Mitigation of Pollution-induced Deterioration of Digital Prints through Low-Temperature Storage

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Abstract

An IPI survey found that approximately 87% of museums, libraries and archives already have digital prints in their collections and that they are concerned about increasing influxes of these materials. The survey also showed that objectionable deterioration has already occurred to some of their prints including fading, yellowing, color bleed, surface cracking and delamination. In total, 71% of institutions have already experienced deterioration in their digital print collections. Previous experimental research, both by IPI and others, has been able to establish a clear connection between ozone and nitrogen dioxide exposure and each of those forms of decay. Development of effective methods to mitigate such damage will, therefore, be critical to the survival of these objects for future generations. This study was aimed specifically at determining the efficacy of one particular approach, mitigating pollutant damage to digital prints through lowered-temperature storage. Since the deterioration due to pollutants occurs through chemical reactions, it may be possible to slow decay through cool or cold storage.

The Arrhenius method was used to predict the times to significant fade or yellowing of prints exposed to 1 ppm ozone or 5 ppm nitrogen dioxide. Test targets were incubated at 25°C, 30°C, 35°C, 40°C, and 45°C at 50% RH for multiple intervals up to 56 days. Cyan, magenta, yellow, and black color patches were monitored using ANSI Status A density for density loss. Unprinted, white areas were monitored using ANSI Status A blue density for paper yellowing. It was found that lower temperature does in fact reduce the rates of decay but not equally for both pollutants. Low temperature was more effective at reducing yellowing caused by nitrogen dioxide than it was at reducing the fade caused by ozone; however, cool or cold storage can clearly mitigate damage and extend the usable life of digital prints in collections.

Introduction

An IPI survey of museums, archives, and libraries found that approximately 87% of cultural heritage institutions already have digital prints in their collections, that they are concerned about continuing influxes of these materials, and that they do not yet feel well informed on how to care for these materials. The same survey showed that objectionable deterioration to these objects has already occurred to portions of these collections including (but not limited to) fading, yellowing, color bleed, surface cracking and delamination. In total, 71% of institutions have already experienced deterioration of some part of their digital print collections [1]. Previous experimental research has established a clear connection between ozone and nitrogen dioxide to each of those forms of decay [2,3]. Ozone has been specifically shown to cause significant fade and delamination/cracking and nitrogen dioxide to induce yellowing and bleed. An understanding of effective methods to mitigate such damage will be critical to the survival of these objects.

Deterioration due to pollutants occurs through chemical reactions, which may potentially be slowed by lower temperature. The specific experiments in this project will define the overall effectiveness of lower temperature in slowing attack by atmospheric ozone and nitrogen dioxide. The problem of pollutant damage to digital prints is a serious issue for museums, archives, and libraries at all levels (national, state, and local). The audience for this project is anyone involved with the care of cultural heritage collections that contain these materials.

Methods

The experiments were based on the well-established Arrhenius method, outlined in ISO *18924 Imaging materials -- Test method for Arrhenius-type predictions* [4]. The Arrhenius method has already successfully been used to determine the thermal aging rates of other cultural property types including color photographic dyes as well as photographic film supports. In this case the additional factor of increased pollutant concentration was added.

Test Target

The test target consisted of a color step wedge containing ten levels of cyan, magenta, yellow, and black (CMYK) and a minimum density (D_{min}) patch. The targets were created using Adobe InDesign and converted to PDF for printing. The target also included vertical and horizontal CMYK lines to monitor for colorant bleed as well as black text on white background and white text on black background text targets with Times New Roman type ranging from 4 – 8 point size to monitor for loss in text readability.

Print Types

The test samples were two different micro-porous type photo papers printed with two different dye-based inkjet printers (including dye black). These prints were selected because they were found to be especially sensitive to pollutant-induced fade, yellowing, bleed, and delamination/cracking in previous IPI experiments. In addition, a printing paper commonly used in electrophotographic (EP) digital presses, and previously shown to be sensitive to yellowing was included. Highly sensitive examples act as a sort of miner's canary and will provide the most conservative results and recommendations. After printing, all samples were allowed to dry for one week in the dark in a climate-controlled room at 21°C and 50% RH before testing. Tables 1 and 2 show the printer-paper combinations selected for the tests.

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Table 1: Test samples for ozone

Printer	Coating	Substrate
Dye inkjet 1	Microporous	RC paper
Dye inkjet 2	Microporous	RC paper

Table 2: Test samples for nitrogen dioxide

Printer	Coating	Substrate
Dye inkjet 1	Microporous	RC paper
Dry-toner EP	Coated glossy	Plain paper

Sample Measurement

Measurements of the color step wedge target were made using a Gretag Spectrolino/Spectroscan spectrophotometer for red, green, blue, and visual ISO Status A density values both pre- and post-pollutant exposure. Measurement of line width was made using an ImageXpert image analysis system for the samples exposed to nitrogen dioxide. Cracking and delamination were assessed visually for the samples exposed to ozone.

Experimental

The ozone and nitrogen dioxide test chambers were custom built by Codori Enterprises. The ozone was produced by means of a UV lamp, while the nitrogen dioxide was provided by a gas tank (2% NO_2 in air) purchased from Airgas. The gas concentration in each chamber was monitored during the extent of the tests and kept within the target values ($\pm$ 0.25 ppm). The samples (in duplicate) were exposed to pollutants (ozone or nitrogen dioxide) at a series of increasing temperatures (25°C, 30°C, 35°C, 40°C, and 45°C) at a relative humidity (RH) of 50% for each. The concentration of pollutant was held at one-part-per-million for ozone or five-part-per-million for nitrogen dioxide. The nitrogen dioxide tests were originally planned to be conducted at 1 ppm; however, after the first temperature trial it was discovered that this concentration was too low and that the time intervals would subsequently need to be increased beyond the project's finish date. For this reason the nitrogen dioxide concentration was increased to 5 ppm.

Test samples were exposed free hanging inside the chamber and were removed at intervals of 1, 2, 4, 7, 10, 14, 21 days for ozone and 14, 21, 28, 35, 42, 49, and 56 days for nitrogen dioxide. Separate samples were used for each incubation temperature and time period.

For the ozone exposures, the incubation times required to reach a 30% fade in the cyan, magenta, yellow and black patches from initial densities of 1.0 for each temperature were determined. The incubation time to reach a blue density gain of 0.05 in the unprinted white areas of the prints (D_{min}) was determined for each temperature for the nitrogen dioxide tests. Using the standardized Arrhenius prediction methodology, the logarithm of the incubation times to reach the 30% fade (or 0.05 D_{min} gain) for each temperature were then plotted against the reciprocal of the absolute test temperatures and the predicted time to reach 30% fade (or 0.05 D_{min} gain) at room and various lower temperatures extrapolated. These lower temperatures represented different levels of reduced-temperature storage commonly used in museums – cool and cold. The low-temperature predictions were then compared to room temperature conditions and the potential benefits of reduced-temperature storage determined. Note that temperatures at or below freezing were not included, since it is not known what physical stresses freezing and thawing might have on the objects. The image analysis measurements of line width and blur were used to predict the potential for lower storage temperatures to minimize pollutant-induced colorant bleed. Visual assessments of cracking and delamination were used to predict the potential for lower storage temperatures to minimize or prevent physical failure of the imaging layers.

Extrapolation of test results to real-life conditions

It is difficult to translate high temperature and high pollutant concentration test data into real-life terms that can be used to confidently assess how significant or insignificant any changes in storage temperatures will be. This is for two reasons. The first is that it is always questionable to assume reciprocity between short–term exposures at high temperature/gas concentrations and long-term exposures in actual collection environments; however, there is no other known methodology other than actually waiting many years to find out when pollution damage will occur. At which point the damage would be done anyway. The point of a prediction is to prevent the damage, so assuming reciprocity between test and real-life experience is, unfortunately, the only choice we currently have. Secondly, any extrapolation to real-life storage environments also assumes that we know what the average pollutant levels will actually be over time. This is not likely as different geographic locations, building designs, air handling systems, etc. will result in different and varying indoor levels of pollutants. It is necessary here to only select a reasonable value as the stand in for the actual values.

While there have been some studies that have looked at pollutant levels in cultural institutions [5], none have resulted in a standardized value that can be used for predicting the long-term behavior of collection objects. This is because, as stated above, levels are highly variable and dependent on a large number of factors that can result in an average daily pollutant level of 1 parts per billion (ppb) in one institution and 100 ppb in another (or even in different areas within the same institution). For this reason, we have chosen 10 ppb as our assumed real-life conditions for ozone and 50 ppb for nitrogen dioxide. These are both $1/100^{th}$ of the test concentrations. Still, no matter which assumed actual-use concentration is used, it will be applied equally to all predictions, and so the ratios of cold storage to room conditions will remain the same, and the relative improvement in pollution mitigation will be accurately described. If an institution knows the actual average daily ppb of ozone or nitrogen dioxide in its storage and exhibition areas, it can recalculate the values described below by dividing the predictions by their actual ppb of ozone or nitrogen dioxide and then multiplying by 10 for ozone or 50 for nitrogen dioxide.

Results

A set of controls for each material was incubated at 45°C (the highest test temperature) for 56 days (the longest test period) in a sealed bag to prevent pollution exposure to ensure that any fade or yellowing of the pollutant exposed samples would be due to the pollutants and not to heat. None of the control samples showed noticeable change, establishing that all changes in the exposed samples are due solely to the pollutants.

The times to endpoint, 30% fade for the ozone exposed samples and 0.05 blue density gain for the nitrogen dioxide exposed samples, for each temperature were used to extrapolate time to endpoint at room (21°C) and various cool-to-cold temperatures (15°C, 10°C, 5°C). The color with the shortest time to endpoint was used as the limiting factor for the ozone tests.

For both samples it was the yellow colorant that faded to 30% loss the fastest during ozone exposure. These values were converted into years and are reported in table 3 below. The correlation coefficient (r^2) for Dye Inkjet 1 was 0.87 and for Dye inkjet 2 was 0.97.

Table 3: Year Predictions to 30% yellow colorant loss - Ozone

	21°C	15°C	10°C	5°C
Dye Inkjet 1	2.6	3.2	4.0	4.9
Dye Inkjet 2	2.6	3.5	4.6	6.0

There is a 1.9x increase in print life for Dye Inkjet 1 when it is moved from room conditions to 5°C cold storage. There is a 2.3x improvement in print life when Dye Inkjet 2 is placed in 5°C cold storage. This means that the life of these dye inkjet prints can be extended approximately 100% by moving them to cold storage. Given the limited life of the materials at room conditions, the extension, even if short, may be worth it.

Table 4: Year Predictions to 0.05 blue density gain – Nitrogen dioxide

	21°C	15°C	10°C	5°C
Dye Inkjet 1	17	27	41	62
Dry-toner EP	9	21	42	87

The effect of temperature on deterioration rates is greater for nitrogen dioxide than for ozone (Table 4). There is a 3.6x increase in time to yellowing for Dye Inkjet 1 when it is moved from room conditions to 5°C cold storage. There is a 9.7x improvement in life when the Dry-toner Electrophotographic Print is placed in 5°C cold storage. These increases are significantly higher than those for ozone-induced decay. The correlation coefficient (r^2) for Dye Inkjet 1 was 0.87 and for Dry-Toner EP was 0.84.

It is important though to put the ozone and nitrogen dioxide data into some context. The samples in these tests were freely exposed to the air in the test chamber as opposed to being housed in enclosures. The airflow was also high to ensure equal distribution of gas throughout the chamber. Additionally, these samples were known to be highly sensitive to pollutants. Prints in collections may contain especially sensitive prints but will likely not leave them constantly exposed to air. For this reason, these numbers are extremely conservative. Prints in collections will likely last much longer, but how much longer is not exactly known. Periodic monitoring of print condition will be critical to catching damage before it occurs.

The test method also called for quantified assessment of colorant bleed. Before and after pollutant exposure, measurements were made; however, the data could not be used because the numerical trends did not match the visual assessments. It is believed that this was due in part to the way in which the image analysis software read the changes in line morphology. If the line spread was uniformly dark then the technique worked; however, when the bleed was of very low density (which it usually was) the image analysis system could not accurately measure the change, as it was below the reading threshold. Therefore, additional study of dye bleed is needed before it can be analyzed instrumentally with a high degree of confidence. Visual assessments of bleed are included below.

Summary of Visual Assessments

The samples were assessed visually for three forms of decay: colorant bleed, surface cracking, and text readability.

For bleed, a single observer used a 50x stereo microscope to look for intact dot shapes. If the dot edges were no longer clear then the sample was considered to have bled. The bleed behavior within the samples appeared somewhat erratic across the test temperatures showing no clear trend (see Table 5). It is not known why this occurred; however, that nitrogen dioxide can induce bleed was once again confirmed. Note that the 40°C data is not included because that test was only run to 35 days as opposed to 56 days like the others, but no samples bled at those conditions. This property deserves further study, though the first step will be to develop precise methods for measuring the phenomenon.

Table 5: Nitrogen Dioxide-Induced Bleed

Temperature	Days to first bleed
25°C	42
30°C	28
35°C	42
45°C	No bleed detected

Cracking was evaluated visually using a 50x stereo microscope after a 90° flexing of one corner of the print by hand. A control was incubated in a sealed bag to prevent pollution exposure at 45°C (the highest test temperature) for 56 days to ensure that any cracking of the pollution exposed samples would be due to the pollutants and not to heat. The Dye Inkjet 1 samples did not crack at either room conditions or after 56 days at 45°C with no pollutant exposure. The ozone exposed Dye Inkjet 1 samples showed a trend indicating that reduced storage temperature will slow the rate of physical deterioration of some inkjet coatings. Table 6 below shows the number of days until cracking is first seen for Dye Inkjet 1. The Dye Inkjet 2 samples cracked even without pollutant exposure. This reaffirmed the sensitivity of some materials to cracking even without exposure to environmental stresses.

Table 6: Ozone-induced Cracking for Dye Inkjet 1

Temperature	Days to first cracking
25°C	No cracking
30°C	No cracking
35°C	21 days
40°C	10 days
45°C	4 days

It is likely that both colorant bleed and cracking/delamination of ink receiver layers in inkjet prints will one day be problematic for collecting institutions. It is not clear whether these adverse effects will occur before or after the fade and yellowing detected and reported on in this project. Existing methodologies do not exist to examine and predict the time to failure for these parameters. Development of such methods as well as in-depth studies of these

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problems will ultimately be highly beneficial to cultural heritage institutions that have or will add these materials to their collections.

The fade, yellowing, or bleeding of the samples in no case impeded the readability of the text samples.

Conclusions

From the data the following conclusions can be made:

- Reduction of storage temperature should have a 1.9x-2.3x impact on the rate of color fade by ozone
- Reduction of storage temperature should have a 3.6x-9.7x impact on the rate of print yellowing by nitrogen dioxide
- Reduction of storage temperature should reduce the rate of physical deterioration for some inkjet coatings by ozone
- More work needs to be done to develop better methods and measures for line bleed and cracking

Reducing airflow over the surfaces of inkjet prints is also known to decrease the rates of pollutant-induced fade [6]. It may be that protective storage enclosures and framing materials can also significantly mitigate damage and possibly to a greater degree than lower temperature storage. Examination of these issues is currently underway at IPI and will be published at a future date. After completion of that work, institutions that collect these materials will be able to decide which approach works best for them.

Additionally, it is believed that this is the first use of Arrhenius incubations simultaneous with elevated pollutant levels to model the interactions between temperature and pollutants on collection objects. Because the approach proved feasible, it is possible that this method may also be used to more fully understand the effects of temperature on deterioration rates for many other pollutant sensitive cultural materials.

Acknowledgements

The authors would like to acknowledge the Institute of Museum and Library Services for their support of the project.

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Daniel M. Burge, Senior Research Scientist, has been a full-time member of the Image Permanence Institute (IPI) staff for over 20 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. Since 2007, he has been leading IPI's investigations into digital print stability and developing recommendations for the use, storage and display of these materials in cultural heritage institutions.