Further Observations of Ozone and Nitrogen Dioxide Pre-Dosed Digital Prints Over Time

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Abstract

There have been numerous reports on the effects of atmospheric pollutants on digitally printed materials that describe fading of colorants, yellowing of substrates, colorant bleed, and delamination of the ink-receiving layer on some digital prints. In 2010, the Image Permanence Institute published the results of an experiment on the effects of ozone and nitrogen dioxide on various digital print types. While it was not the intent of that experiment to determine the long-term effects of pre-exposure to pollutants, it was discovered after publishing the research that some of the samples dramatically yellowed while in storage. This research studied how those same digital prints stored at controlled room conditions changed after being exposed to ozone or nitrogen dioxide prior to storage. The yellowing of papers exposed to ozone before storage was previously documented in studies directed toward the development of test methods for accelerated aging. This paper documents real-time observation of digital prints after several hundred days in storage and addresses the potential damage to digital prints over time after exposure to ozone or nitrogen dioxide. The test samples included inkjet, color and black-and-white electrophotography, dye sublimation, digital press, chromogenic, and offset lithography prints. Paper yellowing, colorant change, further colorant bleed, and additional disintegration of the colorant layer of some prints were observed. Porous-coated materials exposed to ozone yellowed more dramatically in storage than when under direct exposure. This illustrates that initial results of change in these materials do not describe the whole story.

INTRODUCTION

A growing number of digital prints are being accepted into the collections of cultural heritage institutions.[1] Ozone (O_3) and nitrogen dioxide (NO_2) pollutants are commonly found in the indoor environments of institutional collections.[2] Levels of airborne pollutants vary greatly in real world collection environments. For example, the amount of ozone found in indoor environments depends upon outdoor levels, how often outdoor air enters indoors, the indoor surfaces that it comes in contact with, internal sources that can generate ozone, and air purification systems.[2] According to an IPI survey, institutions have already observed the yellowing of inkjet prints in their collections.[1] Collection managers need to know how sensitive these materials are to pollutants in order to take precautionary measures for the prevention of print degradation.

There have been several studies on the sensitivity of digital prints to O_3 and NO_2 exposure.[3,4,5,6] Many authors have reported that O_3, a strong oxidizing agent, is a major pollutant that contributes to the destruction of chromophores in dyes, which results in colorant fade.[5,6,7,8] Inkjet photo papers were found to be especially sensitive to O_3 exposure.[8,9,10] Print degradation depends not only on the colorants used, but also on the combination of colorants and substrate. For instance, the combination of inkjet dyes and porous paper can be very sensitive to colorant fade when exposed to O_3. Yet, the same colorants printed on polymer paper are not as sensitive to colorant fade when exposed to O_3. In addition, the same paper in combination with dye or pigment inks will give different results. One explanation for the sensitivity of porous media to O_3 is because their surface has a high porosity, which allows O_3 to easily penetrate into the substrate and attack the colorants. On the other hand, the protective coatings on polymer papers prevent pollutants from penetrating and degrading the image.

Comstock previously conducted research directed towards the development of standard test methods for image permanence testing, specifically with regards to the thermal testing methods.[11] He found that samples exposed to O_3 prior to the accelerated aging test showed an increase in paper yellowing over samples that were not pre-exposed to O_3. Furthermore, the concentration levels had a small impact on the paper yellowing whereas long time cumulative exposure (concentration multiplied by time) had a greater impact on the rate of paper yellowing. Institutions with low levels of O_3 may still be at risk (this might apply to the other pollutants as well) over long periods of time. The exposure of samples to pollutants prior to storage will be referred to as 'pre-dosing' throughout this paper.

As stated, IPI studied the effects of O_3 and NO_2 on various digital print types and provided tips for cultural heritage institutions.[3,4] After that research was complete, the samples used in the study were sealed and stored in a temperature and humidity controlled room (21°C and 50% RH). While it was not the original intent of the study to determine the long-term effects of pre-dosing, it was later discovered that some of the samples dramatically yellowed while in storage compared to the non pre-dosed samples. This paper reports on the changes to those same digital prints that were pre-dosed with pollutants and stored at controlled room conditions in over time.

METHODOLOGY

Test Samples

The test samples included three major digital printing technologies commonly used for home and office desktop printing, commercial photo kiosks, and short-run publications. Test samples were categorized into two systems: photo printing and document printing. In this report, the discussion of "photo" printing and paper technologies will specifically refer to technologies commonly used to print photographs. Likewise, the discussion of "document" printing will specifically refer to technologies commonly used to print text or mixtures of text and images. Photo printing samples were printed with inkjet, dye sublimation, and chromogenic technologies. Document printing was samples were printed with inkjet, color and black-and-white electrophotography (EP), digital press, and offset lithography technologies. Most technologies included multiple printer and paper combinations. Table 1 shows printing technology, paper type, abbreviation (used in this paper), and number of systems tested in each category.

Paper Types

The inkjet photo papers that were tested included porous-coated photo, polymer-coated photo, porous-coated plain, and fine art papers. Both porous and polymer papers had a resin-coated (RC) layers that are thin plastic layers on both sides of paper which makes the print look and feel like "real" traditional color photographs. The porous-coated photo papers had ink receiver layer (IRL) that consisted of small pores that absorb the ink. The porous coating itself is a thin layer of mineral particles held in a polymer binder that form very small cavities. During printing, the water from the ink is quickly drawn down into a second layer of pores resulting in an "instant" dry print. On other hand, in the polymer-coated photo paper's IRL swells and absorbs the liquid inks during printing and then shrinks back when the ink's solvent evaporates. This print takes several minutes to hours to fully dry compared to the porous-coated photo papers. The porous-coated plain papers are office-type plain papers with the porous IRL coating applied to the surface, usually on both sides. The fine-art papers are various types of high-quality artist papers that have porous ink-receiver layer.

Inkjet document papers consisted of plain office papers and plain inkjet-sized papers with no recycled contents. The plain office papers are chemically treated to absorb inkjet inks without allowing the colorants to spread across the paper. The inkjet-sized paper was a plain office paper with a special IRL that prevents the inks from penetrating the paper fibers keeping it close to the surface and this allows retaining the vibrant colors.

Dye sublimation and chromogenic papers used in the test were specific to their individual technologies. Coated glossy print stock was used for the offset lithography and all the digital press prints.

Table 1: Test samples

Printing Technology	Paper Type	Abbreviation	No. of Systems Tested
Photo Printing Systems			
Inkjet – Dye	Porous-Coated Photo	IJ Dye/Porous-Photo	3
Inkjet – Dye	Polymer-Coated Photo	IJ Dye/Polymer-Photo	3
Inkjet – Dye	Porous-Coated Plain	IJ Dye/Porous-Plain	1
Inkjet – Pigment	Porous-Coated Photo	IJ Pig/Porous-Photo	2
Inkjet – Pigment	Fine Art	IJ Pig/Fine Art	3
Dye Sublimation	Dye Sublimation	Dye Sub	2
Traditional Color Photo	Chromogenic Silver-halide	AgX	2
Document Printing Systems			
Inkjet – Dye	Plain Office	IJ Dye/Plain	3
Inkjet – Dye	Inkjet Office-Inkjet Sized	IJ Dye/Plain-Sized	1
Inkjet – Pigment	Plain Office	IJ Pig/Plain	3
Colour EP	Plain Office	Color EP/Plain	3
B&W EP	Plain Office	B&W EP/Plain	3
Digital Press – Dry Toner	Coated Glossy	DP/Dry Toner	2
Digital Press – Liquid Toner	Coated Glossy	DP/Liquid Toner	1
Offset Lithography	Coated Glossy	Offset	1

Test Targets

The color target contained ten levels of cyan, magenta, yellow, red, green, and blue patches, 20 levels of neutral patches, and two non-printed (white) patches. There was also a pictorial image and text target for illustrative purposes (Figure 1).

(a) (b) (c)

Figure 1: Test targets used in the study. (a) The color target used to measure colorant change and paper yellowing, (b) the pictorial image used for illustrative purposes, and (c) the text target.

Printer Settings

The default printer driver settings were used with default color management settings for desktop printing. "Best Photo" and "Photo Enhanced" printer driver settings were also selected when available for photographic papers. The default settings for plain paper were used for document printer systems. All test targets were in the sRGB color space.

Pollutant Exposure Period

In this paper, the "O_3 exposure period" refers to the measurements taken pre- and post-O_3 exposure at 5 ppm for 14 days. The "NO_2 exposure period" refers to the pre-and post-NO_2 exposure at 5 ppm for 28 days. The colorimetric and densitometric data from this period was already published by IPI. [1,2]

Both O_3 and NO_2 chambers used for pollutant exposure were custom built for IPI by Codori Enterprises. The O_3 was produced by means of an ultra-violet lamp. The samples were exposed at 5 ppm ± 0.25 ppm for 2 weeks. The NO_2 chamber used tanks of 2% NO_2 purchased from Air Products. The samples were exposed at 5 ppm ± 0.25 ppm NO_2 for 4 weeks. The gas concentration was monitored throughout the test period and stayed within the target value. Temperature and humidity were calibrated before testing and were monitored throughout the process. Conditions were 25°C ± 2°C and 50% RH ± 5% RH.

Bagged Period

Following the O_3 and NO_2 pollutant exposure periods, the test samples were measured, placed into hermetically sealed aluminum foil-laminate bags (at 50% RH), and stored in a climate-controlled room at 21°C. The "bagged period" refers to the changes that occurred during the time the samples were stored in the aluminum foil-laminate bags. The bagged period includes changes that occurred 807 days after O_3 exposure and 550 days after NO_2 exposure.

Measurements and Evaluations

Color target patches from pre- and post-pollutant exposure periods and after the bagged period were measured using a Gretag Spectrolino/Spectroscan spectrophotometer. CIELAB (D50, 2° observer, no UV cut filter) and Status A blue density (D_{blue}) values were collected to calculate ΔE^*_{ab} and ΔD_{blue} for all patches to show the colorimetric and densitometric changes. The D_{blue}

density values of the unprinted patch (paper white) were used quantify yellowing of the paper because blue filter absorbs a yellow energy. Figure 2 illustrates the timeline of the experiment and the sample measurements that were taken along the way.

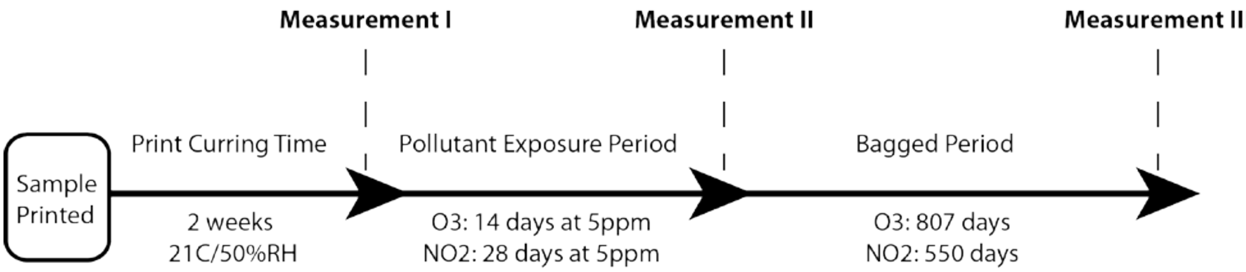


Figure 2: Timeline of the experiment.

RESULTS

Yellowing of the Substrates

Figure 3 shows the average change in density values for the white patch of the papers from the pollutant exposure period, which is shown as dark blue (O_3) or dark green (NO_2) bars. The changes that occurred during the bagged period are shown in light blue and light green bars stacked on the pollutant exposure period bars to show the total average density change for a given paper type. The data in Figure 3 were averaged across paper type.

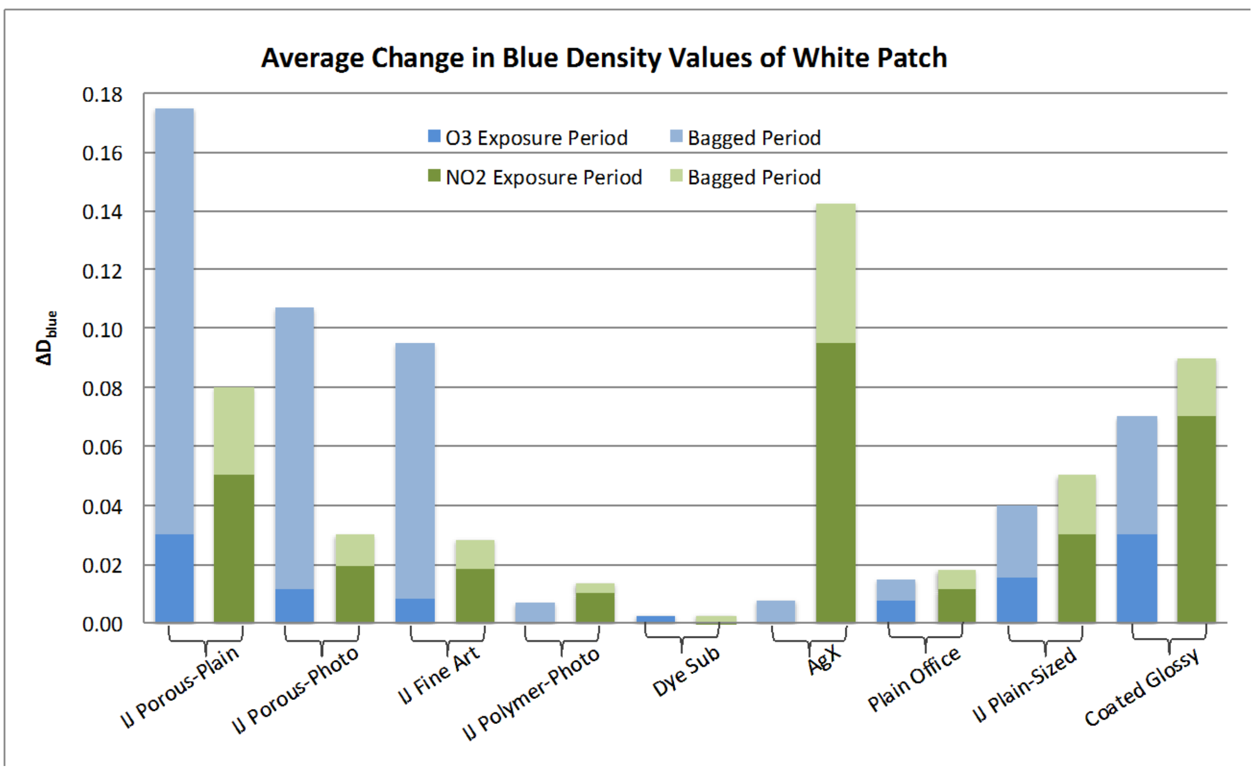


Figure 3: Shows average change in blue density (ΔD_{blue}) of the white patches for pollutant exposure period and bagged period.

The bar graph results confirm previously published research (pollutant exposure period) that NO_2 has a greater overall effect on the yellowing of papers initially than O_3. However, over time the bagged samples that were pre-dosed with O_3 yellowed significantly more than those pre-dosed with NO_2 for all papers except chromogenic. Porous-coated photo papers did not visibly yellow during the O_3 exposure period but after the storage period it significantly yellowed (Figure 4(c)). The bagged samples that were pre-dosed with NO_2 continued to yellow, most noticeably the chromogenic samples.

(a) (b) (c)

Figure 4: Shows yellowing of the porous-coated photo sample. (a) Is the reference image, (b) is the image taken after the O_3 exposure, and (c) is the image taken after the storage period.

The unexposed samples that were stored in a bag were measured to verify that the changes that occurred during the storage period were a result of pollutant pre-dosing. The color differences shown in Figure 5 were between the initial measurements unexposed samples and measurements of those same samples after 908 days of storage. The graph shows small changes that occurred during the bagged period as a result of the natural aging of the prints.

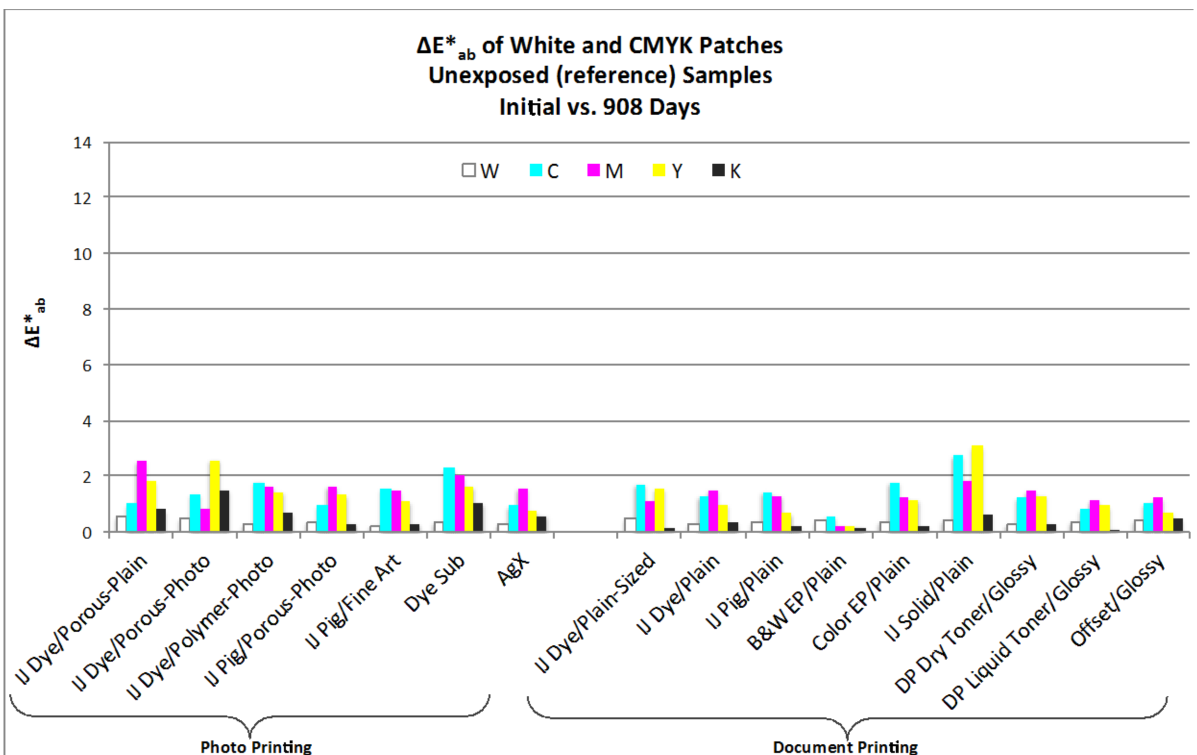


Figure 5: Shows average ΔE^*_{ab} of white and CMYK patches in photo and document printing systems for the unexposed samples.

Colorant Change: Bagged Period (O_3 pre-dosed)

Maximum density patches of cyan, magenta, yellow, and black were measured to analyze colorant change. The white (w) patch was also included as a guide to determine whether paper yellowing influenced colorant change. Figure 6 shows the average ΔE^*_{ab} of the maximum density CMYK patches and white patches in photo printing systems after the bagged period.

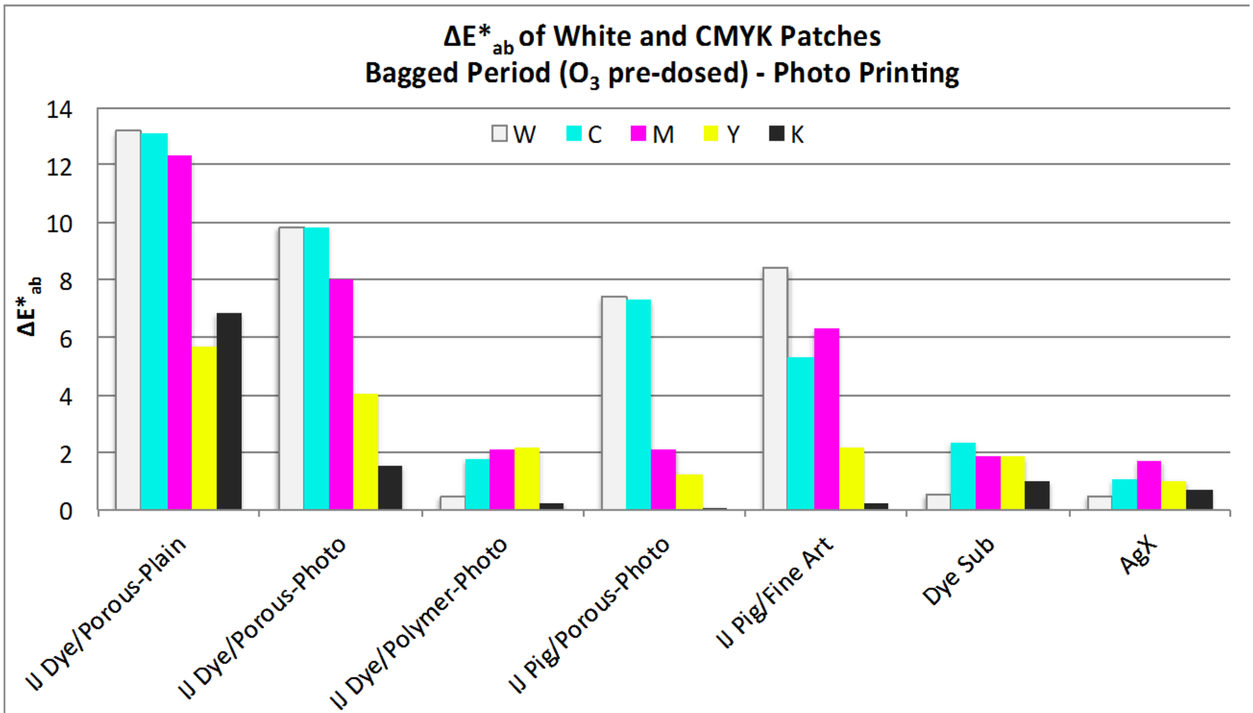


Figure 6: Shows average ΔE^*_{ab} of white and CMYK patches in photo printing systems after the bagged period (O_3 pre-dosed).

The average ΔE^*_{ab} was greater than 5.8 for the white and cyan patches on porous-coated and fine art papers. It is not clear whether the color difference was a result of colorant change independent of paper yellowing or whether the observed colorant change was the result of paper yellowing.

The O_3 results varied even between brands for a single paper type and printer technology. Three porous-coated photo paper brands printed using two dye-based printer brands showed different results. Figure 7(a) is a reference image of one of the porous-coated photo papers. Figure 7(b) through 7(d), are the three brands of porous-coated photo papers. The image in Figure 7(b) appeared to have lost most of its black colorant, which caused its de-saturated, red appearance. Magenta faded significantly in Figure 7(c), but the black still remained. Figure 7(d) shows the overall colorant fade with the black colorant still remaining. Most of these changes occurred during the O_3 exposure period but the data after the bagged period shown in Figure 6 also suggests an average ΔE^*_{ab} above 8.0 for cyan, magenta, and white patches, meaning additional change over time has occurred.

(a) (b) (c) (d)

Figure 7: Shows varied effects of O_3 exposure on the three brands of porous-coated photo paper type. (a) Is the reference image, and (b) through (d) are the three brands of porous-coated photo papers.

Those same three brands of porous-coated photo papers also showed a large range of ΔE^*_{ab} for white patch after bagged period (O_3 pre-dosed). For example, Table 2 shows the ΔE^*_{ab} of the white patch for three different brands of one paper type, porous-coated photo paper.

Table 2: ΔE^*_{ab} of a white patch for three brands of porous-coated photo papers.

	O_3 Exposure Period	***O_3 Bagged Period***
IJ porous-coated photo 1	3.1	15.5
IJ porous-coated photo 2	1.0	9.3
IJ porous-coated photo 3	0.4	4.8

Table 2 demonstrates a large range of ΔE^*_{ab} values resulting from the O_3 bagged period in a single paper type. The ΔE^*_{ab} of the white patch after the bagged period ranged from 4.8 to 15.5. This illustrates that the effect of O_3 exposure on a single paper type can vary within different brands.

In addition to colorant fade and yellowing, porous-coated photo papers showed cracking and disintegration of the image-receiving layer as a result of O_3 exposure. Over the bagged period, the surface became severely fragile, resulting in the image-receiving layer flaking off and a total loss of image. Figures 8, 9, and 10, show cracking and delamination of three brands of porous-coated photo papers. Note that the cracking pattern is different on all three papers. The sample shown in Figure 8 was so sensitive that the ink-receiving layer flaked off during handling. The sample shown in Figure 9 had a few areas that were delaminated. Those areas are shown using 100x magnification.

Figure 8: Shows flaking

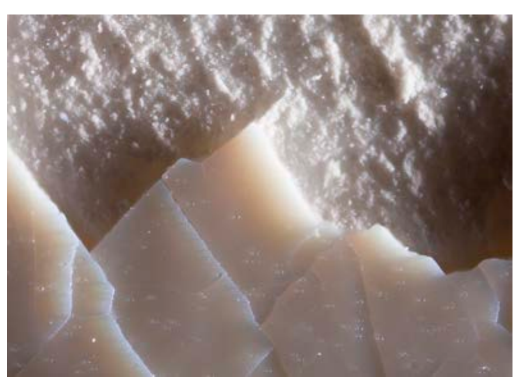
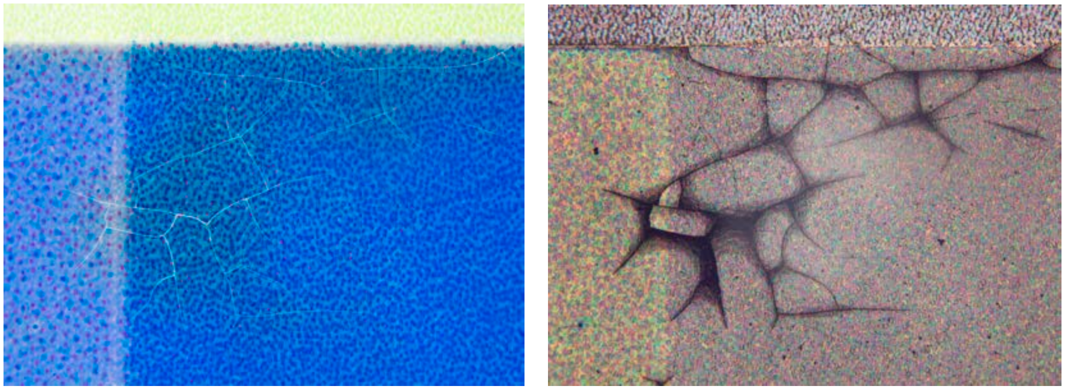


Figure 9: Shows delamination of a small area (100x)

The sample shown in Figure 10 contained minor cracks without flaking. The image in Figure 10(a) was photographed using 45-degree lighting with 50x magnification and the image in Figure 10(b) was taken using axial lighting to reveal cracks more profoundly.



(a) (b)

Figure 10: Shows minor cracking at 50x magnification. (a) The image was photographed using 45-degree lighting and (b) with axial lighting.

As noted above, some of the porous-coated photo papers became more fragile in storage. Figure 11 shows the text target that was photographed after it was removed from the O_3 chamber (Figure 11(a)) and then after storage (Figure 11 (b)). Additional yellowing, colorant fade, and IRL delamination was observed after the storage period.

(a) (b)

Figure 11: Shows additional change over time of the porous-coated sample. (a) The image was made after the O_3 exposure, and (b) after the storage period.

The average ΔE^{*}_{ab} for all document papers was less than 3.6 across all colorants (Figure 12) after the bagged period. These changes may not be as significant as for the photograph papers, but, over longer periods of time, these color differences may continue to increase.

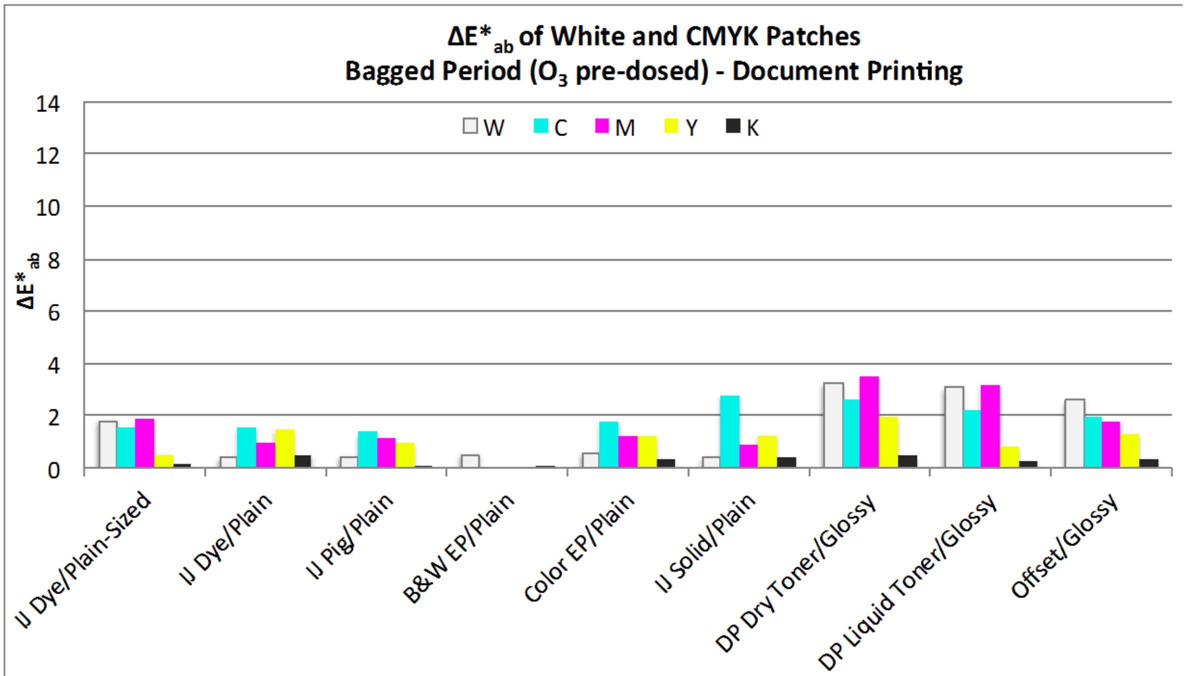


Figure 12: Shows average ΔE^*_{ab} of white and CMYK patches in document printing systems after bagged period (O_3 pre-dosed).

Figure 13 shows samples of the inkjet-sized plain paper printed using a dye printer. Figure 13(a) is the reference print and Figure 13(b) shows the image of the print taken after the bagged period. The bar graph in Figure 12 indicates an average ΔE^*_{ab} of less than 2.0 for all colorants in this sample. Therefore, most of the change in this case occurred during the O_3 exposure period rather than during the bagged period.

(a) (b)

Figure 13: Shows fading of colorants of IJ Dye/Plain-Sized sample. (a) Is the reference image and (b) is the image taken after the bagged period (O_3 pre-dosed).

Colorant Change: Bagged Period (NO_2 pre-dosed)

Figure 14 shows the colorant change that occurred during the bagged period after the NO_2 exposure. The white patch was included as a guide to determine whether paper yellowing influenced the color change. The average ΔE^*_{ab} of the white patch was 0.4 for the polymer-coated papers. However, the cyan patch had an average ΔE^*_{ab} of 4.3, which means that the cyan dye did continue to change over time.

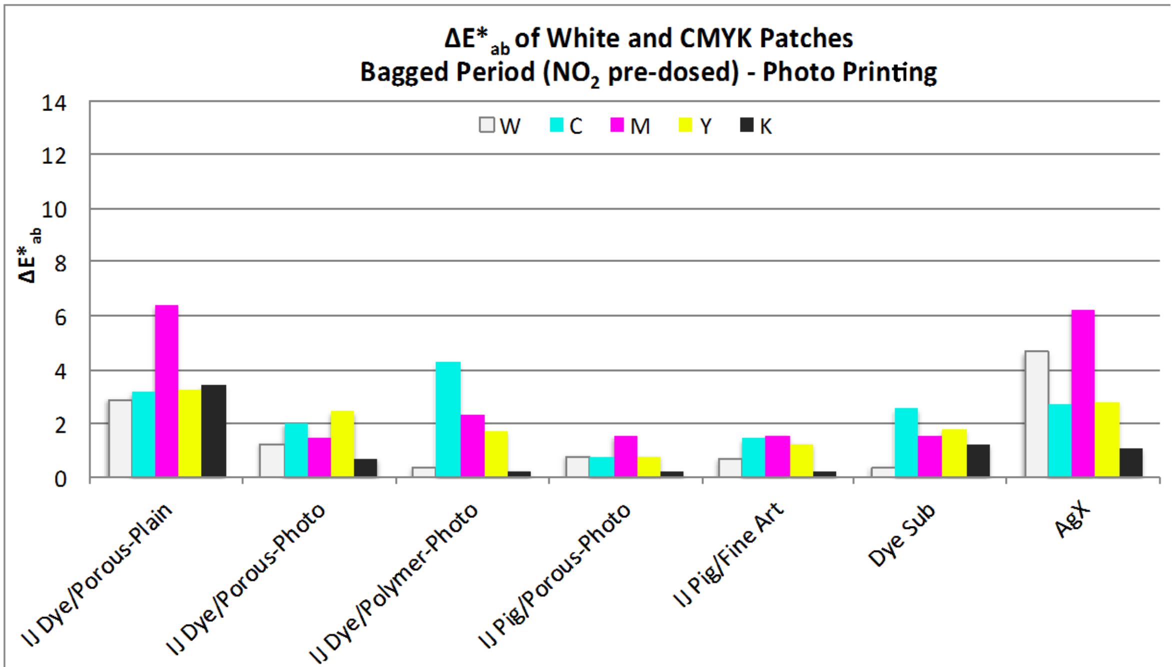
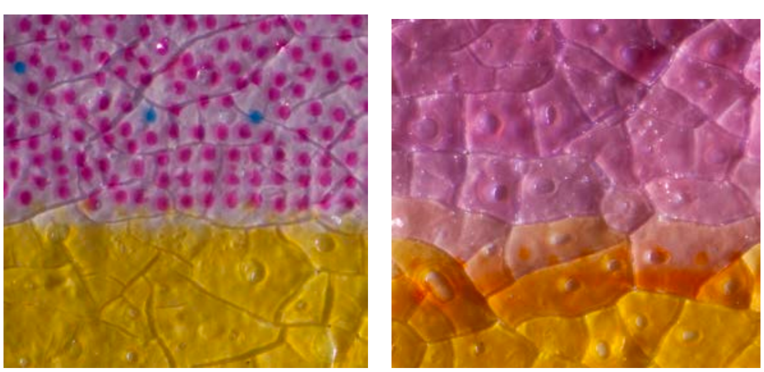


Figure 14: Shows average ΔE^*_{ab} of CMYK and white patches in photo printing systems during the bagged period (NO_2 pre-dosed).

Additionally, there were two papers that showed colorant bleed during the NO_2 exposure period. These samples were inkjet dye print on one of the three porous-photo papers and a porous-coated plain paper. A possible explanation for the colorant bleed is the formation of nitric and nitrous acids, a reaction resulting from the natural water content of the paper and NO_2. There was a large increase in ΔE^*_{ab} for the magenta patch for IJ Dye/Porous-Plain sample (see Figure 14). This could have been due to the increased magenta bleed in the paper over the bagged period. Figure 15(a) is the reference image showing magenta dots, and the Figure 15(b) shows magenta dots bleeding into the yellow patch, filling in the white areas of the print.



(a) (b)

Figure 15: Shows magenta colorant bleed of IJ Dye/Porous-Plain sample at 50x magnification. (a) Is the reference image and (b) is the image taken after the bagged period (NO_2 pre-dosed).

However, colorant bleed in the second print did not show such a large change in average ΔE^*_{ab} for the magenta patch (Figure 14). This was the IJ Dye/Porous-Photo sample (Figure 16). It is often hard to observe bleed directly without magnification. In Figure 16 (b), the bleed is observed as a reddish shift in cloud color. The 100x-magnified image shows the magenta colorant bleed and filling in of the unprinted area.

(a) (b)

Figure 16: Shows magenta colorant bleed of IJ Dye/Porous-Photo sample. (a) Is the reference image and (b) is the image taken after the bagged period (NO_2 pre-dosed).

The average ΔE^*_{ab} increased for all colorants in the chromogenic sample and was especially pronounced for the magenta patch (Figure 14). Figure 17(a) shows the chromogenic sample reference and Figure 17(b) shows an image taken after the bagged period. The sample became more magenta. The NO_2 exposure period for this image did not have a magenta cast. This change occurred during the bagged period.

(a) (b)

Figure 17: Shows magenta hue shift of the chromogenic sample. (a) Is the reference image and (b) is image taken after the bagged period (NO_2 pre-dosed).

Figure 18 shows the colorant change of the document papers that occurred during the bagged period. Cyan and magenta patches in IJ Dye/Plain-Sized samples continued to change, resulting in the highest ΔE^{*}_{ab} across all document papers. All other document samples exposed to NO_2 had slight colorant changes during the bagged period, with an average ΔE^{*}_{ab} of less than 3.5.

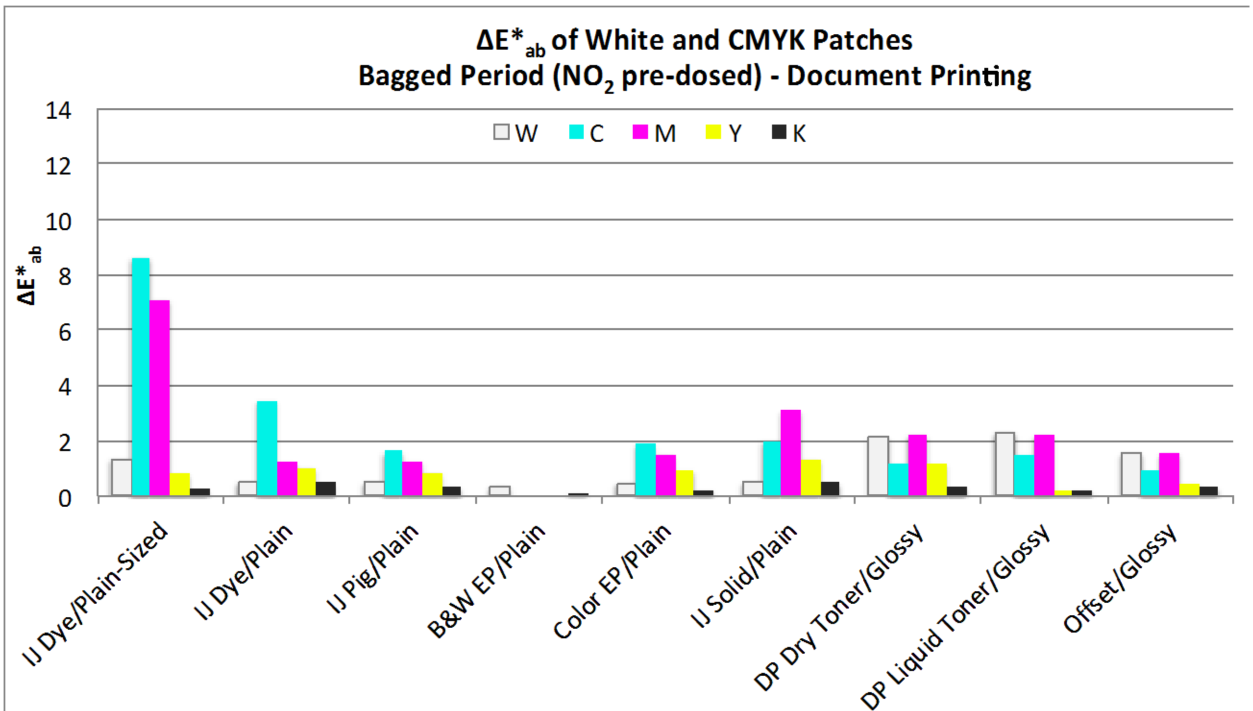


Figure 18: Shows average ΔE^{*}_{ab} of white and CMYK patches in document papers after the bagged period (NO_2 pre-dosed).

Figure 19(a) shows the DP Liquid Toner/Glossy sample reference and Figure 19(b) shows the sample as it looked after the bagged period. Most of the observed yellowing occurred during the NO_2 exposure period because average ΔE^{*}_{ab} for white patch was 7.6. After the bagged period the average ΔE^{*}_{ab} for white patch was only 2.2. The yellowing of text may be more forgiving than the yellowing of photographs because text is still readable and the information is not lost. It may not be objectionable unless the document is of great historic, artistic, or monetary value.

(a) (b)

Figure 19: Shows yellowing of digital press sample. (a) Is the reference and (b) is the image taken after the bagged period (NO_2 pre-dosed).

CONCLUSIONS

The results showed the potential harm caused by the continuous degradation of digital prints during long-term storage after pre-exposure to pollutants regardless of the benign storage environment. Each pollutant affected the prints in different ways. For example, NO_2 exposure had a significant impact on yellowing of some papers initially, and continued to degrade the paper over time. O_3 exposure had a great impact on colorant fade initially, but over time, there was a dramatic increase in paper yellowing. This effect was especially pronounced for porous-coated papers.

While these samples were sealed and stored in the dark over time, the experiment may not have been representative of a real life scenario because samples were sealed in aluminum bags. This research is most applicable in practice for prints that are stored in plastic sleeves or sealed frames. In addition, the high concentration of pollutants produced severe damage in this study because the prints were pre-dosed with 5 ppm. Lower concentrations may or may not result in continuous degradation over time. There is a need for more investigation on this topic to better understand the resistance to collections since the examples in this project were so dramatic. It is still unknown whether lower concentrations, different exposure times, effects of clean air environment after pre-dosing, or varied storage configurations will result in pollution degradation over time. A better understanding of the mechanisms that triggers paper yellowing of pollutant exposed prints in storage over should be investigated.

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