Correlation of ozone test chamber data with real life permanence of inkjet prints

Juerg Reber, Rita Hofmann; Ilford Imaging Switzerland GmbH; Marly, Switzerland

Abstract

Accelerated ozone exposures and real time air exposure were correlated with published outdoor ozone levels. The results showed that ozone represents a major air pollutant causing colorant degradation under the climatic conditions found in Fribourg on the Swiss plateau.

In accelerated ozone chamber tests the real life environment is simulated by choosing defined constant humidity, temperature and ozone concentration levels. On the basis of measurements over one year the statistical variation has been determined and the homogeneity of the test chamber was characterized by colour density loss profiles.

A set of typical inkjet media/ink combinations has been analyzed using this accelerated test and was correlated to real life exposure over more than one year for different locations in a building. As a part of this work, the average ratio of indoor to outdoor ozone level for different locations was also investigated.

Real life and accelerated tests of porous media with dye based and pigment inks were compared. The local climatic conditions for different locations in a building dramatically affected the indoor to outdoor ozone ratio and the real display life of the prints.

The reasons for the different sensitivities of the prints to ozone is on one hand the chemical structure of the colorants and on the other hand the different access of the ozone to the colorant influenced by the media structure as well as its chemical composition and the flow properties around the sample.

Introduction

By the introduction of nanoporous inkjet media fading effects caused by air pollutants became an important factor for print life time. Recent studies investigated in particular the effect of ozone on inkjet prints [2][3][4][5][6] and accelerated testing methods by using an ozone chamber in comparison to real life fading [1]. The European outdoor ozone situation is described in [9] and different measurement networks regularly publish their data [7][8]. Indoor/outdoor ratios for several typical cases are given in [10].

This study tries to determine indoor to outdoor ozone ratios for different exposure locations in one building, propose a reasonable average level for a year of exposure and investigate the correlation of accelerated test with actual real-time display.

Experimental Setup

In this study two sample sets have been used to compare real life performance with ozone test chamber experiments. Set A was one dye based ink set on one nanoporous media exposed to air at thirteen locations in a period from March 2004 to August 2005. Set B comprised two different nanoporous IJ media printed with two commercial aqueous dye based ink sets and exposed at five

different locations, from August 2004 to August 2005. By measuring the outdoor/indoor ozone level ratio for each location and using published outdoor values, the density loss could be related to the individual actual ozone exposure and compared with accelerated ozone fading test data.

Table 1: real life test locations for set A and B

description	building	location number	loc. set A	loc. set B
homelike office, no air cond.	Α	1	1	1
	В	2, 7, 13	2, 7, 13	2
office, air conditioned	С	3	3	3
	F	5	5	
laboratory, air conditioned	В	6, 10	6, 10	
	С	3, 11	3, 11	
	E	4	4	4
	G	9	9	
library, no air condition	D	8	8	8
warehouse, no air condition	Н	12	12	

Accelerated fading tests were done in a Hampden ozone cabinet model 903 using test parameter as described in table 2. Long-term repeatability tests and homogeneity investigations were done by using reference samples made up from a proprietary nanoporous IJ media printed on a typical four color inkjet printer with known and fixed composition of proprietary ink.

Table 2: Ozone test chamber settings

ozone conc.	[ppm]	1.0
temperature	[°C]	30
humidity	[%]	50
air flow	[l/min]	200
exposure	[ppmh]	0, 3, 6, 12, 24,

The test image was composite of full colour patches at 0.5, 1.0 and about 1.5 density for all primary and secondary colours, as well as composite grey. All samples were let to dry before the test for ten days in ambient conditions.

Density measurement was done by Gretag MacBeth Spectrolino.

Ozone levels were determined with a Environnement O3 42M ozone analyzer by UV absorbance method.

Results

Outdoor ozone level

Measurement of outdoor ozone level at Ilford has shown good correlation with published data [7], measured at local measurement station AFU Fribourg/Pérolles, about two miles away from the site. Therefore, the AFU data were used as basis for real life ozone

exposure calculations. The situation for 2004 to 2006 period is presented in figure 1, 2 and 3.

Calculated for one week the average outdoor ozone exposure is 0-1.4 ppmh and for one year about 200 ppmh (170 - 215).

This is about 10% lower than the Swiss average calculated from 16 measurement stations of Swiss NABEL system [8].

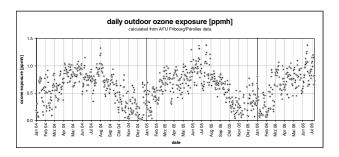


Figure 1. Daily ozone exposure outdoor at Fribourg/Pérolles, Switzerland

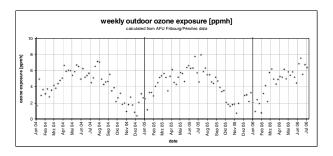


Figure 2. Weekly ozone exposure outdoor at Fribourg/Pérolles, Switzerland

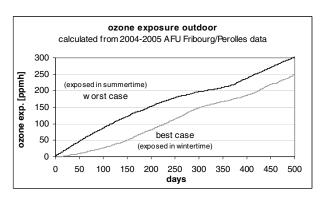


Figure 3. Outdoor ozone levels integrated for best (wintertime) and worst case scenario (summertime) at Fribourg/Pérolles, Switzerland

Accelerated fading test in ozone test chamber

Long-term experimental variation

Long term variation is based on fading curve data from more than 50 reference samples from one year that have been analyzed with each test series. Life time prediction was done by applying the endpoint criteria WIRv3.0 and linear interpolation. This media/ink combination failed first in density loss of pure cyan patches.

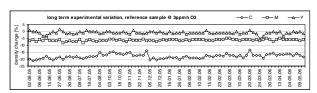


Figure 4. Experimental variation of reference samples, faded in ozone test chamber - for instance density change after 3 ppmh O3 exposure

Table 3: Repeatability and variation in life time prediction

O3 exposure	[ppmh]	3	6	12	24	48	life time pred.	
	stdev	83	56	55	22	11	(failure in pure cyan)	
							[ppmh	O3]
C OD change	avg [%]	-17.8	-25.6	-35.8				
	stdev	1.6	2.6	2.5			avg	8.6
M OD change	avg [%]	-6.2	-12.1	-22.1	-36.9		stdev	1.5
	stdev	0.7	1.3	1.9	2.6		avg+2s	7.1
Y OD change	avg [%]	-0.8	-0.9	-1.6	-2.8	-3.3	avg-2s	10.1
	stdev	1.1	1.1	1.1	1.1	1.5		

Homogeneity of ozone test chamber

Homogeneity was tested with samples containing 5x8=40 fields of pure cyan, magenta and yellow, arranged in a grid of 10mm distance. They were exposed to 12 ppmh of ozone. Results show homogeneous fading for all 48 places in the test chamber.

Table 4: Homogeneity in ozone test cabinet Hampden 903

[ppm]	12
avg	36.4
stdev	0.6
avg	21.0
stdev	0.6
	avg stdev avg

Correlation of real life faded samples to ozone test chamber data for sample set A

Sample set A was exposed to real life conditions and density change curves were recorded. For comparison, the scale had to be transformed from days to ppmh of ozone by calculation from published outdoor values and experimentally determined indoor/outdoor ratio. The influence of light was investigated by control samples without direct light, respectively without air contact. Results have shown light fading to be negligible compared to air pollutant effects for all used test situations. Figure 5 shows one example to illustrate this observation.

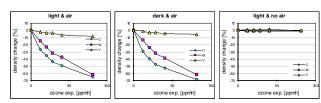


Figure 5. Control samples confirm air pollutants as the main fading factor

Table 5: categorized indoor/outdoor ozone level ratio, measured at Ilford, Marly/Switzerland

location	O ₃ ratio
outdoor	1.00
air conditioned, supplying outdoor air	0.57-0.90
no air cond., windows closed	0.04-0.19

With one exception the fading curves for all locations are showing good correlation to each other and represent the same fading behaviour as observed in ozone chamber test. The cyan to magenta density change ratio that is very selective to different air pollutants showed good agreement.

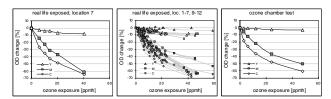


Figure 6. left: real life faded sample at location 7 middle: all locations in comparison (excepted loc. 8) right: The same ink/media combination in accelerated ozone chamber test

Location 8 is a library with no air condition. Fading was very slow and a very different fading behaviour with respect to cyan to magenta ratio could be observed. For this particular location other air pollutants may have become more important than ozone.

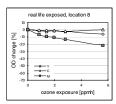


Figure 7. location 8: Magenta fades much more than cyan

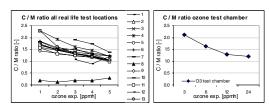


Figure 8. Cyan to magenta ratio of location 8 doesn't correlate with the others and the ozone test chamber result.

Correlation of real life faded samples to ozone test chamber data for sample set B

Sample set B was exposed to real life conditions as described in table 1 and density change curves were recorded. For comparison the scale was transformed from days to ppmh of ozone in the same way as described for sample set A.

printer I, media A

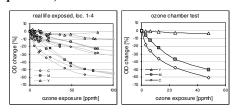


Figure 9. left: real life faded samples, all locations in comparison right: The same ink/media combination in accelerated ozone chamber test

This ink/media combination was the same as used in sample set A and represents a repetition of the first experiment. The results obtained are confirming what was observed in set A. Location 8 (library) showed also the same different fading behaviour as before.

printer I, media B

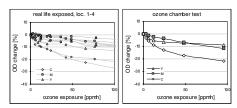


Figure 10. left: real life faded samples, all locations in comparison right: The same ink/media combination in accelerated ozone chamber test

This second ink/media combination faded in reality also similar to what the accelerated testing is showing. Location 8 (library) showed again the same different fading behaviour with magenta being more sensitive than cyan.

printer II, media A

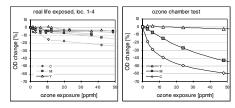


Figure 11. left: real life faded samples, all locations in comparison right: The same ink/media combination in accelerated ozone chamber test

As shown in figure 11, the third ink/media combination used in this set shows no good correlation between accelerated and real life fading. For unknown reasons it fades much less in reality than in the ozone chamber.

Again, samples at location 8 show inverted sensitivity as already discussed.

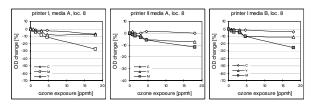


Figure 12. location 8 (library): all printer/media combinations show inverted fading behaviour for magenta and cyan

ozone fading chamber data - performance of todays dye based and pigment inkjet inks on nanoporous media

For each dye based and pigmented ink systems one of today's best performing sets have been used in combination with a typical high end nanoporous media. For life time prediction the endpoint criteria WIRv3.0 were used.

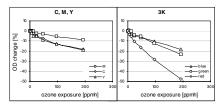


Figure 13. The dye based ink set reached life time prediction of up to 80 ppmh until failure in red density of composite black occurred.

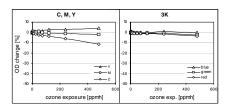


Figure 14. The pigmented ink set is very stable and didn't reach the endpoint until 480ppmh. By interpolation the endpoint is likely be reached somewhere around 1000 ppmh.

Conclusion

The study showed that for well-ventilated locations, indoor ozone levels can be deducted from published outdoor levels that are measured in the vicinity. For the Swiss plateau, the average yearly outdoor level can be best represented by 250 ppmh. Typical indoor/outdoor ratio are 60-90% for a very well ventilated room and 10-30% for a moderately ventilated room. In none ventilated rooms, indoor levels are very low at 0-20% of outdoor levels. The experimental work has confirmed ozone to be a major factor in pollutant fading in locations with sufficient air exchange. However, in locations cut-off from outdoor air exchange, very different pollutant levels and ratios may occur.

In addition there are ink/media interactions that are not well understood. For one media/ink combination real-time fading even showed a less sensitive fading behaviour than accelerated ozone fading test predicted. The reason for this effect is unknown.

For ink/media combinations with confirmed correlation of real life fading to accelerated fading test, life time can be predicted if local outdoor situation and indoor/outdoor ratio are known. Thereby the main difficulty remains the strong variability of ozone levels depending of geographical situation, local air pollutions and indoor air exchange situation. This will be a challenge to the prediction of years of life expectancy of prints for end users. An approach based on ppmh life expectancy would allow end users to estimate air fade for their own location by assuming average outdoor levels and typical indoor to outdoor ratio.

During real life test period, light fade did not seem to contribute to overall fading.

In accelerated fading experiments results were shown to be homogeneous for all chamber locations under the chosen flow and environmental conditions and long term repeatability is given.

Acknowledgements

The authors would like to thank Jean-Pierre Beyeler for the experimental data and Eduard Baumann for contributing to this work with fruitful discussions.

References

- M. Berger and Henry Wilhelm, Evaluating the ozone resistance of inkjet prints: comparison between two types of accelerated ozone tests and ambient air exposure in a home, Proc. IS&T's NIP20, IS&T, Springfield, VA, 2004, p.740
- [2] Y. Kanazawa, Y. Seoka, S. Kishimoto, N. Muro, Indoor pollutant gas concentration and the effect on image stability, Proc. IS&T's NIP20, IS&T, Springfield, VA, 2004, p.748
- [3] M. Thornberry and S. Looman, Air fade and ozone fade on porous media, Proc. IS&T's NIP19, IS&T, Springfield, VA, 2003, p.426
- [4] Y. Oki, K. Kitamura, T. Aoyama, M.Hanmura, H. Fukumoto, The inkjet prints permanence of the latest dye ink, Proc. IS&T's NIP20, IS&T, Springfield, VA, 2004, p.710
- [5] Y. Kanazawa, Y. Seoka, Y. Shibahara, S.Kishimoto, Correlation between gas-resistance testing method and image deterioration in indoor displays: an analysis of phenomena occuring in mixed-gas test with ozone, Proc. IS&T's NIP21, IS&T, Springfield, VA, 2004, p.357
- [6] D. Bugner, R. Van Hanehem, P. Artz, D. Zaccour, Update on reciprocity effects for accelerated ozone fade testing of inkjet photographic prints, Proc. IS&T's NIP19, IS&T, Springfield, VA, 2003, p.397
- [7] Amt für Umwelt, Ozone measurement station at Fribourg/Pérolles, http://appl.fr.ch/sen/fr/air/air.htm
- [8] Bundesamt f
 ür Umwelt BUWAL, O3 monitoring system NABEL, http://www.umwelt-schweiz.ch
- [9] J. Fiala, L. Cernikovsky, F. de Leeuw, P. Kurfuerst, Air pollution by ozone in europe in summer 2004, European Environment Agency, Kopenhagen, 2005, technical report 3/2005
- [10] SR Hayes, "Use of an indoor air quality model (IAQM) to estimate indoor ozone levels", J. Air Waste Manage Assoc., 41(2), 161-70 (1991).

Author Biography

J. Reber studied chemistry at Burgdorf engineering school in Switzerland. He worked for several years in analytical chemistry as test engineer and group leader in a private service laboratory. In 2003 he joined ILFORD and works in the field of image science and performance in research and development. The focus of his activities is in test methods and result characterization for inkjet media.