# A Review of the Evolution of InkJet Print Durability Against Environmental Gases

***Stephan Moeller, Dieter Kaumkoetter, Wolfgang Schmidt, and Gerd Papier; Felix Schoeller jr. GmbH & Co. KG; Osnabrueck, Germany***

## Abstract

*InkJet photo printing became a mature technology within the last 5 years. Higher throughput by increased print speed and higher ink flow required a fundamental change of print media design for photographic prints made by InkJet printing. Since around 2000 a step-by step substitution of so-called swellable type media (low pigment and high polymer content - predominantly PVOH or gelatin) by media based on microporous ink receiving layers took place. Today all major OEM's finished the transition to microporous type media The main drawback of this transition is a fundamental change of the print durability properties. This is due to the fact that the open structures of the receptive layer now allow for the decomposition of dye based inks by environmental gases like ozone, NOx or $SO_2$, resulting in an additional decrease of optical densities or color shifts on top of the regular lightfade degradation. This paper provides a review on how the environmental stability of photographic media changes with the use of different printing technologies such as InkJet, dye-sublimation and silver halide. Influences of the inks in InkJet printouts as well as the influence of the media construction will be discussed. It will also present insight into internally developed test methods for the evaluation of gas-fade stability.*

## Introduction

InkJet photo printing became a mature technology within the last 5 years. Print resolutions improved significantly to a point where non-AgX printed photographs became undistinguishable from the 'classic' silver halide photograph and even benefit from higher color gamut. Trying to break into the domain of mass retail photofinishing higher throughput by increased print speed and the resulting increase in ink flow require a fundamental change of the media design for photographic prints, though. Since around 2000 a step-by-step substitution of swellable type media took place. These media are usually constructed from a paper base with or without resin coating and an ink receptive layer with low pigment and high polymer content - predominantly PVOH or gelatin. The substituting media are based on microporous ink receiving layers with high pigment (mainly alumina or silica) and low binder contents. As of today all major OEM's offer microporous type media in the high volume segments of their product portfolios. While picture quality and resolution remain at a high level - basically determined by printer technology - the main drawback of this transition is a fundamental change of the print durability properties. This is due to the fact that the open structures of the receptive layer now allow for the decomposition of dye based inks by environmental gases like ozone, NOx or SOx, resulting in additional color shift and decrease of optical densities on top of the regular lightfade degradation. The sensitivity of microporous papers to oxidizing gases has been subject to a number of publications in the past [1-7], therefore the focus of this paper will be on a more comprehensive view on how different print technologies compare with respect to gas- and lightfading and what the influences of the media are.

## Experimental

For the evaluations a number of commercially available papers were printed using InkJet, dye-sublimation and traditional silver halide as printing technologies. InkJet prints were made on the following printers (ink type, technology): hp Photosmart 8260 ('Vivera' dye-based, thermal), Canon PIXMA iP8500 ('#6' dye-based, thermal), Epson R200 ('T0481-86' dye-based, piezo), Epson R360 ('Claria' dye-based, piezo), Epson R800 ('Ultrachrome' pigmented, piezo), hp Photosmart Pro B9180 ('Vivera pigment', thermal). The inks were exclusively commercially obtained OEM inks recommended for the printer model used for printing. Dye-sublimation prints were made on a Kodak EasyShare Photo Printer 500 and a Mitsubishi CP9550DW printer. The silver halide prints were obtained through regular retail channels. A listing of all media used for this evaluation is given in Table 1.

**Table 1: list of media used for fading experiments**

| | |
|---|---|
| **InkJet** | Epson Premium Glossy Photo Paper; Epson Photo Paper Glossy; Canon PP101; Canon PR101; HP Advanced Photo Paper; HP Premium Plus Photo Paper; Fuji WPA430 Pro; Felix Schoeller UltraWhite; Felix Schoeller Premium Paper Glossy; Felix Schoeller Ultra 6 |
| **Dye-Sublimation** | Kodak Kombipack PH 160; Mitsubishi CK9046 |
| **Silver Halide** | Fuji Crystal Archive Paper |

All samples were printed with 7 color patches consisting of the primary and secondary print colors C, M, Y, K, R, G, and B. The prepared samples were then exposed to defined atmospheres of the main oxidative gases $NO_2$, $SO_2$ and $O_3$ that are present as pollutants in today's ground atmosphere and to accelerated lightfading. No sample was exposed to more than one condition. $O_3$ was generated 'in situ' from ambient atmosphere using an Innotec OGK-10MG electric discharge ozone generator in an Innotec OKA 1-75L chamber. The ozone concentration was controlled with a Monitor Europe ML9810B $O_3$ Photometric Analyzer. $NO_2$ and $SO_2$ were taken from gas cylinders and mixed into ambient atmosphere with a MKS gas controller 647B in Heraeus Voetsch HC 2033/S chambers. The $NO_2$ concentration was controlled with an Environment S.A. Analyser $NO_X$ AC31M, the $SO_2$ concentration was controlled with an Environment S.A.

Analyser $SO_2$ AF21M. For overall comparability of the results the gas concentrations and exposure times were chosen to simulate 6 months of exposure to average atmospheric conditions in urban areas of Germany [8] and are given in Table 2. Climate conditions in all chamber tests were set to 23°C and 50% relative humidity.

**Table 2: gases and concentrations used for fading experiments**

| | $O_3$ | $SO_2$ | $NO_2$ |
|---|---|---|---|
| **avg. conc. urban area (µg/m³)** | 40 | <10 | 55 |
| **avg. conc. urban area (ppb)** | 19.4 | 3.75 | 28.7 |
| **Half year exposure (ppmhrs.)** | 84 | 16.2 | 124 |
| **Chamber conc. (ppm)** | 3.5 | 0.35 | 1.3 |
| **Exposure time (hrs.)** | 24 | 48 | 96 |

Accelerated fading was conducted in an Atlas Weatherometer Ci3000+ with Xenon lamp irradiation (2kW; sodalime filter; irradiance 1.2 W/cm² at 420 nm; illuminance 144kLux) for 50h at 23°C and 60% relative humidity. This exposure is equivalent to 3.7 years with an assumed daily exposure of 450 lux for 12 hrs. For comparability reasons to the gas-fade results the results were standardized to a 6 month exposure.

The amount of fading of the printed colors was determined relative to unexposed samples with a delta E calculation:

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \quad (1)$$

The L*, a* and b* values were measured with a Gretag McBeth Spectrolino, D65 illuminant, UV source on.

## Results and Discussion

In Figure 1 the combined results of the fading experiments with $NO_2$, $SO_2$, $O_3$ and light on InkJet printers with dye and pigmented inks are shown.

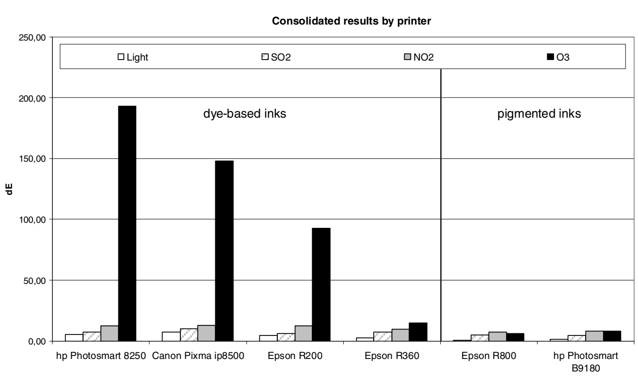


*Figure 1. gas- and light-fading of InkJet prints printed with dye and pigmented inks*

Ozone fading plays the dominant role in the degradation of InkJet prints made with dye based inks, with magnitudes in ΔE-values that are almost 4 times bigger than the sum of all other evaluated factors, i.e. on the Epson R200 $\Delta E(O_3) = 92.8$ vs. $\Delta E$ ($NO_2$ + $SO_2$ + light) = 23.3. Across the printers the magnitude of $NO_2$ (avg. $\Delta E = 10.5$) and $SO_2$ (avg. $\Delta E = 6.8$) induced fading is in the same order and with little variation ($\Delta\Delta E \sim 2$) between the ink types. Exceptionally results are achieved on the Epson R360 printer with 'Claria' inks, which yields an ozone fade resistance that is by a magnitude of 5 – 10x better than the other dye based inks in the test field. With an average ΔΔE of 9 this is already very close to the performance of pigmented inks. The pigmented ink sets of the Epson R800 and the hp Photosmart Pro B9180 yield the overall best environmental stability of photographic prints generated by InkJet printing technology and a lightfade stability that exceeds that of silver halide. Surprisingly, although the ozone fade resistance of the pigment inks improves by magnitudes over dye based inks, this magnitude does not scale to their $NO_2$ and $SO_2$ fade resistance. This finding, however, can be explained from a chemical perspective in a way that the main reaction mechanism of $O_3$ is ozonolysis of any double bond and the resulting destruction of chromophoric groups. $NO_2$ and $SO_2$ are more likely for nucleophilic attack of exposed functional groups which may lead to color shifts.

In Figure 2 microporous and swellable media constructions are compared side-by-side to the overall print results that are achieved by the Epson R360 with 'Claria' inks. As stated earlier, ozone fading is predominant on microporous media printed with either the hp 8250, Epson R200 or Canon iP8500. In strong contrast to that ozone fading on the swellable hp Premium Plus Photo Paper is reduced such that it becomes similar to the degree of fading with $NO_2$ and $SO_2$ across all printers with very little difference between the printers including the Epson R360. Interestingly the $NO_2$ and $SO_2$ fade values are again comparable in magnitude regardless of the media construction.

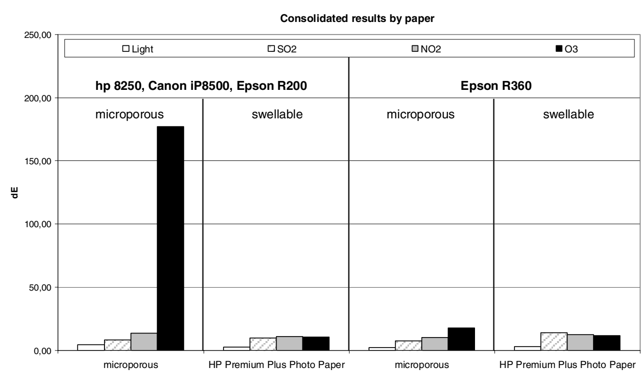


*Figure 2. comparison of gas- and light-fading properties of swellable and microporous media printed with dye-based inks*

Looking at the ozone fade results of the Epson R360 on microporous media it is obvious, however, that the ink technology of the Epson 'Claria' inks has advanced printing on microporous media such that their environmental stability becomes directly comparable to the performance of flagship swellable media or InkJet prints generated with pigmented inks, respectively. But how do they compare to the performance of silver halide and dye-sublimation generated prints? In Figure 3 the gas- and lightfade results of dye-sublimation prints made on a Mitsubishi CP9550DW and a Kodak EasyShare printer are compared to a traditional silver halide photograph on Fuji paper and prints on microporous photo paper made with the Epson R360 and 'Claria' inks. As expected the overall best performance is achieved by the silver halide print with ΔE-values ranging from 2.7 ($NO_2$, highest) to 1.5 (light, lowest). Slightly worse results – approximately by 2x in lightfade, $NO_2$- and $SO_2$-fade – are achieved by the Kodak EasyShare printer. The lightfade results gained with the Mitsubishi printer are already 5x away from silver halide lighstability. $NO_2$- and $SO_2$-fade values are also slightly worse than on the Kodak printer and comparable to the Epson R360 printer. The Epson R360 achieves a lightfade resistance that is better than with dye-sublimation but the poorest ozone fade resistance in this class of products.

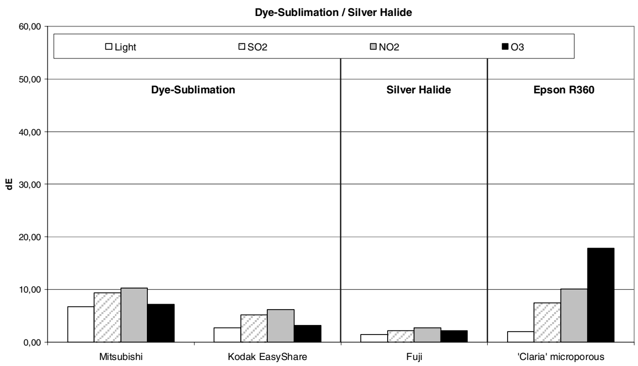


***Figure 3**. gas- and lightfading of pictures generated by dye-sublimation and the silver halide process vs. Epson R360*

In all previous graphs, the gas- and light-induced fading contribution of the paper bases has been neglected as their avg. $\Delta E$-values are very low in magnitude compared to the shown results of the printed samples. For completeness, the $\Delta E$-values of the unprinted paper samples are shown in Figure 4.

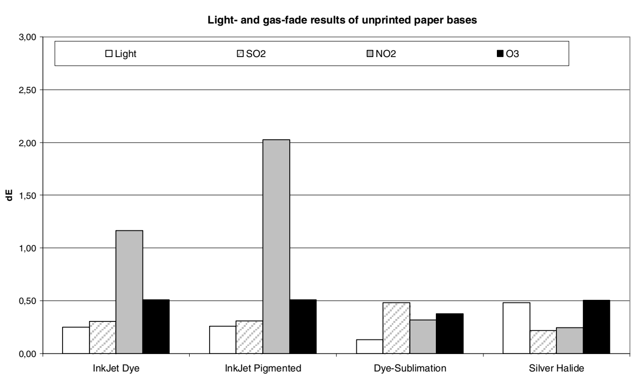


***Figure 4**. gas- and lightfading of unprinted paper bases*

## Summary and Outlook

As described in the previous sections, the environmental stability especially of the ink / media combination of InkJet prints is one of the critical factors for lasting photographic prints. From the main oxidative gases present in today's ground atmosphere Ozone plays the major role in the degradation of InkJet printed photographs with dye-based inks on microporous paper. $NO_2$ and $SO_2$ do contribute to gas-fade in all printing processes at nearly the same magnitude but always to a lesser extent than ozone. In the 6 month window that was tested, light fading has the least contribution to print degradation. The silver halide process still provides the overall best durability of all evaluated technologies, but InkJet prints made with pigmented inks already outperform both dye-sublimation technology and silver halide in terms of lightfastness and are just margins away from the performance of a silver halide photograph in terms of gas-fastness. It could be shown, that advances in the ink composition of dye-based inks can provide a significant leap forward in the gas fade-stability of prints made on microporous papers such that their overall performance falls into the same category as prints made by dye-sublimation. Further evaluation is needed though, on how gas-fade performance develops over extended periods of time beyond a simulated 6 month exposure time. A comprehensive overview over all results is given in Figure 5.

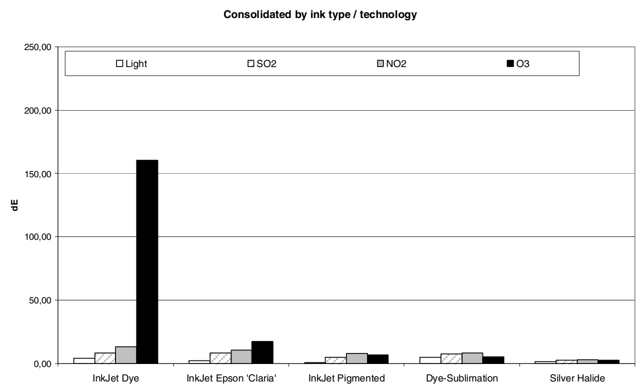


***Figure 5**. comparison of gas- and lightfading of pictures generated by InkJet, dye-sublimation and the silver halide process*

## Acknowledgement

We would like to thank the Fraunhofer Institute for Chemical Technology in Karlsruhe, Germany, for the opportunity to use their $NO_2$ and $SO_2$ chambers.

## References

[1] R. Barcock and A. Lavery, "Ozone Degradation of InkJet Photoquality Images", Journal of Imaging Science and Technology, 48, 2, pg. 153 (2004).

[2] M. Berger and H. Wilhelm, "Comparison of Different Methods for Estimating the Sensitivity of InkJet Images to Gas Fading", Final Program and Proceedings of IS&T´s NIP19: International Conference on Digital Printing Technologies, New Orleans, Louisiana, pg. 438 (2003).

[3] M. Berger and H. Wilhelm, "Evaluating the Ozone Resistance of Inkjet Prints: Comparisons Between Two Types of Accelerated Ozone Tests and Ambient Air Exposure in a Home ", Final Program and Proceedings of IS&T´s NIP20: International Conference on Digital Printing Technologies, Salt Lake City, Utah, pg. 740 (2004).

[4] J. Reber, R. Hofmann, "Correlation of ozone test chamber data with real life permanence of inkjet prints", Final Program and Proceedings of IS&T´s NIP22: International Conference on Digital Printing Technologies, Denver, Colorado, pg. 231 (2006).

[5] D. Bugner and P. Artz, "A Comparison of the Image Stability of Digital Photographic Prints Produced by Various Desktop Output Systems", "Features of Reciprocity Failure and Ozone Fading in InkJet Images", Final Program and Proceedings of IS&T´s NIP1: International Conference on Digital Printing Technologies, San Diego, California, pg. 306 (2002).

[6] K. Kitamura, H. Hayashi and Y. Oki, "Gas-fastness of Photographic Prints of Epson PM-950C", International Congress of Imaging Science, Tokyo, Japan, pg. 539 (2002).
[7] D. Bugner et al., "Update on Reciprocity Effects for Accelerated Ozone Fade Testing of InkJet Photographic Prints ", Final Program and Proceedings of IS&T´s NIP19: International Conference on Digital Printing Technologies, New Orleans, Louisiana, pg. 497 (2003).
[8] Umweltbundesamt Deutschland; Messnetze der Bundesländer und des Umweltbundesamtes (2006).

## Author Biography

*Stephan Moeller received his doctor of chemistry from the University of Wuerzburg, Germany, in 1994. Since 1997 he works with Felix Schoeller, first in a technical marketing position. Since 2006 he is head of the application technologies and analytical labs.*