers show a linear decay with total exposure as demonstrated by the HP Photosmart 7960 dye-based inks printed on HP Premium Plus Glossy Photo Paper. Figure 2 also demonstrates the principal of "reciprocity," where fading is proportional to the total exposure, whether achieved by a low concentration of ozone over a long time or by a high concentration of ozone over a shorter time period. In general, reciprocity behavior was relatively good for the systems studied.

Relative Ranking of Different Systems in Terms of Susceptibility to Ozone

Table 2 rank-orders the susceptibility to fading of the test samples at the maximum exposure (500 ppm-hours) and compares the fading at 25 ppm-hours for both UV and ED generated ozone. The greatest percentage density loss of either red, green, or blue density in a 1.0 neutral patch is used for the ranking. Table 2 shows: 1) The rank ordering is identical at the higher exposure compared to the ranking at the lower exposure; and, 2) The ranking and degree of fading are very similar between the UV and ED ozone chambers. One benefit of exposure to higher concentrations of ozone is better discrimination of resistance to fading between the more ozone-resistant samples.

Higher concentration ozone exposures are also desirable in evaluating prints overcoats and additives. Barcock and Lavery[8] showed that a 0.5 micron aqueous polymer overcoat could protect Epson Stylus Photo 890 prints from ozone fading for up to 24 hours at 3.5 ppm ozone exposure. In our testing, the sample sprayed with a protective overcoat showed only a small loss at 25 ppm-hours total exposure, but showed increasingly greater losses at greater exposures (see Figure 3). Indeed at a total exposure of 500 ppm-hours, the sprayed and non-sprayed samples had substantial and nearly identical losses in density. This delay in density loss for the sprayed sample is similar to the behavior of media containing ozone

Table 2. Relative Ranking – Susceptibility to Ozone

	Greatest Density Loss 500 ppm-hours @ 5ppm "ED ozone"	Greatest Density Loss 25 ppm-hours @ 1ppm "ED ozone"	Greatest Density Loss 25 ppm-hours @ 1ppm "UV ozone"	Ink Type Paper Type
Canon S900/ Canon Photo Paper Pro PR-101	-88%	-61%	-72%	Dye Microporous
Epson Stylus Photo 960/Epson Premium Glossy Photo Paper v.2001	-78%	-30%	-37%	Dye Microporous
Canon S900/Canon Photo Paper Pro PR-101/LumiJet Spray	-74%	-3%	-7%	Dye Microporous + Spray
Epson R300/Epson Premium Glossy Photo Paper v.2001	-32%	-6%	-9%	Dye Microporous
HP PhotoSmart 7960/HP 57,58,59 inks/HP Premium Plus Glossy Paper (2003)	-15%	-3%	-6%	Dye Swellable Polymer
Epson Stylus Photo 2000P/Epson Archival/Epson UltraSmooth Fine Art Paper	-8%	-3%	-4%	Pigment Matte Porous
Epson Stylus Pro 4000/Epson UltraChrome/Epson UltraSmooth Fine Art Paper	-5%	-2%	-2%	Pigment Matte Porous
Canon S900/ Kodak Ultima Picture Paper High Gloss ColorLast (2003)	-4%	-2%	-3%	Dye Swellable Polymer
Epson Stylus Photo 960/Epson ColorLife Photo Paper	-1%	0%	-1%	Dye Swellable Polymer

Table 3. Reciprocity Study – Density Loss at 50 ppm-hours (IN USA Model OTC-1 Chamber)

	0.2 ppm % Density Loss			1.0 ppm % Density Loss			5.0 ppm % Density Loss		
	C	M	Y	C	M	Y	C	M	Y
Canon S900/ Canon Photo Paper Pro PR-101	-64.0%	-27.0%	-4.6%	-73.0%	-49.0%	-9.8%	-73.0%	-55.3%	-10.6%
Epson Stylus Photo 960/Epson Premium Glossy Photo Paper v.2001	-43.0%	-39.7%	-0.2%	-43.3%	-41.7%	0.7%	-33.0%	-21.0%	-7.0%
Epson R300/Epson Premium Glossy Photo Paper v.2001	-10.0%	-8.2%	-7.9%	-10.5%	-8.6%	-7.5%	-9.0%	-7.8%	-6.8%
HP PhotoSmart 7960/HP 57,58,59 inks/HP Premium Plus Glossy Photo Paper (2003)	-4.4%	-6.4%	-3.0%	-5.0%	-5.4%	-1.2%	-3.8%	-4.2%	-1.5%
Epson Stylus Photo 2000P/Epson Archival/Epson UltraSmooth Fine Art Paper	-3.7%	-4.4%	0.3%	-3.6%	-4.6%	0.2%	-3.2%	-4.2%	0.3%
Epson Stylus Pro 4000/Epson UltraChrome/Epson UltraSmooth Fine Art Paper	-2.5%	-2.5%	-0.2%	-2.5%	-2.6%	-0.2%	-2.1%	-2.3%	0.0%
Canon S900/ Kodak Ultima Picture Paper High Gloss ColorLast (2003)	-1.8%	-0.5%	-1.1%	-2.2%	-0.6%	-0.9%	-2.3%	-1.3%	0.0%
Epson Stylus Photo 960/Epson ColorLife Photo Paper	-0.7%	-0.5%	1.7%	-0.6%	-0.5%	-0.4%	-0.8%	-0.5%	-0.6%

scavengers;[2] once the scavengers have been consumed, normal fading resumes. This is a special case of reciprocity failure.

Reciprocity Behavior in Ozone Fading

The characterization of the reciprocity behavior of a system is important, because if a system obeys the reciprocity relationship, then short-term accelerated tests with high concentrations of ozone can be used to predict fading in ambient conditions. Often, but not always, an accelerated test can overestimate the stability and thus the predicted lifetime. Bugner et al[2] have reported that HP and Canon inks printed on swellable polymer receivers exhibit reciprocity failure, exhibiting between 20 and 30% more fading at lower ozone concentrations than predicted by studies at higher ozone concentrations.

The thoroughly studied Epson Stylus Photo 960/Epson Premium Glossy Photo Paper (v.2001) system demonstrates

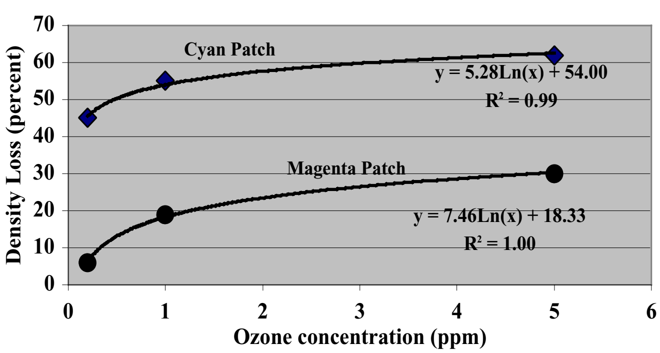

Figure 4. Density loss for constant total ozone exposure of 25 ppm hours with prints made with a Canon S900 printer and Canon Photo Paper Pro PR-101 (a microporous glossy photo paper).

excellent reciprocity behavior as seen in Figure 2. These results agree with previous studies.[1,2] However Barcock and Lavery[8] found that the same Epson inks when printed on another porous coating did not exhibit reciprocity showing less fading at lower ozone concentrations. There is growing evidence that specific dyes and receivers can strongly influence the observed overall reciprocity behavior. The inks used in the Canon S900, for example, have demonstrated a range of behaviors. Good reciprocity behavior was found with the cyan ink on Canon Photo Paper Pro PR-101 (this study); more fading than predicted by the reciprocity law at low ozone concentrations occurred with Office Depot Premium Photo Paper;[2] and less fading at lower ozone concentrations than predicted by the reciprocity law was found with the magenta ink on Canon Photo Paper Pro PR-101 (this study).

If the reciprocity law is obeyed, the results at a total exposure of 50 ppm-hours should show the same degree of fading regardless of the ozone concentration. Table 3 compares the greatest percentage density loss in the 1.0 neutral patch of the test samples tested with three different ozone concentrations: 5 ppm ozone for 10 hours, and 1 ppm ozone for 50 hours, and 0.2 ppm for 125 hours.

For a majority of the samples, there were only small differences in the percentage of density loss between different ozone concentrations. The exception is the Canon S900/ Canon Photo Paper Pro PR-101 system, which clearly shows an increase in fading at higher concentrations of ozone for equal total ozone exposures, especially for the magenta ink. This trend is also observed at 25 ppm-hours and is plotted in Figure 4.

Although the authors previously reported reasonably good reciprocity behavior over the same range of ozone

Table 4. Comparison of Density Loss for ED and UV Generated Ozone and with Ambient Indoor Home Conditions

	ED % Density Loss			UV % Density Loss			Ambient % Density Loss		
	C	M	Y	C	M	Y	C	M	Y
	(25 hours @ 1ppm Ozone, 60% RH and 24C)						(29 days @ 70% RH, 24 C)		
Canon S900/ Canon Photo Paper Pro PR-101	-61%	-35%	-6%	-72%	-56%	-12%	-65%	-26%	6%
Epson Stylus Photo 960/Epson Premium Glossy Photo Paper v.2001	-30%	-25%	2%	-37%	-32%	-3%	-33%	-21%	-7%
Epson R300/Epson Premium Glossy Photo Paper v.2001	-6%	-5%	-5%	-9%	-8%	-9%	-8%	-3%	-9%
HP PhotoSmart 7960/HP 57,58,59 inks/HP Premium Plus Glossy Paper (2003)	-3%	-3%	-1%	-6%	-5%	-2%	-2%	-4%	1%
Epson Stylus Photo 2000P/Epson Archival/Epson UltraSmooth Fine Art Paper	-3%	-3%	0%	-3%	-4%	0%	-4%	-5%	0%
Epson Stylus Pro 4000/Epson UltraChrome/Epson UltraSmooth Fine Art Paper	-2%	-2%	0%	-2%	-2%	0%	-2%	-2%	0%
Canon S900/ Kodak Ultima Picture Paper High Gloss ColorLast (2003)	-2%	0%	1%	-3%	0%	1%	-2%	5%	13%
Epson Stylus Photo 960/Epson ColorLife Photo Paper	0%	0%	0%	-1%	-1%	2%	0%	0%	7%

concentrations and total exposures for this Canon system, we believe the results of the study reported here are more representative because of improved control over the test conditions, including temperature and relative humidity.

Rate of Degradation as a Function of Ozone Concentration

By examining the amount of fading at different ozone concentrations, it is possible to study fading kinetics and possible mechanisms for the different systems. Figure 5 shows the dependence of the rate of density loss with 50 hours exposure at a variety of ozone concentrations for the HP 7960/ HP Premium Plus Glossy Photo Paper.

The HP ink/media system exhibits behavior consistent with zero order kinetics with respect to dye concentration. A fading mechanism consistent with a linear dependence on ozone concentration could be a fast reaction between the dye and ozone, but limited by the slower diffusion of the ozone through the swellable polymer receiver system.

In general the dye/porous or dye/microporous based systems showed first order kinetic behavior and the dye/swellable polymer receiver systems exhibited zero order kinetics. There were exceptions to this rule, indicating that different rate-limiting kinetics and processes predominate in those systems. For example, the Canon S900/Kodak Ultima Picture Paper High Gloss ColorLast system (dye/swellable polymer) exhibited first order kinetics, and the Epson R300/Epson Premium Glossy Photo Paper system (dye/microporous) showed zero order kinetics.

Comparison of Fading for ED and UV Generated Ozone and Ambient Conditions

Table 4 addresses the following questions: 1) Do ED and UV ozone chambers give comparable results? and, 2) Is the accelerated fading observed in ozone chambers comparable to that which occurs in ambient conditions? A comparison of the density losses in the neutral patches after a total of 25 ppm-hours exposure (1 ppm ozone, 60% RH, 24°C) in the commercial ozone chambers, and in the ambient indoor home condition (28 ppm-hours exposure, 70% RH, 24°C) indicates that, in general, there is very good agreement between the ED and UV chambers and also with the ambient conditions. It appears that there may be slightly more fading

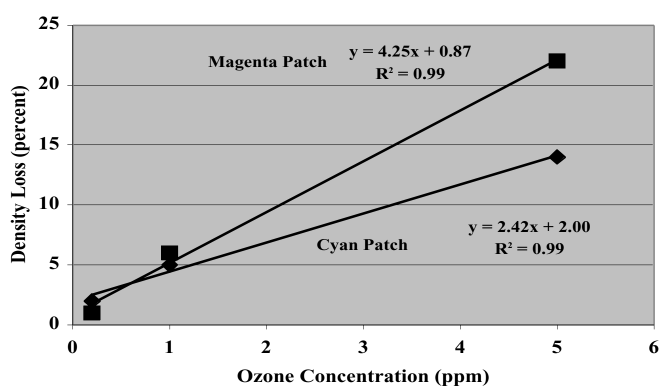

Figure 5. Density loss with prints made with a Hewlett-Packard Photosmart 7960 printer (using HP 57, 58, and 59 ink cartridges) and HP Premium Plus Glossy Photo Paper after 50 hours of ozone exposure at different ozone concentrations.

in the UV chamber than in the ED chamber, especially for the magenta dye. This may be due to the greater air exchange rate in the UV chamber (3 times per minute) compared to the ED chamber (1.5 times per minute). Moving air has been found to increase the rate of fading of Canon S800 images printed on a microporous paper by a factor of four over the rate in still air.[8] More research is needed to quantify the effect of air-flow in ozone fading, as it appears that at least for some ink/media combinations, airflow is a major factor in their fading rates.

There are several samples in the ambient condition (Table 4) that showed an increase in yellow density after 29 days; in particular, the dye/swellable polymer systems showed increases of 1%, 13% and 7%. In general, the increases in yellow density were not as great for samples tested in the ozone chambers as compared to ambient exposure. The average ambient humidity (60–90% RH with an average of 70% RH) was substantially higher than the 60% RH in the ozone chambers. It has been shown that many dye/swellable polymer systems undergo dye migration at high humidity.[9,10] The sensitivity of each media/ink combination to dye migration due to high humidity must be taken into account when evaluating correlations between accelerated and ambient conditions.

Conclusions

Our results indicate that for a wide range of inks and inkjet media, ozone induced fading did not depend on how the ozone was generated. Reciprocity was generally obeyed and observed deviations were small, except for a system with a sprayed protective coating. There was also good correlation between the fading results from testing in ozone chambers and testing in "real world" conditions with ambient indoor air in a home. Further work is underway to gather additional data comparing chambers using UV lamp generated ozone and corona electrical discharge generated ozone at greater total exposures. Additional research is also needed to quantify the effects of air-flow on ozone fading.

Acknowledgements

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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 aspects of photochemistry, atmospheric chemistry, and digital imaging, and he holds nine patents. Dr. Berger is currently working with Wilhelm Imaging Research on the characterization of gas fading of traditional silver halide and digital photographs by atmospheric pollutants.