# Effects of Nitrogen Dioxide on the Various Digital Print Technologies: Photographs and Documents

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## Abstract

*The purpose of this study was to survey the most common types of digital print materials to determine their resistance to fade or yellowing by nitrogen dioxide ($NO_2$), a pollutant commonly found in indoor environments to different degrees. For this experiment, various types of inkjet, dye sublimation, and electrophotographic prints (including digital press) were exposed to 5 ppm $NO_2$ for four weeks. The sensitivities of the digital prints were then compared to those of traditionally printed materials (black-and-white electrophotographic, color photographic, and offset lithographic). Inkjet dye inks and the color dyes in traditional photographic prints were the most prone to fade by $NO_2$. Traditional photographic, digital press, and offset lithographic papers were the most prone to yellowing by $NO_2$. Black colorants were fairly robust indicating that most text-only documents should be very resistant to $NO_2$ induced fade, though the papers may still yellow. Additionally, some inkjet dyes bled slightly to severely, depending on the printer and paper combination, causing the prints to appear discolored and blurred. This could result in loss of detail in images or a reduction in the readability of text in documents. This effect has not been reported with ozone exposures.*

## Introduction

Examples of the most common digital print materials were surveyed for their resistance to fade or yellowing by nitrogen dioxide ($NO_2$) a pollutant commonly found in cultural heritage institutions [1]. Digital prints already exist within cultural heritage collections and are expected to continually increase in quantity. Deterioration of these materials in collections has already been reported [2]. Collection managers need a general overview of which digital print materials are sensitive to $NO_2$ and to what degree so that they can take precautionary measures to prevent decay. While some work has been done to examine the effects of $NO_2$ on individual or small numbers of digital print types, there has been no major survey that has incorporated the great variety of digital printing technologies, colorants, and papers [3, 4]. Additionally, previous work has focused on damage to pictorial images. This project includes examining the effects of $NO_2$ on text-based documents as well as images. There has also been little work to simultaneously examine digitally and traditionally printed materials to develop a context of risk for the modern materials. Because collection care professionals will likely not be able to identify prints in their collections by specific products (printers, inks, and papers), the results are presented by printing technology categories (e.g. dye sublimation, dye inkjet, etc.) that can be differentiated by print identification schema. The audience for this study is collection care professionals at cultural heritage institutions; however, others, such as professional photographers, art galleries, and imaging manufacturers may find the results helpful.

## Methods

The types of digital print materials examined included inkjet (IJ), color electrophotographic (EP), dye sublimation (D2T2) and dry- and liquid-electrophotographic digital press (DP). Silver-halide color photographic prints were used as the traditional print comparators for the digitally printed photos. Black-and-white electrophotographic and offset lithographic prints were used as the traditional print comparators for the digitally printed documents.

The inkjet prints were further sub-divided into dye and pigment ink prints on both photo and document papers. The inkjet photo papers used in the tests included porous-coated plain, polymer resin-coated (RC), porous-coated RC, and fine art papers. Document inkjet papers included plain office paper, a plain paper that had been chemically treated to minimize ink absorption into the paper fibers, and a plain paper coated with a special sizing to keep the colorant close to the surface to maximize the density and brilliance of the printed image.

The dye sublimation papers used were those that matched their particular printer models. Chromogenic silver-halide papers were used to create the traditional color photographs. Plain papers and a paper treated especially to receive color electrophotographic toners were used for the electrophotographic prints. Coated glossy print stock was used for the offset lithographic and all the digital press prints.

Tables 1 and 2 show the types of printers and papers tested as well as the number of systems (printer/colorant/paper combinations) tested for each type of digital print.

**Table 1. Photo printing systems tested**

| *Printer* | *Paper* | *No. Tested* |
|---|---|---|
| IJ – dye | Porous-coated RC | 3 |
| IJ – dye | Polymer-coated RC | 3 |
| IJ – dye | Porous-coated plain | 1 |
| IJ – pigment | Porous-coated RC | 2 |
| IJ – pigment | Fine art | 3 |
| D2T2 | Dye sublimation | 2 |
| Silver-halide | Chromogenic | 2 |

**Table 2. Document printing systems tested**

| *Printer* | *Paper* | *No. Tested* |
|---|---|---|
| IJ – dye | Plain office | 3 |
| IJ – dye | IJ office - treated | 1 |
| IJ – dye | IJ office - IJ sized | 1 |
| IJ – pigment | Plain office | 3 |
| Color EP | Plain office | 3 |
| Color EP | Color laser | 1 |
| DP – dry toner | Coated glossy | 2 |
| DP – liquid toner | Coated glossy | 1 |
| B&W EP | Plain office | 3 |
| Offset lithography | Coated glossy | 1 |

Color step-wedge and text targets were printed in duplicate for each system. The color step-wedge targets consisted of cyan, magenta, and yellow patches in ten approximately equal intervals of low to maximum density (Dmax), neutral patches with 20 intervals, as well as three non-printed patches (Dmin). The text targets consisted of black text on a white field and white text on a black field. The font was Times New 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 the inkjet photos. Default printer settings were used for printing the inkjet documents and all electrophotographic and dye sublimation prints. After printing, all samples were left to dry at 21ºC and 50%RH 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 $NO_2$ exposure. Delta E values were then calculated. Results for all of the printers and papers within each printing technology (e.g. inkjet dye on polymer-coated photo paper) were averaged to predict that technology's sensitivity to $NO_2$. Text targets were assessed visually to determine the smallest readable font after $NO_2$ exposure.

The $NO_2$-exposure chamber used for the project was custom built for IPI by Codori Enterprises. The tanks of 2% $NO_2$ were purchased from Air Products. The samples were exposed at 5 ppm ± 0.25 ppm $NO_2$ for 4 weeks. The temperature and humidity within the chamber were held constant at 25°C ± 2°C and 50% RH ± 5%. The gas concentration was monitored with an Interscan RM15-10.0m Analyzer using an Interscan 115-LD10m sensor. A Watlow Anafaze CLS216 controller was used to maintain temperature, humidity and gas concentration.

If the average level of $NO_2$ concentration in an actual collection area (storage or display) was assumed to be 60 ppb [1], then the various prints tested could potentially show the damage indicated in the tables below after only 6.4 years of use. Longer periods of storage or display could, of course, result in even greater changes than demonstrated by these experiments. It is important to note that these sorts of extrapolations of experimental data into real life predictions are problematic as many variables will ultimately affect the rate of fading and yellowing of collection materials including air exchange rates, enclosures materials and designs, and the temperatures and humidities of the storage and display environments.

## Results

### *Digitally Printed Photos*

Table 3 shows the average delta E values for the maximum density cyan, magenta, and yellow patches for each printer and paper type for the photo printing systems. Table 4 shows the average delta E values for a mid-tone neutral patch (approximately 70% of Dmax so as to include the three primary colors plus black inks) and the maximum density neutral patch for each printer and paper type. While most grey tones in color prints are mixtures of cyan, magenta, yellow, and black colorants, the maximum density black is often black colorant only. The exceptions are the dye sublimation and silver-halide color prints which include only cyan, magenta, and yellow and contain no black. Table 5 shows the average delta E values for each technology for the minimum density (white) areas of the print.

**Table 3. Effect of $NO_2$ on delta E of cyan, magenta, and yellow colorants on the photo papers**

| *Printer* | *Paper* | *C* | *M* | *Y* |
|---|---|---|---|---|
| IJ – dye | Porous-coated RC | 2 | 7 | 5 |
| IJ – dye | Polymer-coated RC | 5 | 8 | 1 |
| IJ – dye | Porous-coated plain | 10 | 31 | 8 |
| IJ – pigment | Porous-coated RC | 1 | 2 | 1 |
| IJ – pigment | Fine art | 2 | 2 | 0 |
| D2T2 | Dye sublimation | 6 | 2 | 3 |
| Silver-halide | Chromogenic | 14 | 14 | 4 |

**Table 4. Effect of $NO_2$ on delta E of mid-tone grey and maximum black on the photo papers**

| *Printer* | *Paper* | *Dmid* | *Dmax* |
|---|---|---|---|
| IJ – dye | Porous-coated RC | 5 | 2 |
| IJ – dye | Polymer-coated RC | 4 | 0 |
| IJ – dye | Porous-coated plain | 20 | 20 |
| IJ – pigment | Porous-coated RC | 1 | 1 |
| IJ – pigment | Fine art | 0 | 0 |
| D2T2 | Dye sublimation | 4 | 2 |
| Silver-halide | Chromogenic | 12 | 11 |

**Table 5. Effect of $NO_2$ on delta E of white areas of the photo papers**

| *Printer* | *Paper* | *Dmin* |
|---|---|---|
| IJ – dye | Porous-coated RC | 3 |
| IJ – dye | Polymer-coated RC | 1 |
| IJ – dye | Porous-coated plain | 4 |
| IJ – pigment | Porous-coated RC | 1 |
| IJ – pigment | Fine art | 2 |
| D2T2 | Dye sublimation | 0 |
| Silver-halide | Chromogenic | 9 |

All of the digitally printed photos showed some degree of fade (delta E > 2) except the pigment inkjet prints. However, with the exception of the inkjet dye on porous-coated plain paper, all of the digitally printed photos were more resistant to fade than the traditional photographic print materials. Additionally, all of the digitally printed photographs were significantly more resistant to yellowing than the traditional photographs.

### *Digitally Printed Documents*

Table 6 shows the average delta E values for the maximum density cyan, magenta, and yellow patches for each printer and paper type for the document printing systems. Table 7 shows the average delta E values for a mid-tone neutral patch and the maximum density neutral patch for each printer and paper type. Table 8 shows the average delta E values for each technology for the minimum density (white) areas of the print.

**Table 6. Effect of $NO_2$ on delta E of cyan, magenta, and yellow colorants on the document papers**

| *Printer* | *Paper* | *C* | *M* | *Y* |
|---|---|---|---|---|
| IJ – Dye | Plain office | 4 | 4 | 2 |
| IJ – Dye | IJ office - treated | 4 | 5 | 2 |
| IJ – Dye | IJ office - IJ sized | 14 | 22 | 1 |
| IJ – Pigment | Plain office | 1 | 2 | 0 |
| Color EP | Plain office | 6 | 5 | 5 |
| Color EP | Color laser | 4 | 4 | 2 |
| DP – Dry Toner | Coated glossy | 6 | 9 | 1 |
| DP – Liquid Toner | Coated glossy | 7 | 5 | 1 |
| Offset Litho | Coated glossy | 5 | 3 | 1 |

**Table 7. Effect of $NO_2$ on delta E of mid-tone grey and maximum black on the document papers**

| *Printer* | *Paper* | *Dmid* | *Dmax* |
|---|---|---|---|
| IJ – Dye | Plain office | 1 | 1 |
| IJ – Dye | IJ office - treated | 1 | 0 |
| IJ – Dye | IJ office - IJ sized | 6 | 0 |
| IJ – Pigment | Plain office | 1 | 0 |
| Color EP | Plain office | 4 | 2 |
| Color EP | Color laser | 4 | 2 |
| DP – Dry Toner | Coated glossy | 3 | 2 |
| DP – Liquid Toner | Coated glossy | 2 | 0 |
| B&W EP | Plain office | 1 | 1 |
| Offset Litho | Coated glossy | 1 | 0 |

**Table 8. Effect of $NO_2$ on delta E of white areas of the document papers**

| *Printer* | *Paper* | *Dmin* |
|---|---|---|
| IJ – Dye | Plain office | 1 |
| IJ – Dye | IJ office - treated | 1 |
| IJ – Dye | IJ office - IJ sized | 5 |
| IJ – Pigment | Plain office | 1 |
| Color EP | Plain office | 2 |
| Color EP | Color laser | 4 |
| DP – Dry Toner | Coated glossy | 7 |
| DP – Liquid Toner | Coated glossy | 8 |
| B&W EP | Plain office | 2 |
| Offset Litho | Coated glossy | 7 |

With the exception of pigment inkjet documents, all of the digitally printed documents showed some degree of fade of the cyan, magenta, and yellow colorants. The black colorants, however, were considerably more robust and faded very little, if at all. As stated above, this is probably due to the fact that most grey tones in color digital prints are made up of cyan, magenta, yellow, and black colorants together. The maximum density black, however, is often black colorant only, and it is usually a pigment colorant even for many dye inkjet systems. Because of this, the text was not compromised and all samples were still readable after $NO_2$ exposure. All of the papers used in production printing, either for digital presses or traditional offset lithography were prone to yellowing.

In addition to fading and yellowing, the magenta ink bled in dye inkjet photos printed on the porous-coated plain paper and on one of the porous-coated photo papers. Bleed is sometimes seen when dye inkjet prints are exposed to high humidity; however, these samples were exposed in a pollution chamber held constant at 25°C ± 2°C and 50% RH ± 5%. It is not known why the ink bled; however, many inks are dependent on opposing charges between the ink and the paper to adhere properly. It is possible that the $NO_2$ dissolved in the natural water content of the paper resulted in the formation of nitric and nitrous acids. This alteration in the pH of the system might cause the ink and paper coating to disassociate. Photomicrographs illustrating ink bleed are shown in Figures 1 and 2 below. The print was dye inkjet on porous-coated plain paper.


***Figure 1.*** *Unexposed text*


***Figure 2.*** *Text exposed to $NO_2$*

## Conclusions

From the data the following conclusions were drawn:

- Dye inkjet prints on porous-coated plain papers and inkjet-sized office papers as well as the dyes in traditional color photographic papers were the most sensitive to fade by $NO_2$.

- The traditional photographic, digital press, and offset lithographic papers were the most prone to yellowing by $NO_2$.
- Black colorants were fairly robust, so text-only documents should be very resistant to $NO_2$ induced fade, though the papers may yellow.
- Exposure of some digital prints may result in colorant bleed which is potentially more objectionable than fade or yellowing as image detail may be lost or text readability diminished. Further research into this phenomenon is highly recommended.

This project only examined the effects of $NO_2$ on digitally printed materials; it did not take into consideration other decay forces such as other atmospheric pollutants (i.e. ozone), temperature, humidity, light, etc. Best practices for preservation of digitally printed materials should take into consideration the potential for damage by all of these forces.

## References


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## Author Biography

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