

Effects of Pollutant Vapors on Image Permanence

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Abstract

In the complex situation of a real archives or library, the contribution that air pollution makes to the fading of images is not easy to measure or observe. The effects are subtle and occur slowly, blending in with the action of light, heat, humidity, and the inherent stability (or instability) of each individual type of photograph. We are not able to say what percentage of the fading of a color print is due to air pollution. We know it causes some fading, but the thermal fading characteristics of color materials are probably the major factors.

Because of the chemical nature of images (including in that term products commonly used in still photography, cinema, microforms, and color hard copy output from computers), it is a reasonable expectation that airborne pollutants would act to destroy them. Color images are usually comprised of organic dyes, which depend on complex structural arrangements within the dye molecule to absorb light. Disturb that precise structure at the right spot, and a yellow dye becomes colorless, or a cyan dye becomes a weak yellow. Black-and-white photographic images are comprised of metallic silver, which must first become oxidized before it can degrade; but, with silver, the response to atmospheric pollutants is complex and depends on more than just the presence of an oxidant. The subtle interactions of the component gases of air pollution are an intriguing problem and were a major focus of this research.

Introduction

This study investigates the threat posed by the ingress of polluted air into library and archival storage environments. The study attempted to, not only identify those photographic materials that were at risk by exposure to pollutants in the environment, but also to evaluate the possible mitigating effects offered by typical storage enclosures. This three year research project was funded by the National Endowment for the Humanities, Division of Preservation and Access, the New York State Program for the Conservation and Preservation of Library Research Materials and the Rochester Institute of Technology.

Background

Ozone and Objects Indoors

In recent years, considerable investigation has been done on the effects of atmospheric ozone on modern and traditional artists' pigments.^{1,2,3,4,5} Ozone is a concern because it is such

a strong oxidizing agent, especially reactive toward the double bonds in organic dyes, which often are part of the key chromophoric groups on dye molecules. The research (much of which was done at an O₃ concentration of 0.40 ppm, the approximate peak outdoor ozone levels in a polluted area) found that colorants vary in susceptibility, and that some are quite sensitive. A very important determinant of susceptibility to attack was not only the dye structure itself but also whether or not the dye was protected by a binder material, for example, gum arabic or linseed oil.

Other related research (much of which resulted from a broad initiative on environmental effects conducted by the Getty Conservation Institute) attempted to both directly measure and predict from a model the ozone concentrations that would actually be encountered inside southern California museums.^{6,7,8} These studies and others outside the conservation field have found that indoor ozone concentrations can be as much as 70% of outdoor concentrations and that relatively simple models can predict indoor ozone concentrations.

Leaving aside for the moment any air purification system or internal sources of ozone such as copiers, the amount of ozone in indoor air will be determined by: (1) outside levels, (2) the rate at which outdoor air is admitted to the indoor environment, and (3) the area and nature of surfaces indoors. Ozone is decomposed by reaction with any surface (floors, walls, etc.) so the ratio of indoor surfaces to the volume of air circulating through the space becomes important.

Items freely exposed to indoor air in a building could accumulate very large ozone doses over time. Most images, however, are encased in boxes or other forms of storage enclosure. Based on this model of the behavior of a building, there are two reasons why ozone damage would be mitigated inside a storage box. First, the air exchange rate between the inside and the outside of the box is normally low, so the total accumulated ozone exposure inside would be less than outside. Second, there is also the chance that ozone that does enter the box would react with the walls and not the contents.

Sulfur Dioxide and Nitrogen Oxides Indoors

Many of the studies of these acid gases have been devoted to the effects of acid rain on outdoor stone and metal objects.^{9,10,11,12,13} However, levels of both of these oxides are relatively high in museums, raising concern about books, paper, and works of fine art. Hackney made measurements of sulfur dioxide at the National Gallery of Ireland, the Victoria and Albert Museum, and the Tate Gallery.¹⁴

Nitrogen dioxide levels were also measured at the Tate Gallery. Hackney found significant levels of nitrogen dioxide in unconditioned galleries, which correlated well with the sulfur dioxide measurements. Levels of SO_2 were also significant in all three museums and varied irregularly with weather conditions. Levels fell rapidly after a rain, although winter weather brought levels up. Grosjean and Hisham similarly found that indoor levels of sulfur dioxide and nitrogen dioxide in southern California museums were a significant proportion of the outdoor levels.^{15,16}

Limited studies have been performed on the effects of air pollutants on cellulose, cotton, and paper, but these experiments have concentrated on the acid gases, sulfur dioxide and nitrogen dioxide.^{17,18,19,20} Of particular significance to accelerated aging research have been studies by Havermans on the influences of sulfur dioxide and nitrogen oxides on accelerated aging of paper.²¹ Havermans showed that in the presence of sulfur and nitrogen oxides, acid hydrolysis of the paper was the dominant deterioration mechanism. Buffered paper tended to perform much better than nonbuffered paper although measurable amounts of nitrates and sulfates were found only in buffered paper.

Enclosures and Air Pollution

Enclosures are a very important aspect of storing photographs. Collection managers cannot change the nature of photographic materials to make them fade and stain more slowly or to be more physically robust. Nevertheless, among the things that collection managers *can* control are handling practices, environmental conditions, and the choice of storage enclosures. Although temperature and RH are the primary factors in the survival of images, enclosures and handling practices are next in importance. Whether for still photography or motion pictures, enclosures add to the useful life of collections by providing physical protection, by buffering rapid environmental changes, and by being inert, harmless containers during years of storage.

There is no one ideal enclosure design for a particular type of photograph; the handling patterns, storage environment, use environment, and economic circumstances of every collection are different. Enclosures are always part of a multilevel system where each object has an individual enclosure, which in turn is matched to a box or folder, which finally is placed in a third level consisting of shelving or cabinets. Ease and safety in handling and the ability to integrate with the other levels should be designed into the overall system from the beginning.

Test Apparatus

The specially designed incubation chambers used in this project are one of a kind and are designed to withstand the rigors of constant exposure to varying levels of corrosive gases and extremes of temperature and humidity. These chambers have a large capacity (21 cubic feet) and are designed to maintain constant temperature, humidity, and gas concentration while providing recirculation and adequate mixing of the test atmosphere. Figure 1 shows the inside of one of the incubation chambers. All wetted

components of the chamber are constructed of Teflon, polyvinylidene fluoride (PVDF), or stainless steel. The chamber is depicted without the removable rear panel to show the circulation fans, heating coil, gas and humidity inlets, sample outlet, and cooling and dehumidification coils. Test conditions are maintained from a desktop PC that is networked with two ANAFAZE 8 loop PID controllers that allow operator input and monitoring of PID function.

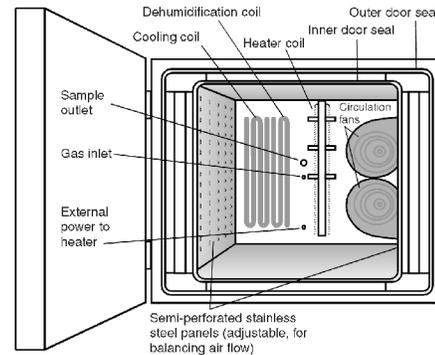


Figure 1. Interior of incubation chamber.

The test gases are injected into the chambers from large gas cylinders. NO_2 , SO_2 , and H_2S are supplied on demand via the controllers and dedicated Teflon solenoid valves for each gas. The ozone injection system is outlined in Figure 3. Ozone can be regulated by air volume and variable output from the PID controller. Ozone is generated on demand using a high-voltage discharge ozone generator (Figures 2 and 3).

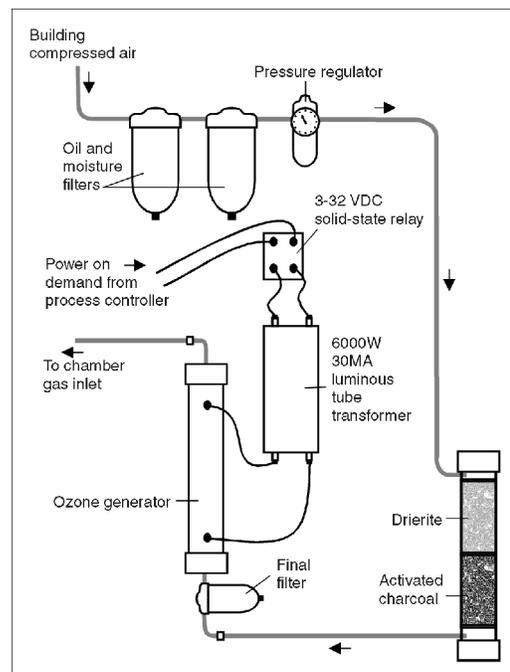


Figure 2. Schematic drawing of ozone injection system used in project.

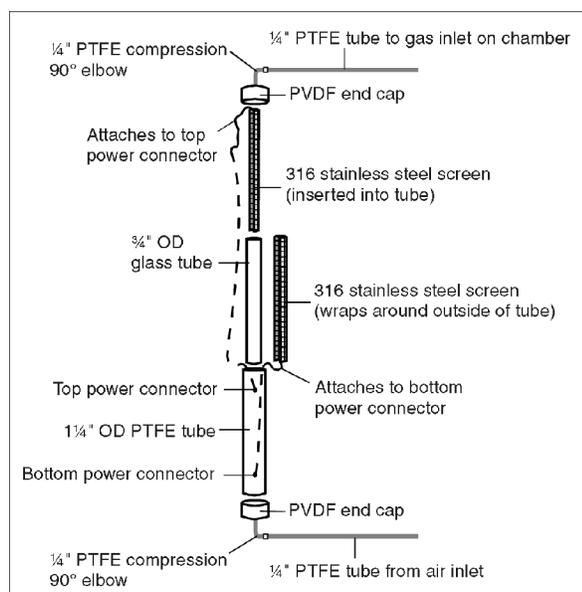


Figure 3. Exploded view of ozone generator.

Monitoring of the chamber atmospheres is accomplished by withdrawing a sample from the chamber outlet and analyzing it with the appropriate gas analyzer. Monitoring equipment (all manufactured by Monitor Labs) includes the following:

Ozone	Model 8810 U.V. Photometric Ozone Analyzer
Nitrogen dioxide	Model 8840 Chemiluminescent Nitrogen Oxides Analyzer
Sulfur dioxide	Model 8850 Fluorescent SO ₂ Analyzer
Hydrogen sulfide	Model 8850 Fluorescent SO ₂ Analyzer equipped with Model 8770 H ₂ S Converter

The monitoring equipment is mounted in an instrumentation rack placed between the two chambers and is calibrated by a Monitor Labs 8500 calibrator. All of the equipment is interfaced with the controllers and subsequently with the computer.

Overview of Test Design

This study was divided into three individual phases. In many cases, the phases overlapped each other and materials used in one phase were also included in one or both of the other phases.

Phase I: Study of Pure Oxidizing Gases at Ambient Conditions

In this phase, pure oxidants were run at low concentrations for an extended time period. Only the pollutants ozone and nitrogen dioxide were studied at a 0.1 ppm (100 parts per billion) concentration. The tests were run for one year at 25°C, 50% RH. To separate the effects

of the pollutants from normal aging, all samples were also incubated for the same time period in a humidity-controlled chamber at 25°C, 50% RH without any pollutant gases present.

A wide and broadly representative variety of common photographic materials were tested. A listing of the photographic materials included is shown here:

1. Negative motion picture film (Kodak 5272).
2. Positive motion picture film (Kodak 5384).
3. Conventional chromogenic color print (Ektacolor).
4. Diazo microfilm (Xidex).
5. Source document microfilm (Fuji HR2).
6. Source document microfilm, polysulfide treated (Fuji HR2).
7. Direct duplicating microfilm (Kodak 2468).
8. Colloidal silver film (detector used in the ANSI Photographic Activity Test).
9. Ilfochrome color micrographic film (Cibachrome CMM).
10. Resin-coated black-and-white paper print (Ilford Polycontrast).
11. Fiber-base black-and-white paper print (Kodak Polyfiber).
12. Thermal dye diffusion print (Kodak Ektatherm).
13. Electrophotographic color print (Canon Color Copier).
14. Color ink-jet print (Hewlett Packard Paint Jet).

Specimens were removed from the pollution chamber every four months, measured for density, and then replaced in the chamber. Samples were suspended in the chamber and freely exposed to the chamber atmosphere. This approach simplified the specimen preparation, requiring only two specimens of each material type per chamber.

All black-and-white samples had a step wedge of seven density blocks ranging from D_{min} to D_{max}, a range of approximately 0.05 to 2.0 blue density, including 1.0 above D_{min}. Color materials had three sets of color patches (cyan, magenta, and yellow dyes), each color having four density steps.

Status A blue densities were measured on the seven black-and-white (or neutral tone) materials, while blue, green, and red densities were measured on the seven color images. Density change and visual inspection for silver mirroring or redox blemish formation were the only criteria for this phase.

Phase II: Study of Synergistic Effects

Earlier research showed that filamentary silver is relatively resistant to the effects of pure ozone, nitrogen dioxide, and sulfur dioxide. However, there are numerous practical examples of silver images showing mirroring and/or fading when exposed to an environment having elevated pollutant levels. It is now believed that this is the result of the interaction of two or more pollutants. It was considered important to determine if this synergistic effect takes place under more practical conditions, particularly in the case of NO₂ and H₂S.

Two specimens each of the same materials studied in Phase I were studied in Phase II, using the same density

measurements. Densities were determined at intervals of two or four months, resulting in three sets of determinations for the six-month studies and three sets for the one-year study. After each measurement the specimens were returned to the chamber for further incubation.

Phase III: Study of Enclosures

Under practical storage conditions, control of pollutants is frequently impossible because of the expense of installing and operating the necessary equipment. However, photographic materials are usually placed in enclosures such as sleeves or boxes. It has been shown that these enclosures will mitigate the effect of pollutants. The unanswered questions were by how much, and what types of enclosures are to be preferred with each type of photographic material. These practical considerations were the primary focus of Phase III.

Four photographic materials were chosen for this study:

1. Thermal dye diffusion print (Kodak Ektatherm)
2. Positive motion picture film (Kodak 5384).
3. Direct duplicating microfilm (Kodak 2468).
4. Resin-coated black-and-white paper print. (Ilford Polycontrast)
5. The commonly available enclosures studied were:
6. Buffered paper envelope (Light Impressions Straight Cut Envelopes made from 80-lb. Apollo Paper™).
7. Nonbuffered paper envelope (Light Impressions Straight Cut Envelopes made from 80-lb. Renaissance Paper™).
8. Polyethylene sleeve (Print File 35-1M Polyethylene Sleeve).
9. Polypropylene sleeve (Light Impressions 3-mil FoldLock™ Sleeve).
10. Polyester sleeve (Light Impressions 3-mil Mylar D sleeve).
11. Metal-edge box made from lignin-free buffered cardboard (Conservation Resources Lig-free Type I 35mm Archival Microfilm Boxes).
12. Polyester sleeve inside a metal-edge box (Light Impressions 3-mil Mylar D sleeve).
13. Buffered paper envelope inside a metal-edge box (Light Impressions Straight Cut Envelopes made from 80-lb. Apollo Paper™).

The first configuration in this phase was designed to mimic sleeved negatives or prints that were placed vertically in a drawer. In real life, photographs in this type of configuration can be placed loosely in the drawer or be packed tightly together. In this test, in order to limit the number of samples required, a normal filing cabinet drawer was not used. Samples were instead prepared to fit into a collapsible 3½" computer floppy disk storage box. This box allowed the three samples of each material to be placed in a separate compartment in the box. Placing three samples in each compartment caused a slight pressure to be placed on the samples and restricted air flow into the package.

Sleeved prints and negatives are also stored

horizontally in boxes where the box itself could act as an impediment to attack from pollutants in the atmosphere. The second configuration consisted of one sleeved sample placed in a roll microfilm storage box (Figure 4). These boxes are not well-sealed. Therefore, it was presumed that they offered little protection from ingress of the outside atmosphere, but the extent or lack of benefit was unknown. Three individual boxes were required for each sleeve/sample material combination. The boxed samples were placed on a perforated stainless steel rack at the bottom of the chamber (Figure 5).

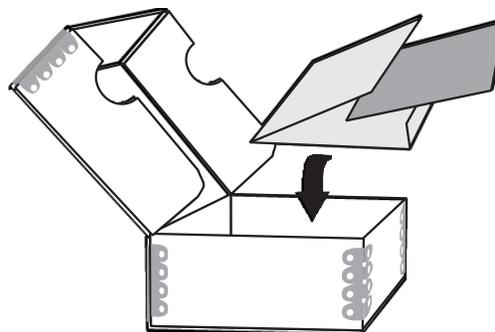


Figure 4. Single sleeved sample in roll microfilm storage box.



Figure 5. Arrangement of boxed samples in incubation chamber. Spacing boxes a half-inch apart on raised rack permitted free flow of air around samples.

Another box configuration included in this phase was intended to explore the commonly seen stack of unsleeved negatives or prints in a box. In this configuration, five separate samples of each of the four materials were stacked on top of each other and placed in the same roll microfilm storage box as above (Figure 6). In a normal storage situation there would be many more objects stacked together—typically whatever the box would hold. This represented a problem, in that the more objects there are in the box, the more weight and subsequent pressure there is placed on objects in the stack. Creating large stacks of samples in each box for testing was impractical, so this configuration included only five samples, and only the top, middle, and bottom samples were measured.

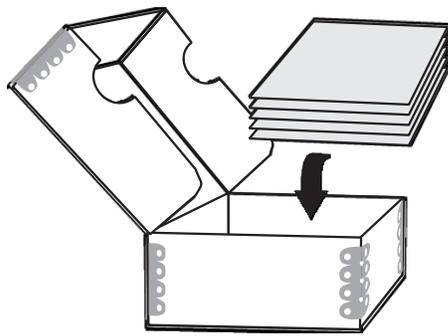


Figure 6. Stack of five sample sheets without sleeves in roll microfilm storage box.

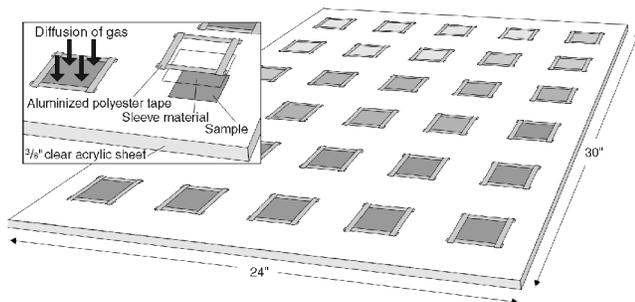


Figure 7. Sleeve permeability test.

The *sleeve permeability test* was devised to evaluate a sleeve's diffusion resistance or pollutant-trapping capacity (see Figure 7).

In this test, 2" x 2" pieces of thermal print material and Kodak 2468 direct duplicating film were arranged on a 24" x 30" sheet of clear polycarbonate. Each sample was then covered by a 2 1/2" x 2 1/2" piece of one of the five sleeve materials. There were three separate samples of each sleeve material for both the thermal print and the 2468 film. The sleeve materials were affixed to the sheet with aluminized polyester tape. The samples were thus completely covered and sealed from the environment. The pollutant gases could affect the samples only by diffusing through the plastic or paper sleeve material.

All samples in Phase III were made as one uniform density patch of approximately 1.0 density. The single field of 1.0 density was used to track edge effects, as the gases were expected to penetrate and cause fading only at the edges of the samples inside the sleeves. Color patches of only cyan dye, with a density of 1.0 above D_{min} , were used for the two color materials. The cyan dye had previously been shown to be very sensitive to oxidants for both the movie-print film and the thermal print material. A single patch with a blue density of 1.0 above D_{min} was used for the two black-and-white samples. Measurements were taken at five different positions on each sample before incubation. A template of clear polyester was used to ensure measurement of the same areas on each sample. Since removing the specimens from the enclosure would disturb the gaseous distribution, it was necessary to use separate

specimens for each time period.

The duration of each test was eight weeks, and there were three sample time periods: two and one half weeks, five weeks, and eight weeks. Since the primary purpose of this phase was to determine the relative degree of improvement afforded by the various enclosures, tests were conducted at 5 ppm of the various pollutants at 25°C, 50% RH. It was recognized that these conditions were more severe than those found in practice, but longer incubation times at lower concentrations were not possible within the time allowed.

How Incubation Conditions Relate to Real Life

The test conditions used in this study were planned with different goals in mind. The short-term, high-concentration tests were meant to acquire as much data as possible in a short-term experiment. Relying on data from previous IPI research, we were confident that measurable density change was possible at the 5-ppm gas concentration in the proposed time frame. In the long-term tests, the purpose was to simulate as closely as possible real-life exposures. Tables 1 and 2 show a general relationship between real-life concentrations of pollutant gases and the project test conditions. Table 1 compares the two conditions used in the current study and shows how long it would take at real-life conditions (assuming an average level of 0.025 ppm) to attain the same exposure received in both of the test conditions. The .025 ppm gas concentration represents a typical average concentration that might be found in a storage space that has no filtering or HVAC control. The comparison is hypothetical and based on ozone only; it assumes a linearity of concentration versus time and does not consider the variability of the test materials.

According to Table 1, the short-term tests in this project would be equal to approximately 33 years at room conditions. The long-term tests would require about four years at ambient indoor conditions to reach the test exposure levels.

Table 1: Relationships between test atmospheres and exposure times

Ozone Concentration	Elapsed Time (days)	Total Exposure (ppm hours)	Equivalent Exposure at .025 ppm (years)
0.05 ppm	6000	7200	33
0.10 ppm*	3000	7200	33
0.50 ppm	600	7200	33
1 ppm	300	7200	33
2 ppm	150	7200	33
5 ppm*	60	7200	33
10 ppm	30	7200	33

* Concentrations used in current study

Table 2: Comparison of the two test atmospheres in the current study

Ozone Concentration	Elapsed Time (days)	Total Exposure (ppm hours)	Equivalent Exposure at 0.025 ppm (years)
0.10 ppm	365 (3000 days = 5 ppm exposure)	876	4
5 ppm	60 (7.3 days = 365 days at 0.10 ppm)	7200	33

Results

Table 3 shows an overview of the sensitivity of each sample material used in the project to each of the incubation conditions that they were exposed to. Only four sample materials were used in the short-term experiments, so data is

seen for only those four materials in incubations H through M. The legend for the table lists the test atmosphere and duration for each incubation and provides a key for the various levels of attack and any other manifestations of the exposure.

The table shows that the filamentary silver film materials were only slightly affected by these gaseous atmospheres. In the real world, examples of filamentary silver fading are everywhere, but this project's use of plausible real-life storage atmospheres failed to produce much effect in the time allowed. The mixed-gas incubations sought to mimic the oxidation/reduction cycle that is known to be the mechanism of silver image fading, but they did not reproduce real-life fading. The one variable that was not equivalent to real life was time. As noted above, the low-concentration incubations would only approximate four or five years' exposure to real-life conditions. Nevertheless, silver mirroring and redox blemish formation in only a year's time at room temperatures and ambient gas concentrations have been observed in the IPI lab.

Table 3: Relative sensitivity of the sample materials to test conditions.

Material	A	B	C	D	E	F	G	H	I	J	K	L	M	N
5272	0	0	0	0	0	0	0							0
5384	0	0	0	0	0	0	0	1-BS/CBS	0	0BS/CBS	1+BS/CBS	0BS/CBS	0	0
Ektacolor	0BS	2-	0BS	0BS	0	0BS	0BS							0
Xidex	2-BS	2-	1-BS	2-BS	2-	2-BS	2-BS							0
HR2	0	0	0	0	0	0	0							0
HR2 Toned	0	0	0	0	0	0	0							0
2468	RB	0	0	RB	0	0	0	RB	0	0	0	0	0	0
Colloidal silver	2+	2-	2+	1+	1-	1+	1+							0
CMM	0	0	0	0	0	0	0							0
B&W RC	0BS/M	0	0BS	0BS/M	0	0BS	0BS	0M/BS	M/BS	0BS	0BS	0BS	0	0
B&W Fiberbased	0BS	0	0BS	0BS	0	0BS	0BS							0
Ektatherm	4-BS/CBS	4-	3-BS/CBS	4-BS/CBS	4-	2-BS/CBS	2-BS/CBS	4-BS/CBS	4-	4-BS/CBS	4-BS/CBS	4-BS/CBS	3-BS/CBS	0
Electro-photographic	0	0	0	0	0	0	0							0
Ink jet	1-BS	3-	2-BS	2-BS	3-	1-BS	1-BS							0

LEGEND FOR GAS ATMOSPHERES

	Gas Concentration	Test Duration	Level of Attack
A	0.1 ppm NO ₂	1 year	0 = No density loss (-) or gain (+)
B	0.1 ppm O ₃	1 year	1 = Slight density loss (-) or gain (+)
C	0.1 ppm NO ₂ and 0.05 ppm H ₂ S	1 year	2 = Moderate density loss (-) or gain (+)
D	0.1 ppm O ₃ and 0.1 ppm NO ₂	6 months	3 = Severe density loss (-) or gain (+)
E	0.1 ppm O ₃ and 0.05 ppm SO ₂	6 months	4 = Very severe density loss (-) or gain (+)
F	0.1 ppm NO ₂ and 0.05 ppm SO ₂	6 months	
G	0.1 ppm NO ₂ , 0.1 ppm O ₃ , and 0.05 ppm H ₂ S	6 months	
H	5 ppm NO ₂	8 weeks	RB = Redox blemishes
I	5 ppm O ₃	8 weeks	M = Mirroring
J	5 ppm NO ₂ and 5 ppm O ₃	8 weeks	DY = Dmin yellowing
K	5 ppm NO ₂ and 5 ppm H ₂ S	8 weeks	BS = Base stain
L	5 ppm NO ₂ , 5 ppm O ₃ , and 5 ppm H ₂ S	8 weeks	CBS = Color balance shift
M	5 ppm O ₃ and 5 ppm H ₂ S	8 weeks	
N	Control (no gas)	1 year	

Conclusions

1. Although some of the most sensitive imaging materials

in Phase I did display a great deal of dye fading, most of the popular color and silver-based photographic output materials were not affected by the pure oxidizing

atmospheres they were exposed to. The total exposure represented by these incubations would only be equivalent to about four years in a fairly polluted urban setting with no HVAC system controlling the input air of a storage space. Using higher concentrations of pollutant gas has proven that many of the commonly used modern photographic materials are sensitive to oxidative attack. This is especially true of chromogenic color materials whose dyes fade rapidly in the presence of high levels of oxidants; in real life, however, the time required for equivalent pollutant dosage would require several decades at ambient levels. In this time frame the inherent sensitivity of these dyes to heat would have caused them to fade a great deal more than the oxidant gases. If the materials were stored in a cool/cold environment, the dye fading would be much reduced, but the action of any oxidants would be diminished by an equal amount as their mechanisms are temperature-dependent also. It can be concluded that, although chromogenic color materials are sensitive to oxidant gases, they are more sensitive to high temperature and are not overly threatened by typical ambient concentrations of pollutant gases in the storage environment.

2. Silver-based imaging materials, as has been noted in previous research, are not highly sensitive to pure oxidant gases. Ionic silver is formed by oxidation, but, if no reducing agent is present, the oxidation/reduction cycle of silver image deterioration can not move forward. There is little doubt that high levels of oxidant gases combined with background levels of acidic/reducing gases in storage atmospheres will attack image silver over time. Therefore, supplementary HVAC and filtering is recommended for these collections. As mentioned above, cool/cold storage will further mitigate deterioration of silver images.
3. Phase II of this project explored the synergistic effects of gas combinations. Its primary aim was to recreate the oxidation/reduction deterioration cycle of silver images. While there were occurrences of some forms of image degradation in these experiments, the most interesting finding is the fact that interactions between the constituent gases diminished the effectiveness of gas combinations. Reduced dye fading of the color materials was noted in all of the gas mixtures. This would seem to indicate that gases in the atmosphere act upon each other to reduce their individual concentrations and lessen their effects, but this study did not evaluate the long-term ramifications of absorbed gases and their role in future deterioration.
4. As seen in Phase III, enclosures for photographic materials offer physical protection against handling damage and add extra support to delicate objects, but their advantages in stopping the diffusion of atmospheric gases is minimal. Enclosures made of multiple layers (an object in a sleeve, in a box, in a drawer), will certainly slow down the ingress of polluted air, but the inside and outside atmospheres will equilibrate relatively rapidly. Enclosures made of plastic can protect objects to the extent that they are in

intimate contact with them, while paper enclosures will not stop the diffusion of gas into the enclosure package. Encapsulation in plastic offers almost complete protection against the atmosphere but also traps any deterioration by-products in the enclosure, thereby accelerating any autocatalytic forms of deterioration. Buffered paper did not give any extra protection against pollutant attack, but buffering does prolong the service life of the enclosure itself.

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