Fade Stability of Color Photographic Images in the Presence of Ozone Gas – Part II

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Abstract

The Image Stability Technical Center of Eastman Kodak Company is continuing its evaluation of various media in a new system for testing image permanence in the presence of elevated levels of ozone. An initial presentation of system uniformity was made at the Digital Photo Fulfillment Conference in February, 2009. This second follow-on paper will report on experimental findings to date relating to ozone gas impingement method and gas velocity at 1 ppm concentration as well as initial reciprocity studies for dye-based inks on one porous photo paper. Future studies will include repeat experiments with other industry media types, tests with lower velocities, and temperature/RH effects.

Introduction

It is well documented that exposure to the common air contaminant ozone is one of the more important factors impacting the life of printed images [1]. With this recognition, the digital print industry has been working toward the goal of adopting a standardized test method for establishing image permanence claims based on ozone exposure. Consensus on methodology is sometimes hampered by the lack of test data and need for further study.

Commercially available environmental chambers used in ozone testing can be costly and may afford only limited experimental flexibility because of fundamental capabilities or as-manufactured design impediments.

In the fall of 2008, Eastman Kodak Company completed development of a custom environmental chamber (Fig. 1) for dedicated use in understanding and quantifying the impact of ozone exposure on printed images [2].

Figure 1. *New ozone environmental chamber from Kodak .*

In addition to controlling temperature, humidity, and ozone concentration, this new chamber affords the ability to study other variables such as impingement method and velocity. Key parameters are monitored and controlled using a programmable logic controller. Refer to Fig. 2 for general design.

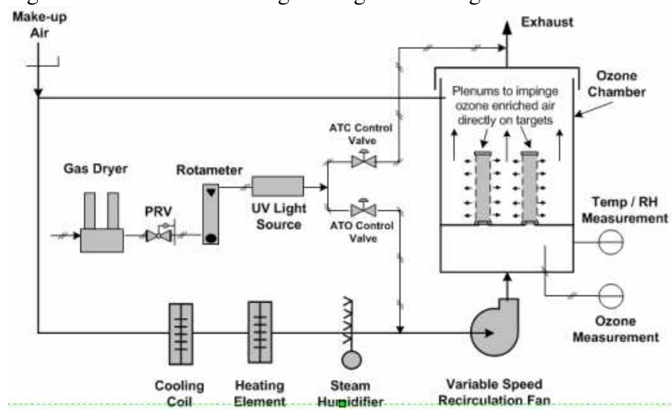

Figure 2. *Chamber design schematic.*

The chamber design employs a variable speed centrifugal blower to regulate the gas volume being recirculated. Impingement velocity is controlled via fan speed, the number of installed plenums, the design of the perforation pattern in the impingement plenum, and the target standoff distance. Figure 3 pictures one style of impingement plenum.

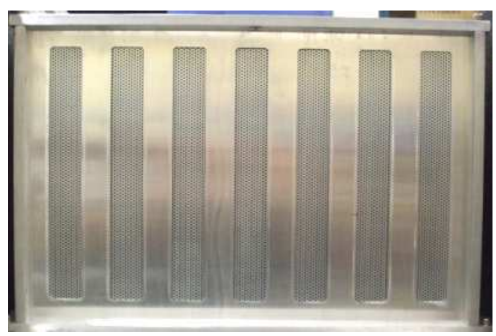

Figure 3. *Face of impingement plenum.*

A UV light source is used to generate ozone, which eliminates potential contamination from the by-products associated with ozone generation using the corona discharge method. Ozone concentration as supplied to the targets is measured within the chamber and is precisely controlled by continuously regulating the position of two control valves, either directing ozone-enriched instrument air to the chamber or to an external exhaust. Ozone enters the chamber at the inlet of the centrifugal fan to achieve good mixing. The air in the room where the chamber resides is scrubbed using carbon filters to reduce ambient ozone concentration to ~2 ppb. A small amount of continuous exhaust ensures that some fresh make-up air is continually introduced into the chamber to avoid build-up of any potential contaminants.

Experiment Background

For these experiments, the media chosen was identical to that used in the earlier uniformity studies and employed dye-based inks on porous photo paper. The particular system chosen was thought to have a high sensitivity to ozone exposure. A test target was designed having 18 patches each of neutral, magenta, and cyan, all at respective equal d_{max} densities, as shown in Fig. 4. Three neutral d_{min} patches are also included. (Prior testing has revealed that magenta and cyan are typically the first colors to fail when exposed to ozone) [1].

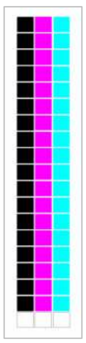

Figure 4. *Test target.-(57 blocks, neutral d_{max} on left, magenta center, cyan on right, neutral d_{min} on bottom).*

Fresh samples were printed just prior to the start of the experiments from the same lot of paper and ink. Initial density measurements were made just prior to the start of each event, using the Gretag Spectroscan spectrophotometer. Reported results are the loss in density over the life span of the test.

Test targets were held on three sides in a frame for precise and constant positioning throughout the experiment. A target blade having seven mounted targets on one face is shown in Fig. 5. This mount allowed for only single-sided target exposure to ozone during the experiment. The number and position of targets varied depending on the particular test design.

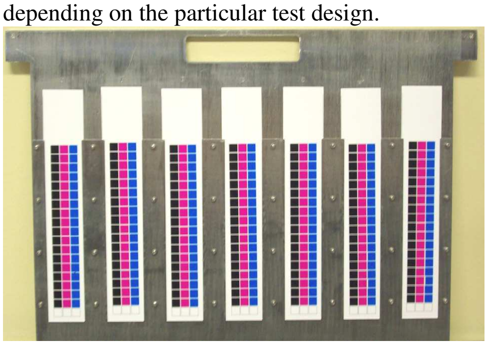

Figure 5. *Target mounting blade with targets.*

The following equipment was used in support of these experiments:

- InUSA IN-2000 LoCon UV adsorption ozone analyzer
- General Eastern Hygro M2 hygrometer
- Gretag Macbeth/Spectroscan spectrophotometer
- Kodak's custom designed environmental chamber as described above

Temperature and humidity conditions were confirmed prior to the start of the experiment using a hygrometer with traceable calibration. Ozone concentration was measured with an InUSA ozone analyzer with traceable calibration to 1 ppm and confirmed with a redundant analyzer. Conditions were monitored and confirmed throughout the experiment duration.

Experiment A – Impingement Method/Velocity

This first experiment examined fade results over a set of identical targets at controlled conditions of 22.2 ºC (72 F) dry bulb, 50% RH, and an elevated ozone concentration of 1 ppm, all under closed loop control with differing impingement methods and velocities. Ozone concentration supplied to the targets was held constant for a duration of 13 days during each of four test phases. In the chamber, all test targets were equally spaced off impingement plenums using fixed position target mounts.

A total of 18 targets were positioned in the center six rows and center three columns of the chamber and were impinged with ozone-enriched air from a plenum of orifice jets at 90º to the target surface.

Another six targets were positioned in the two outermost rows using the center three columns but, in this case, the plenums were blocked so that these targets had no direct impingement. Instead, return grilles were left open so the targets were only exposed to the volumetric turnover of ozone-enriched air, which would be flowing mostly parallel to the surface.

The four test phases of this experiment were conducted based on equal changes in fan speed (900, 1550, 2200, and 2850 rpm) supplying the ozone-enriched air. New targets from the same original batch were loaded, exposed and evaluated for each phase, using equal exposure hours and chamber conditions. Fan laws dictate that the equal rpm changes represent equal changes in fan volumetric output. Based on the fan curve, rpm, static discharge pressure, and open orifice area of the test chamber, it was calculated that these fan speeds represented plenum discharge velocities of 120, 240, 360, and 480 fpm.

The data for impinged targets is published against these four velocities of ozone-enriched gas. For the nonimpinged targets, the fan speed settings were converted to approximate volumetric turnover per hour, as the fan discharge CFM and chamber volume are known. For the nonimpinged targets the data is plotted against these volumetric turnover rate estimates. The four conditions roughly equate to 925, 1850, 2775, and 3700 volume turns/h [VT/h].

The goal of this experiment was to assess whether impingement velocity or method had any discernable impact on fade results. The data represents the average density loss of all patches of the same color record for all targets.

Experiment A – Results and Discussion

Figure 6 displays the average fade results of the cyan, magenta, and neutral component colors for all color patches on the 18 impinged targets against the four velocities tested.

Figure 7 displays the average fade results of the cyan, magenta, and neutral component colors for all color patches for the six nonimpinged targets against the four velocities as converted into volumetric turnover.

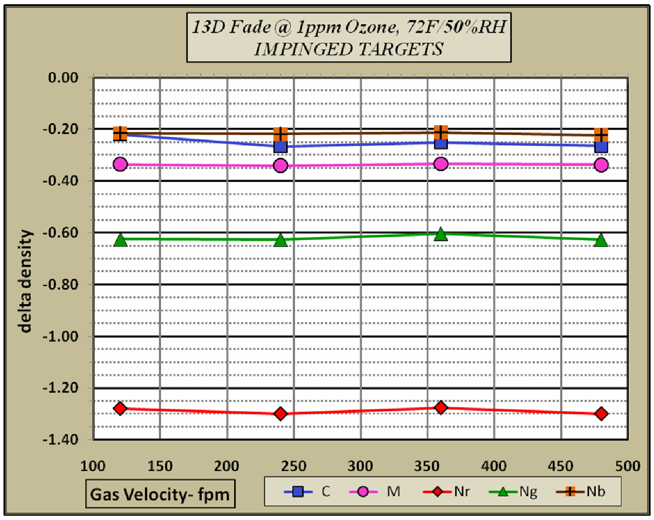

Figure 6. Impinged target fade vs gas velocity.

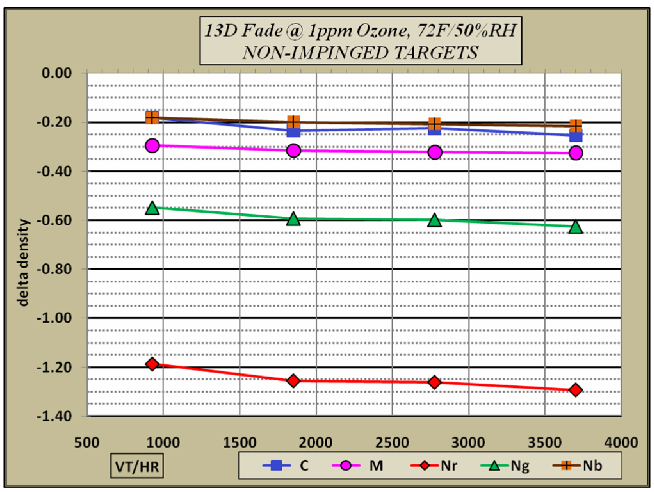

Figure 7. Nonimpinged target fade vs volume turnover ratio.

Some caution must be used in interpreting the results as this only represents one trial with one media type. Multiple trials, media variability, other media, and test noise may yield different results. With that understanding, these results might suggest the following preliminary conclusions:

- For impinged targets with impinged velocities of 100 fpm or more, impingement velocity does not appear to impact fade, as fade results in each color record are essentially constant.
- For the nonimpinged targets, the data may suggest that the rate of volumetric turnover can influence fade results, as all fade results show some minor increase in fade with increasing volumetric turnover rates. Note that these were fairly high turnover rates tested.
- In most cases, the fade results for the nonimpinged targets were slightly less than similar results for the impinged targets, except at very high turnovers. This may suggest that a chamber incorporating impinged target design with a minimum impingement velocity of 100 fpm may be a more "robust" test bed. Standard deviations of the data set tend to support this as well.

Experiment B – Reciprocity

This second experiment examined fade results over a set of identical targets at controlled conditions of 22.2 °C (72 F) dry bulb, 50% RH, a fixed velocity, and a constant ozone cumulative exposure of 504 ppm-h. This was accomplished by setting a desired ozone concentration and determining the required test duration. Ozone concentrations of 1.0, 1.5, 2.1, 3, and 5 ppm were tested, with durations per Table 1. Reciprocity data was collected on impinged and nonimpinged targets tested simultaneously within the chamber. For all tests, the fan speed was set at a fixed speed of 1750 rpm.

Table 1. Ozone Concentration vs. Test Duration

Test phase	#1	#2	#3	#4	#5
ppm	1.0	1.5	2.1	3.0	5.0
h	504	336	240	168	101
days	21	14	10	7	4.2
ppm-h	504	504	504	504	504

As before, all test targets were equally spaced off impingement plenums using fixed position target mounts.

A total of 18 targets were positioned in the center six rows and center three columns of the chamber and were impinged with ozone-enriched air from a plenum of orifice jets at 90 degrees to the target surface.

Another ten targets were positioned in the two outermost rows using the center five columns but, in this case, the plenums were blocked so that these targets had no direct impingement. Instead, return grilles were left open so the targets were only exposed to the volumetric turnover of ozone-enriched air which would be flowing mostly parallel to the surface.

The results are summarized graphically in Figs. 8-12 for the cyan, magenta and neutral component color records. In these graphs, the impinged targets are to the left (hashed bars) and the nonimpinged targets are to the right (solid bars). Ozone concentrations increase from 1.0, 1.5, 2.1, 3.0, and 5.0 ppm from left to right in each series.

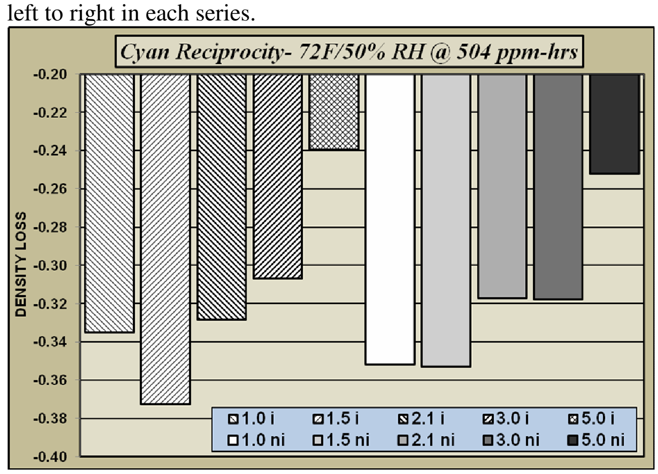

Figure 8. Cyan reciprocity results for impinged and nonimpinged targets.

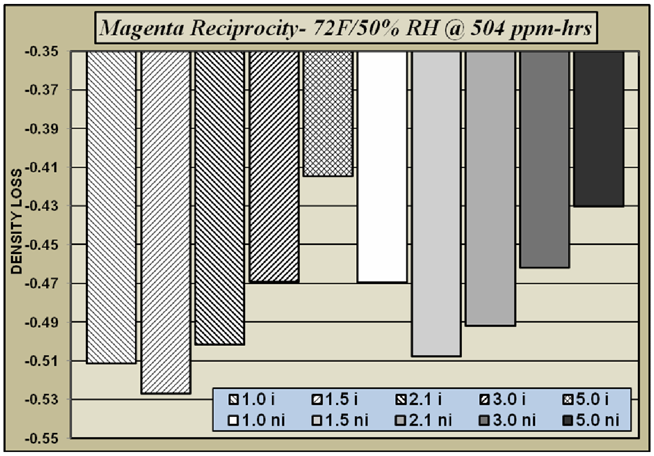

Figure 9. Magenta reciprocity results for impinged and nonimpinged targets.

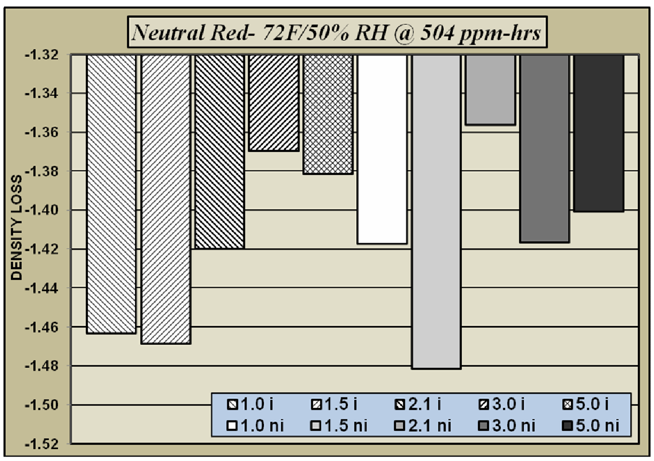

Figure 10. Neutral red reciprocity results for impinged and nonimpinged targets.

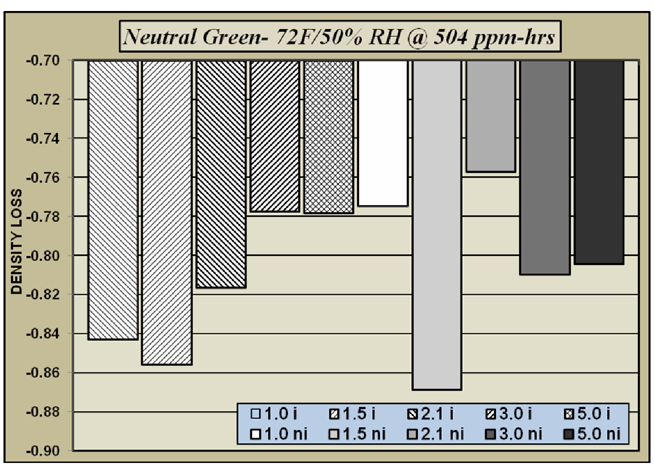

Figure 11. Neutral green reciprocity results for impinged and nonimpinged targets.

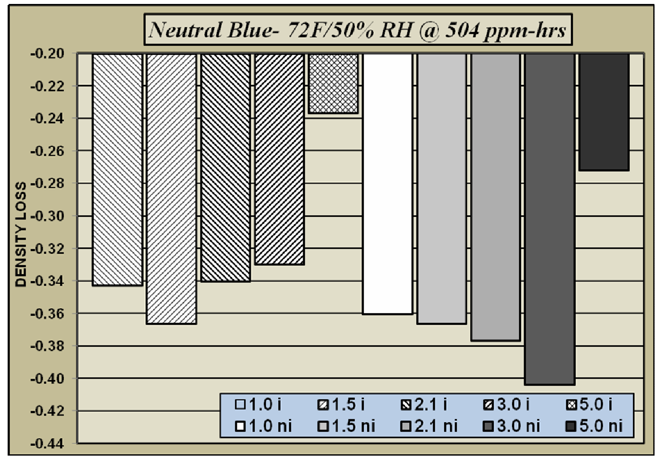

Figure 12. Neutral blue reciprocity results for impinged and nonimpinged targets.

Experiment B – Results and Discussion

The goal of this experiment was to test the theory of reciprocity, i.e., equal cumulative exposure results in equal fade. In addition to testing the basic theory, we also sought to test whether the method of impingement made a difference in results.

Clearly, this data is more difficult to interpret. One could argue that the impinged results showed a fairly consistent trend in all color records. The nonimpinged results do not exhibit that same consistency. This may be partly explained by the observation in experiment A that using impingement at 100 fpm or more may be a more robust testing position.

We would exercise the same caution stated for experiment A, which was that these results only represent one trial with one media type. Multiple trials, media variability, other media, and test noise may yield different results. With that understanding, these results might suggest the following preliminary conclusions:

- that reciprocity does not hold between low and high levels of ozone concentration. It may be that this is a real failure of reciprocity or "apparent reciprocity," at least for this specific media. However, one concern we would have with this conclusion is the lack of a standard calibration method above 1 ppm concentrations for readily available commercial ozone analyzers. There is a tendency to assume that these systems are linear above their 1 ppm calibration points, when extrapolating out to higher operating conditions. The failure of the data to show reciprocity at all levels might easily be explained by the suggestion that we were not actually testing at the desired aim concentrations indicated but at something less or more. A more precise measurement method would be required to better understand this failure.
- that the lack of consistency across the impingement methods during simultaneous testing in the same chamber would suggest that impingement method does play a role in results.
- perhaps equally as concerning is that peak fade results occurred at a test level other than 1.0 or 5.0 and that 5.0 always showed the least fade in this reciprocity experiment. If this is not a calibration issue or related to some other test phenomenon and held true across other

media types, it would complicate fair comparison of media and testing systems across various sites that use differing methodologies.

Conclusions/Future Studies

Definitely, the results generated by these experiments warrant further testing and exploration. The ability to draw sound conclusions based on a sample size of one has inherent risks. However, the insights gained are worth sharing if they prompt further discussion and lead to additional testing.

Future Studies

The results reported here suggest the following additional testing be executed:

- Repeat testing with this same media along with other media types.
- Exploring more sophisticated means of confirming ozone concentrations at levels above 1 ppm.
- Reconfiguring the environmental chamber to test at impingement velocities less than 100 fpm. All testing done here was conveniently executed over the range of available fan speeds with a fixed chamber configuration. Altering the chamber configuration (number, type, and open area of plenums) will permit lower velocities to be explored.
- Dry-bulb temperature and RH affects.

References

[1] D. Bugner, R. Van Hanehem, M. Oakland, P. Artz, D. Zaccour, and R. Levesque, "Ozone Concentration Effects on the Dark Fade of Ink Jet Photographic Prints," J. Imaging Sci. Technol., 49, 6 (2005).

[2] D. Miller, "New Equipment Designs for Evaluation of Fade Stability of Color Photographic Images in the Presence of Ozone Gas – Part One," Proc. IS&T's Int. Symp. on Technologies for Digital Photo Fulfillment, pp.68-70 (2009).

Author Biography

David (Dave) Miller is a senior research engineer at Eastman Kodak Company. He received his B.S. in mechanical engineering from Clarkson College of Technology (1974). In 1999, Mr. Miller was accredited as a Six Sigma Black Belt quality practitioner. Since joining Kodak, he has held roles as a mechanical design engineer, project manager, process engineer, operations supervisor, maintenance engineer, and most recently, ITSC process engineer for the Image Stability Technical Center, Consumer Digital Group, Eastman Kodak Company.