Effects of Ozone on the Various Digital Print Technologies: Photographs and Documents

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Abstract. The harmful effects of ozone on inkjet photographs have been well documented. This project expands on that research by performing ozone tests on a greater variety of digital prints including colour electrophotographic and dye sublimation. The sensitivities of these materials are compared to traditionally printed materials (black-and-white electrophotographic, colour photographic and offset lithographic) to determine if the digital prints require special care practices. In general, the digital prints were more sensitive to ozone than traditional prints. Dye inkjet prints were more sensitive to fade than pigment inkjet, though pigment was not immune. The dye sublimation, colour electrophotographic (dry and liquid toner), and traditional print systems were relatively resistant to ozone. Text-based documents were evaluated in addition to photographic images, since little work has been done to determine if the type of object (image or text) has an impact on its sensitivity to ozone. The results showed that documents can be more resistant to ozone than photographs even when created using the same printer and inks. It is recommended that cultural heritage institutions not expose their porous-coated, dye-based inkjet photos to open air for extended periods of time. Other inkjet prints should be monitored for early signs of change.

Introduction

The purpose of this project was to survey the most common digital print materials for their resistance to ozone. Digital prints already exist within cultural heritage collections and are expected to continually increase in quantity [1]. Deterioration of these materials in collections has already been reported [1]. Collection managers need a general overview of which digitally printed materials are sensitive to ozone and to what degree so that they can take measures to prevent decay as well as develop usage policies which restrict exposure. While much work has been done to examine the effects of ozone on individual or small numbers of digital print types [2], there has been no major survey that has incorporated the great variety of digital printing technologies, colorants, and papers. Additionally, previous work has focused on damage to pictorial images. This project includes examining the effects of ozone on text-based documents as well. There has also been little work to simultaneously examine digitally and traditionally printed materials to develop a context of risk for the modern materials. The audience for this report is collection care professionals at cultural heritage institutions; however, others, such as professional photographers and imaging manufacturers may find the results helpful.

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Methods

The test samples included inkjet, colour electrophotographic, dye sublimation, and digital press to represent digital prints. Chromogenic photo, black-and-white (B&W) electrophotographic, and offset lithography were used to represent traditional prints.

The inkjet prints were further sub-divided into dye and pigment, photo and document. The inkjet photo papers included cast-coat, porous photo-coated, polymer photo-coated, and fine art papers. Cast-coat papers are plain papers with a simple, porous ink-receiver layer applied to the surface (usually both sides). Porous-coated photo papers are resin-coated (also known as RC) papers with a more complex porous ink-receiver layer. These look and feel most like traditional colour photographs. Fine art inkjet papers use various types of high-quality artist's papers to which a porous ink-receiver layer has been applied. Porous-coated photo and fine art papers are usually coated on only one side of the paper. The porous coating on all these papers consists of mineral particles in a binder. The spaces between the particles form extremely small cavities that can absorb the inkjet ink during printing. Polymer-coated inkjet photo papers are resin-coated papers with an ink-receiver layer that swells when the ink is applied and then shrinks when the ink's solvent evaporates. The inkjet document papers used included both plain office and office papers treated specifically (either by chemical treatment or coating) to receive inkjet inks.

Plain papers and papers treated especially to receive electrophotographic toners (both black-and-white and colour) were used for the electrophotographic prints. Coated glossy print stock was used for the offset lithographic and all the digital press prints. Note that the digital presses were production-scale electrophotographic printers that use either dry or liquid toners. Multiple systems (printer/ink/paper combinations) were tested when possible. Table 1 shows the types of printers and papers tested as well as the number of systems (printer/ink/paper combinations) tested for each.

Table 1. Printers and papers tested.

Printer	***Paper***	***Purpose***	***No. of Systems Tested***
Inkjet – Dye	Porous Photo	Photo	3
Inkjet – Dye	Polymer Photo	Photo	3
Inkjet – Dye	Cast Coat	Photo	1
Inkjet – Dye	Plain Office	Document	3
Inkjet – Dye	Inkjet Office - Uncoated	Document	1
Inkjet – Dye	Inkjet Office - Coated	Document	1
Inkjet – Pigment	Porous Photo	Photo	2
Inkjet – Pigment	Fine Art Photo	Photo	3
Inkjet – Pigment	Plain Office	Document	3
B&W Electrophotographic	Plain Office	Document	3
B&W Electrophotographic	Laser	Document	1
Colour Electrophotographic	Plain Office	Document	3
Colour Electrophotographic	Colour Laser	Document	1
Dye Sublimation	Dye Sublimation	Photo	2
Digital Press – Dry Toner	Coated Glossy	Document	2
Digital Press – Liquid Toner	Coated Glossy	Document	1
Chromogenic Silver-Halide	Chromogenic Silver-Halide	Photo	2
Offset Lithography	Coated Glossy	Document	1

Colour test targets for each system were printed in duplicate. The targets consisted of cyan, magenta, and yellow patches in ten approximately equal intervals of density from minimum density

(Dmin) to maximum density (Dmax), neutral patches with 20 intervals, as well as two non-printed patches (Dmin). Text targets consisted of black text on a white field and white text on a black field. The font was New Times Roman and the text ranged in size from 8 point to 14 point. “Best Photo” and “Photo Enhanced” printer settings were selected when available for photo-specific printing systems. Default settings were used for document printing systems. After printing, all samples were left to dry at 21ºC and 50% RH in the dark for two weeks before testing. All targets were read using a Gretag Spectrolino/Spectroscan (no UV filter, 2º observer, D50 illuminant) for CIELAB L*a*b* both before and after ozone exposure. Delta E values were then calculated. Results for each printer and paper type were averaged to determine that technology’s sensitivity to ozone. Text targets were assessed visually to determine the smallest readable font after ozone exposure.

The ozone-exposure chamber used was custom built for IPI by Codori Enterprises. The ozone was produced by means of an ultra-violet lamp. The samples were exposed at 5 ppm ± 0.25 ppm for 2 weeks. The temperature and humidity within the chamber were held constant at 25°C ± 2°C and 50% RH ± 5% RH.

Results

Table 2 shows the average delta E values for the maximum cyan, magenta, and yellow density patches for each printer and paper type. Table 3 shows the average delta E values for a mid-tone neutral patch (approximately 70% of Dmax so as to include the three primary colours plus black inks) and the maximum density neutral patch for each printer and paper type. While most grey tones in colour digital prints are made up of cyan, magenta, yellow, and black colorants together, the maximum density black is often black colorant only. Additionally, some inkjet systems use dyes for the cyan, magenta, and yellow colours and a pigment for black.

Table 2. Effect of ozone on delta E of cyan, magenta, and yellow colorants.

Printer	*Paper*	*Cyan*	*Magenta*	*Yellow*
Inkjet – Dye	Porous Photo	33	62	44
Inkjet – Dye	Polymer Photo	6	2	1
Inkjet – Dye	Cast Coat	46	96	73
Inkjet – Dye	Plain Office	8	7	4
Inkjet – Dye	Inkjet Office - Uncoated	9	6	5
Inkjet – Dye	Inkjet Office - Coated	25	57	51
Inkjet – Pigment	Porous Photo	12	5	3
Inkjet – Pigment	Fine Art Photo	10	8	1
Inkjet – Pigment	Plain Office	8	7	2
B&W Electrophotographic	Plain Office	NA[a]	NA[a]	NA[a]
B&W Electrophotographic	Laser Office	NA[a]	NA[a]	NA[a]
Colour Electrophotographic	Plain Office	4	1	2
Colour Electrophotographic	Colour Laser Office	8	2	2
Dye Sublimation	Dye Sublimation	2	3	2
Digital Press – Dry Toner	Coated Glossy	3	3	1
Digital Press – Liquid Toner	Coated Glossy	8	7	1
Chromogenic	Chromogenic	1	0	1
Offset Lithography	Coated Glossy	4	3	1

[a] NA = not applicable. B&W electrophotographic does not have cyan, magenta, and yellow toners, only black.

Table 3. Effect of ozone on delta E of mid-tone and maximum black.

Printer	*Paper*	*Mid-tone*	*Dmax*
Inkjet – Dye	Porous Photo	48	36
Inkjet – Dye	Polymer Photo	4	1
Inkjet – Dye	Cast Coat	56	65
Inkjet – Dye	Plain Office	3	1
Inkjet – Dye	Inkjet Office - Uncoated	5	1
Inkjet – Dye	Inkjet Office - Coated	14	1
Inkjet – Pigment	Porous Photo	5	1
Inkjet – Pigment	Fine Art Photo	3	0
Inkjet – Pigment	Plain Office	2	1
B&W Electrophotographic	Plain Office	1	1
B&W Electrophotographic	Laser	1	0
Colour Electrophotographic	Plain Office	2	2
Colour Electrophotographic	Colour Laser	4	5
Dye Sublimation	Dye Sublimation	3	2
Digital Press – Dry Toner	Coated Glossy	1	2
Digital Press – Liquid Toner	Coated Glossy	3	1
Chromogenic Silver-Halide	Chromogenic Silver-Halide	0	0
Offset Lithography	Coated Glossy	1	0

Both ink and paper selections have a significant effect on the overall sensitivity of the system as a whole (printer/ink/paper combination). The porous-coated photo paper, cast-coated paper, and coated-office paper printed with dye inkjet were all more likely to fade than those printed with dye inkjet using polymer or plain office papers or any paper printed with pigment inks. While the pigment inkjet prints were less sensitive to damage by ozone than dye inkjet, they were not immune. The electrophotographic and dye sublimation as well as the traditional print types were more resistant to ozone-induced fade than dye or pigment inkjet. In several cases, the maximum density neutral patches faded at a slower rate than mid-tone neutral patches suggesting that text and line art that uses full density black may be more resistant to ozone-induced decay over time. This applied to both dye and pigment inkjet with the exception of dye inkjet on porous photo- or cast-coated paper. The text targets were all readable at all font sizes for all print technologies after exposure to ozone even though some of the inkjet prints were severely faded.

Table 4 shows the average delta E values for each technology for the density minimum (white) areas of the print.

Table 4. Effect of ozone on delta E of white areas of the print.

Printer	*Paper*	*Average ΔE*
Inkjet – Dye	Porous Photo	1
Inkjet – Dye	Polymer Photo	0
Inkjet – Dye	Cast Coat	4
Inkjet – Dye	Plain Office	1
Inkjet – Dye	Inkjet Office - Uncoated	1
Inkjet – Dye	Inkjet Office - Coated	3
Inkjet – Pigment	Porous Photo	1
Inkjet – Pigment	Fine Art Photo	1
Inkjet – Pigment	Plain Office	1

B&W Electrophotographic	Plain Office	1
B&W Electrophotographic	Laser	1
Colour Electrophotographic	Plain Office	1
Colour Electrophotographic	Colour Laser	1
Dye Sublimation	Dye Sublimation	1
Digital Press – Dry Toner	Coated Glossy	3
Digital Press – Liquid Toner	Coated Glossy	3
Chromogenic Silver-Halide	Chromogenic Silver-Halide	0
Offset Lithography	Coated Glossy	5

Visually, none of the papers discoloured severely, but several did yellow slightly, most noticeably the digital press and offset lithographic prints. The cast-coat inkjet and coated-inkjet office papers also yellowed.

In addition to fading and yellowing, one of the porous photo-coated papers also showed cracking and delamination of the ink-receiver layer. While rare, this is more objectionable because a faded print may still be readable/viewable, but a print that has lost some or its entire ink-receiver layer would be considered a total loss.

Previous work by the field had already shown that dye-based inkjet printed on porous-coated photo papers could be highly sensitive to ozone attack. That result was replicated here; however, it was unexpected that the dye inkjet on plain paper would be so much less sensitive to ozone exposure. It had been assumed that with plain papers, ozone would be able to attack the image from both sides making it more sensitive to ozone. It is not clear why this did not happen. Since the prints on the plain and porous photo papers in this test were made using different printers, a second experiment to compare prints made with the same printers was performed to validate the effect. The methodology was the same as above including the 5 ppm for two weeks exposure. Three printers were tested using both porous photo paper and plain office paper. Table 4 shows the delta E values for neutral mid-tone patches printed on both photo and plain papers on each of three dye inkjet printers.

Table 5. Delta E values of mid-tone neutral on photo and plain papers.

Printer	***Photo Paper***	***Plain paper***
Printer 1	31	2
Printer 2	57	2
Printer 3	66	2

In each case, the inks on plain paper were more resistant to ozone-induced fade than the same inks on porous photo paper.

Conclusions

As a result of the research the following conclusions were drawn:

- Exposing inkjet photographs to ozone can cause fading of colorants, yellowing of print papers, and cracking of ink-receiver coatings.
- Both dye and pigment inkjet printed materials are more sensitive to ozone-induced deterioration than electrophotographic, dye sublimation, or traditionally printed materials.
- Dye inkjet prints on porous-coated papers (photo, cast, fine art, and coated inkjet office) are significantly more sensitive to ozone-induced fade than any other type of printer/ink/paper combination.
- Inkjet documents on plain papers can be more resistant to ozone than inkjet photographs.
- Exposure to ozone can cause yellowing of digital press and offset lithographic print papers.

It is therefore recommended that cultural heritage institutions not expose their porous-coated, dye-based inkjet photos to open air for extended periods of time. Use of inert, plastic enclosures during handling is highly advised. Pigment-based inkjet photos, dye-based inkjet on polymer photo paper, and all inkjet printed documents are all more resistant to fade than dye inkjet on porous paper but they should be monitored over time for early signs of decay. Dye sublimation photographs and all electrophotographic prints may be treated using the same care practices that are currently being used for traditionally printed materials.

References

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Daniel M. Burge, Senior Research Scientist, has been a full-time member of the Image Permanence Institute (IPI) staff for the last 19 years. He received his B.S. degree in Imaging and Photographic Technology from the Rochester Institute of Technology in 1991. He managed IPI's enclosure testing services from 1991 to 2004. In 2004, he took over responsibility for all of IPI's corporate-sponsored research projects. Currently he is investigating digital print stability and storage issues.