Colorant Fade and Page Yellowing of Bound and Unbound Materials Printed Using Digital Presses and Offset Lithography when Exposed to O_3 or NO_2

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Abstract

The printing industry has seen growth in the number of bound digitally-printed materials since the introduction of commercial digital presses. Many short-run publications, such as research monographs, periodicals, and books have already entered the collections of cultural heritage institutions. It is vital that information be made available regarding the care of these materials. There is no known previous research on the effects of pollutants, such as O_3 (ozone) or NO_2 (nitrogen dioxide), on bound digitally-printed materials. This study was undertaken to specifically investigate the susceptibility of digital press and offset printed bound materials to page yellowing and colorant change when exposed to O_3 and NO_2 independently. The research findings demonstrated that bound digitally-printed materials are at risk to damage by these airborne pollutants. Cultural heritage institutions that have these materials within their collections should take precautions to mitigate deterioration through the use of air filtration, reduced temperature storage, or low permeability enclosures. The method chosen should match the use and size of the collection and the resources of the institution.

Introduction

Offset lithography dominated the commercial printing market for the past 50 years and now high-speed electrophotographic and inkjet digital press systems are changing the market [1]. The print quality of digital presses has been improving and it has more application capabilities and short-run capabilities, than offset lithography [2]. Digital press systems also provide versatility in terms of the wide range of substrates on which they can print [3]. However, the permanence issues with bound materials created by digital presses have yet to be fully investigated.

The permanence of bound digitally-printed materials is vital because they already exist in collections. According to Wilhelm, the images in photobooks are as valuable as traditional silver-halide photographs, since the majority of them are not produced in any other hardcopy form [4]. The greatest concerns with regards to the permanence of bound digitally-printed materials are the yellowing of the pages over time and the potential for colorant fade. Although books most often remained closed and stored on bookshelves, the cover might be susceptible to fade, or if the book is opened and is displayed on a table, then the pages might be susceptible to fade [4]. The book bindings are also an important factor; however, the durability of bindings will not be covered in this paper. This paper is the first published research on the sensitivities of digitally printed bound materials to O_3 or NO_2 exposure.

Methodology

Bound and Unbound Materials

The bound materials were printed using three different digital press systems (dry-toner electrophotography (EP), liquid-toner EP, pigment inkjet) and offset lithography. Except for the pigment inkjet prints, the sheets were bound in three different configurations: stitched-hardcover book, glued-softcover book, and stapled periodical. Each binding type was paired with a specific paper (hardcover with uncoated paper, softcover with glossy paper, stapled periodical with glossy paper containing 30% recycled content) commonly used with each type of binding. The pigment inkjet prints, which used a glossy inkjet-primed paper, were only bound as stapled periodicals.

Unbound sheets from the sample set were also tested to compare the effect of pollutants on free-hanging samples versus samples in bound form. Table 1 shows printing technology, paper type, binding type, and sample codes used in this experiment. Note that DP stands for "digital press."

Test Targets

The bound pages contained printed test targets to quantify the yellowing and colorant fade that resulted from the pollutant exposure. The following test elements were included on each page spread (see Figure 1):

- Edge yellowing was assessed using paper measurements at positions indicated by arrows at the paper corners, along the edges (including the gutter), and in the center of page
- Colorant fade was evaluated using D_{max} (maximum density) CMYK (13mm x 26mm) patches
- Two pictorial images and a text target for illustrative purposes
- A 73-patch color target was cut out and used for the unbound free-hanging portion of the experiment. This target included cyan, magenta, yellow, red, green, blue, and neutral ten-step tint ladders, as well as a white (non-printed) patch used to measure paper yellowing. Only D_{max} CMYK and a white patch data will be reported in this paper.

Measurements

Color change and page edge yellowing were measured using a GretagMacbeth Spectrolino/Spectroscan (D50, 2° Observer, with the UV component included). CIELAB values were collected for both pre- and post-pollutant exposures to calculate ΔE^*_{ab}. The bound volume measurements were made from pages located at the beginning, middle, and near the end of the book using a white backing material. All test samples were conditioned

Table 1. Materials Tested.

Printing Technology	Paper	Binding Type	Sample Codes
Dry Toner DP	Uncoated	Stitched Hardcover	DT_Uncoated
Liquid Toner DP	Uncoated	Stitched Hardcover	LT_Uncoated
Offset Lithography	Uncoated	Stitched Hardcover	Offset_Uncoated
Dry Toner DP	Glossy	Glued Softcover	DT_Glossy
Liquid Toner DP	Glossy	Glued Softcover	LT_Glossy
Offset Lithography	Glossy	Glued Softcover	Offset_Glossy
Dry Toner DP	Glossy w/30% Recycled	Stapled	DT_Glossy (Rec)
Liquid Toner DP	Glossy w/30% Recycled	Stapled	DT_Glossy (Rec)
Offset Lithography	Glossy w/30% Recycled	Stapled	Offset_Glossy (Rec)
Pigment Inkjet DP	Inkjet Glossy	Stapled	Inkjet_Glossy

Figure 1. *Example of the pages in a stitched hardcover book.*

for two weeks in a climate-controlled room at 21°C and 50% RH before testing.

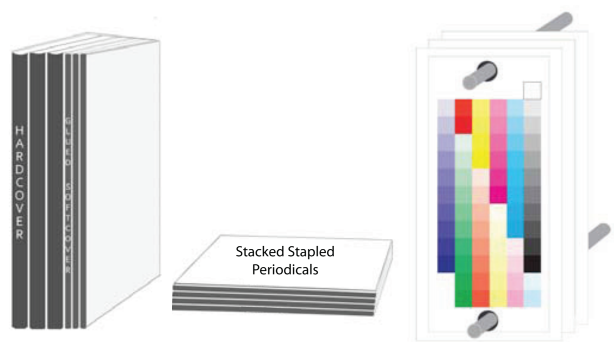
Chambers and Exposure Times

The O_3 and NO_2 chambers were custom built by IPI by Codori Enterprises. The O_3 was produced by means of an ultraviolet lamp. The NO_2 chamber used tanks of 2% NO_2 purchased from Air Products. The temperature and humidity within chambers were held constant at 25°C ± 2C and 50% RH ± 5% RH.

The bound and unbound materials placed in the O_3 chamber were exposed to 1 ppm O_3 for six weeks and those placed in the NO_2 chamber were exposed to 5 ppm NO_2 for six weeks. These conditions were selected because these were chamber conditions already in use for testing samples for a different experiment.

Sample Arrangements in the Chambers

The bound materials were placed independently in the NO_2 and O_3 chambers as follows. The hardcover and glued softcover books printed using three different presses were placed vertically next to each other, as they would be found on library shelves (Figure 2a). The stapled periodicals printed using four different presses were laid flat as one might find them in a librarys magazine section (Figure 2b). In addition, the unbound sheets were hung freely in the pollution chambers on a rod with 2 cm gaps between the samples (Figure 2c).



(a) (b) (c)

Figure 2. *Sample arrangements in the pollution chambers: (a) illustrates vertically placed hardcover and softcover books, (b) stacked stapled periodicals, (c) unbound free-hanging samples.*

Results

Unbound Free-Hanging Samples

Figure 3 shows the ΔE^*_{ab} of a white patch after the O_3 exposure for all papers tested. Visually, yellowing of the papers was not observed after O_3 exposure, and the data only showed a small change in ΔE^*_{ab}.

Figure 4 shows the ΔE^*_{ab} of a white patch after the NO_2 exposure. Glossy and glossy paper with 30% recycled content showed the greatest increase in ΔE^*_{ab}. Visually, NO_2 exposure caused yellowing of all substrates except for the inkjet glossy paper, for which there was no noticeable change.

O_3 exposure had a greater impact on colorant fade than NO_2 exposure. Figure 5 shows the ΔE^*_{ab} of white and D_{max} CMYK patches after O_3 exposure. The liquid-toner digital press showed the largest cyan and magenta colorant fade regardless of the paper on which it was printed. The inkjet digital press had the highest ΔE^*_{ab} of 13.8 for the cyan patch. Dry toner EP and offset press samples had ΔE^*_{ab} color differences below 3.1 for all colorants.

Figure 6 shows ΔE^*_{ab} color differences for D_{max} CMYK patches after NO_2 exposure. A white patch was also included

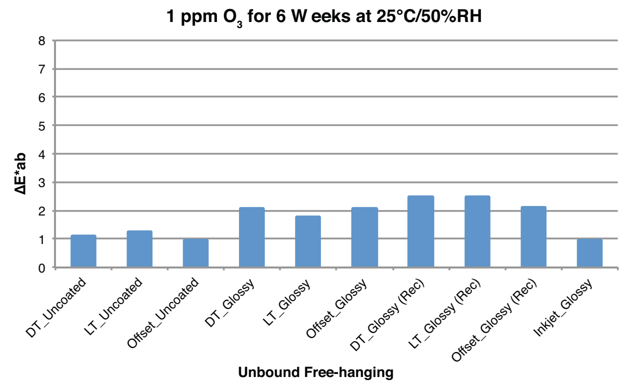


Figure 3. *Average ΔE^*_{ab} of the white patch after the O_3 exposure.*

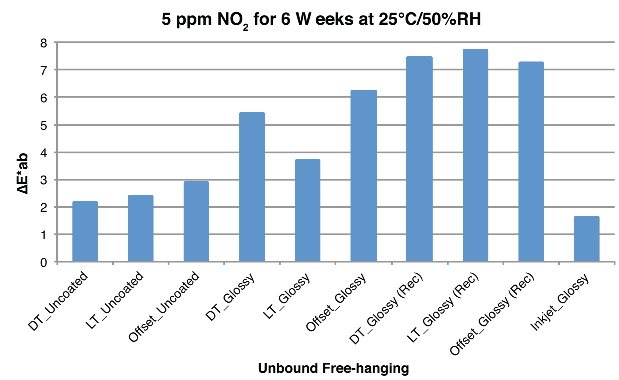


Figure 4. *Average ΔE^*_{ab} of the white patch after NO_2 exposure.*

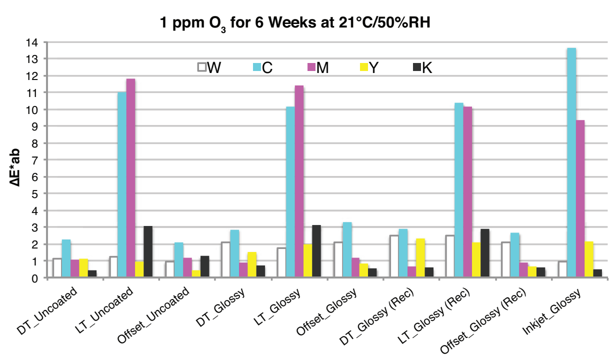


Figure 5. *ΔE^*_{ab} of D_{max} CMYK patches after O_3 exposure.*

as a guide to determine whether paper yellowing influenced colorant change. The cyan and white patches had the highest ΔE^*_{ab} changes. The ΔE^*_{ab} of a white patch in this case suggests that paper yellowing might have influenced the large ΔE^*_{ab} values for the cyan patch. Examination of the data revealed a similar magnitude and direction of change in the CIELAB color space between paper white and the cyan patch, suggesting that the cyan colorant change was most likely due to the yellowing of the substrate and not the loss of cyan colorant. However, paper yellowing did not seem to have as big of an effect on the yellow, magenta, and black colorants. The black patch, on the other hand, did not reflect or transmit much light at all, and thus its color was minimally affected by the paper yellowing.

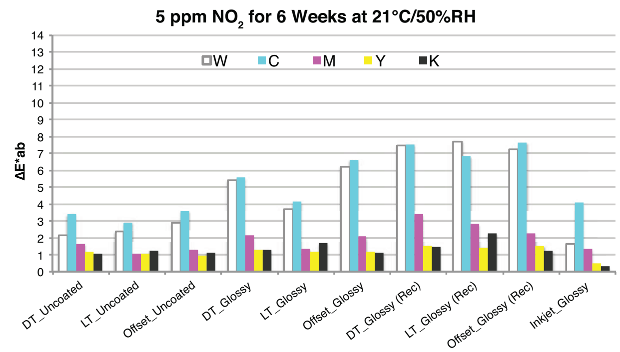


Figure 6. *ΔE^*_{ab} of white and CMYK patches after NO_2 exposure.*

Bound Materials

There was a very small change in the yellowing of the substrates after O_3 exposure in bound materials and free-hanging samples. Therefore, the O_3 data from the bound materials for paper yellowing was omitted from this paper. Likewise, the colorant data after the NO_2 exposure showed confounding ΔE^*_{ab} results in bound materials due to the substrate yellowing. Thus, the NO_2 data for color patches from bound materials was omitted.

Overall, the bound materials did not show the same degree of yellowing throughout the pages as the free-hanging samples after the NO_2 exposure. While the book cover or the text block as a whole might have protected the center of the pages from pollutant penetration, yellowing was still observed on the edges and in the gutter. Figure 7 shows ΔE^*_{ab} values for the white patch after NO_2 exposure. The bar graph plots data read from the center of the book against data from the middle of the gutter and the edges of the pages. All of the bound materials had ΔE^*_{ab} values greater than 1.0 for the paper edges. However, stapled periodicals had the largest ΔE^*_{ab} values for all page sections (center, gutter, and edges). The larger gaps between pages in the stapled periodical, a result of the pages being less densely packed together, allowed NO_2 to penetrate easily (see Figure 8). Although the hardcover book shielded the center and the middle of the gutter from yellowing, the edges were still affected. The softcover book showed yellowing in the middle of the gutter and at the edges, but not it the center.

One of the stapled periodical samples from the graph in Figure 7, Liquid-Toner_Glossy (Rec), is shown in Figure 9 below. Yellowing was severe at the page edges and gutter. The center of the page did not show as much yellowing as the other sections. Additionally, this example shows the yellowing effect in the middle pages of the book, which had a gap when closed due to the stapled binding, allowing for pollutant penetration. In Figure 8, the image was manipulated in Adobe Photoshop using the Hue/Saturation tool to improve reproduction of yellowing of the page edges and the gutter resulting from NO_2 exposure in both B&W and color publications. Dark areas illustrate where the yellowing has occurred.

The colorant fade in bound materials after O_3 exposure was not as dramatic as in the free-hanging samples. However, the sta-

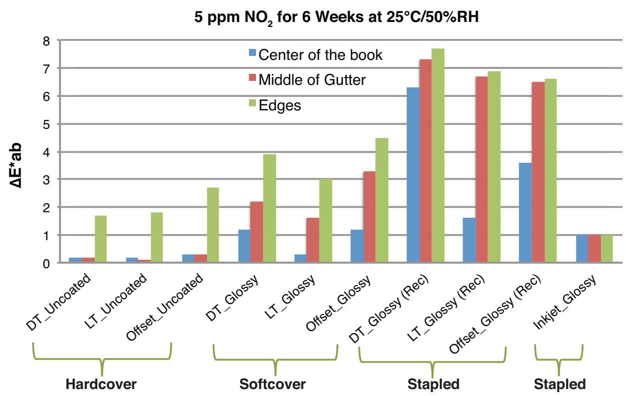


Figure 7. *ΔE^{*}_{ab} of the white patch after the NO_2 exposure for bound materials.*

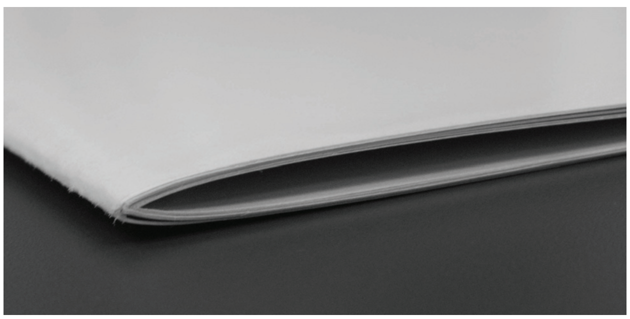


Figure 8. *Gaps were present between the pages in the stapled periodical.*

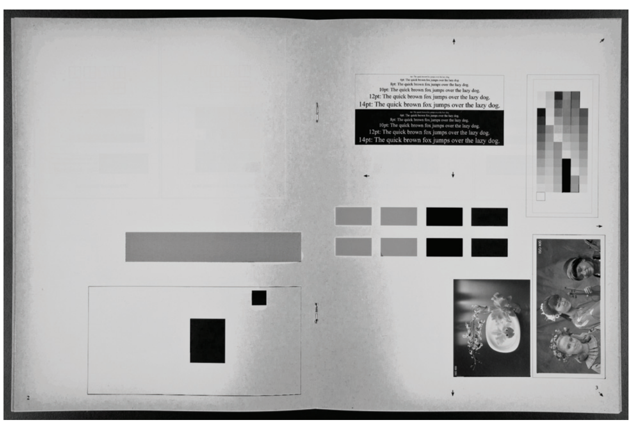


Figure 9. *Yellowing of the glossy paper with 30% recycled content in a stapled periodical after NO_2 exposure.*

pled Inkjet_Glossy periodical had the highest ΔE^{*}_{ab} for cyan and magenta patches (Figure 10). The rest of the books had ΔE^{*}_{ab} color differences below 2.0. It appears that the hardcover, softcover, and stapled bindings protected the sheets from O_3 penetration for EP and Offset. Overall, it appears that all of the bindings, except for the stapled Inkjet_Glossy periodical, protected colorants from fading after O_3 exposure.

Conclusions

The study showed that bound digitally-printed and unbound materials were affected by the exposure to O_3 and NO_2. Exposure to O_3 contributed more to the fading of the colorants, while exposure to NO_2 contributed to substrate yellowing. This research revealed that the free-hanging samples yellowed across the entire surface as a result of NO_2 exposure while the bound materials only exhibited yellowing on the edges. In general, the page centers were shielded by the hardcover and softcover bindings. However, the stapled periodical showed yellowing in the page centers and in the middle of the gutter due to the large gaps between the pages allowing for greater NO_2 penetration. It was also noted that the cyan patch exhibited colorant change after NO_2 exposure, which was more likely due to the substrate yellowing than cyan colorant loss. With regard to the O_3 exposure of the free-hanging samples, the liquid-toner EP and inkjet press samples showed the greatest cyan and magenta fade regardless of the paper it was printed on. However, the bindings mitigated O_3 penetration inside the books and reduced colorant degradation, except for the stapled inkjet periodical, which showed cyan and magenta colorant fade. There is still more research needed to be done on this matter. In this experiment, binding types were only paired with a specific paper. In future work, a wider selection of papers with different bindings, pollutant concentrations, page numbers, and different sample arrangements should be considered.

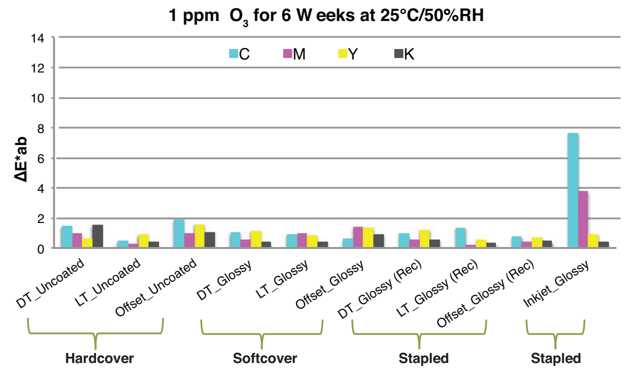


Figure 10. *ΔE^{*}_{ab} of CMYK patches after O_3 exposure in bound materials.*

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Nino Gordeladze, Research Associate, has been working for the Image Permanence Institute since 2008. She graduated from Rochester Institute of Technology with a Bachelor of Science in Imaging and Photographic Technology in 2010. She also received an Associate degree in Business Administration from Hudson Valley Community College in 2007. Currently she is working on the DP3 (digital print preservation portal) research projects funded by IMLS and the A. W. Mellon Foundation. Some of her work includes investigating the stability of digital prints in bound forms, the pollution-mitigations strategies, and thermal stability of the digital print colorants.