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Original Paper

Influence of Fumigation on Photographic Images and Their Stability in Long-Term Preservation

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Abstract: The influence of fumigation on several types of photographic images and a colloidal silver film was examined using various fumigants (propylene oxide, ethylene oxide, methyl iodide, sulfuryl fluoride, cyphenothrin, methyl bromide, and carbon dioxide). The effect on the long-term stability of the images was also examined via accelerated aging experiments on the fumigated samples. Although methyl iodide and bromide are known to react with colloidal silver, these reagents did not affect photographic silver images. The other fumigants also negligibly affected all of the photographic specimens examined. Even when long-term storage tests were conducted, fumigation did not cause notable changes to typical photographic images.

Key words: Gelatin, Fumigation, Aging, Photographic image

1. Introduction

Throughout history, proteins, gelatin and albumin have been used as the primary photographic binders. Under humid conditions, binders undergo not only physicochemical deterioration, but also biological deterioration due to mold. In order to avoid biological deterioration, fumigation is generally applied to most cultural properties prior to storage in museums. To date, however, fumigation has not been used on photographs. Methyl bromide (MeBr) has been widely used in combination with other fumigants to enhance the characteristic merits and to compensate for the weak points of each reagent [1]. Use of a mixture of methyl bromide and ethylene oxide (MBEO, one of the most common fumigation agents) is known to be effective against both insects and bacteria for in cultural properties for extended periods of time. It has been reported that MBEO affects sulfur-containing materials, and it has therefore been suspected that similar chemical reactions would take place with photographic materials [2].

However, museum conservators desire fumigation treatment of photographs of cultural importance because all such resources are generally kept in the same physical storage space. It is therefore necessary for our museums to understand the effects of fumigation on photographic images. This work evaluates the applicability of various fumigants to various types of photographs.

MeBr was historically one of the most widely-used soil fumigants, but the "Montreal Protocol on Substances that Deplete the Ozone Layer" identified MeBr as an ozone depleting substance. In 1997, it was agreed that the use, sale, and production of MeBr would be totally prohibited by 2005 in advanced countries, including Japan [3].

A mixture containing MeBr has been widely used for the fumigation of cultural properties in museums, because it works incredibly well to protect against damage from insects, bacteria, and fungi. However, following the Montreal Protocol, various alternative fumigants have been increasingly used. The effects of various pesticides, ovicides, and fungicides on a wide variety of cultural artifacts — from inorganic materials such as metals to organic materials such as zoological specimens — have been examined by several groups [2, 4–7].

However, the effects on photographic images of these major fumigants have not been reported. Although photographs are not currently fumigated to avoid fouling the images, conservators must be diligent in order to avoid contaminating other museum acquisitions with material from non-fumigated photographs. (Of course, since biological deterioration does occur on photographs, fumigation would also be an attractive way to conserve the photographs themselves.) In view of this, the effects of major fumigants on a wide variety of photographic images were examined. In order to evaluate these effects under practical museum conditions, the experiments shown in Scheme 1 were planned, and the following evaluations were conducted on a variety of types of unaltered photographic samples (Stage i):

(1) Direct effects of fumigation on photographic images (Stage ii)
(2) Effects after long-term preservation of the fumigated photographic images (Stages iii and vi)
(3) Effects of re-fumigation (Stage iv)
(4) Effects after long-term preservation of the re-fumigated photographic images (Stage v).

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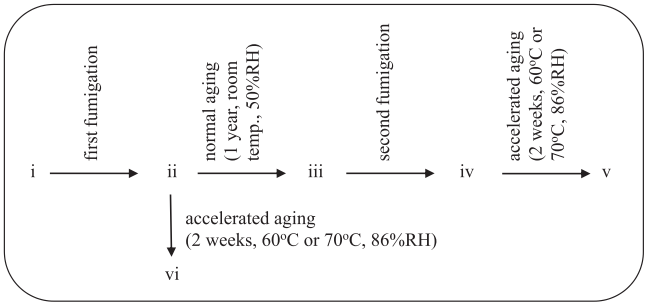

Scheme 1. Flow chart of experiments and stages of fumigation and aging.

Stage iii is considered to be the situation after the loan out of museum works, as fumigation is preferred before re-storage.

2. Materials and Methods

2.1 Photographic Samples

Various types of photographs (from conventional to modern/digital-based; Fig. 1 and summarized in Table 1) were treated with a fumigant. Samples Fiber-base gelatin silver print (FB) and Resin coated gelatin silver print (RC) were contact exposed to the tungsten-halogen lamp filtered by a UV filter with Kodak Photographic Step Tablet no. 2 (uncalibrated; hereafter referred to as "Step Tablet"), then were developed with Kodak's D72 diluted 1:2 with water, fixed with Kodak F-5, washed and dried. Recipes of Samples Albumen print (AP) and Cyanotype (CT) are indicated in Tables 1 and 2. Images on them were produced as photographs contact-printed out with Step Tablet with the metal halide lamp, then were washed, fixed with Kodak F-5, washed and dried. Sample Ink-jet print (IJ) was printed by a printer Epson PM-G720 with digital data that has been copied from the Macbeth ColorChecker Chart. Sample Chromogenic print (CP) was also printed from the same digital data.

A colloidal silver film (CS, colloidal silver in gelatin on a polyester film base) was utilized as a sensitive sensor to detect substances affecting the silver image. CS is commonly used to test photograph storage enclosure materials [8], and is reported to be one of the most sensitive materials under the incubation conditions [9].

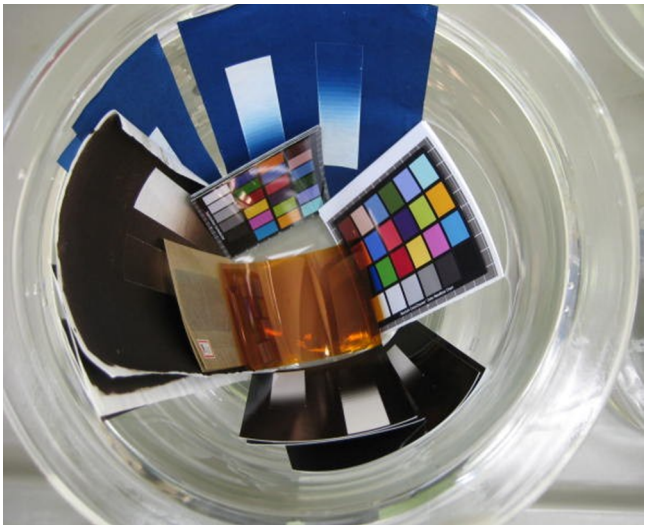

Fig. 1. Photographic samples examined.

2.2 Fumigation

The fumigant characteristics and fumigation conditions are summarized in Table 4. The fumigation conditions are essentially based on the specifications of the Institute of Insect Damage to Cultural Properties [1]. The primary MeBr substitutes were exam-

Table 2. Ingredients of Albumen print.

Sizing/salting solution is:
45 g albumin
7 g sodium chloride
150 ml distilled water
Sensitizer is:
10 g silver nitrate
2 drops 1N nitric acide
100 ml distilled water

Table 3. Ingredients of Cyanotype.

Mixing Sensitizer;
Solution A is:
20 g ferric ammonium citrate
100 ml distilled water
Solution B is:
9 g potassium ferricyanide
100 ml distilled water

Table 1. Constituent materials and manufacturers of photographic samples examined.

Sample	Manufacturer	Binder	Support	Image material
Ink-jet print (IJ)	Photofinishing, Advance Hi Double weight, Fujifilm and Epson PM-G720	polymer	resin coated paper	dye
Chromogenic print (CP)	Kodak paper	gelatin	resin coated paper	dye
Gelatin silver print (FB)	Fuji Bromide Rembrandt VG2, Fujifilm	gelatin	fiber-based paper	silver
Gelatin silver print (RC)	Super SP Gekko VR2, Mitsubishi Paper Mills Limited	gelatin	resin coated paper	silver
Albumen print (AP)	hand made	albumen	acid-free paper (Tokushu Paper Mfg.)	silver
Cyanotype (CT)	hand made	—	acid-free paper (Tokushu Paper Mfg.)	iron compounds
Colloidal silver film (CS)	Agfa-Gevaert	gelatin	polyester film	silver
Gelatin dry plate (GD)	unknown	gelatin	glass	silver
Nitrocellulose film (NC)	unknown	gelatin	cellulose nitrate film	silver

Table 4. Treatment conditions of samples.

Fumigant or treatment	Temperature °C	Humidity %RH	Concentration	Treatment time	Effects
Mixed methyl bromide and ethylene oxide reagent (MBEO) [a)]	25.0	40	98–92 g/m^3	48 hours	insect repellent, bacterial killing
Methyl iodide (MI) [b)]	18.0	54–59	1.1–2.1%	48 hours	insect repellent, bacterial killing
Propylene oxide (PO) [c)]	17.5–18.0	52–59	2.0–2.3%	48 hours	insect repellent, bacterial killing
Ethylene oxide (EO) [d)]	18.0–18.5	54–60	2.6–2.7%	48 hours	insect repellent, bacterial killing
Sulfuryl fluoride (SF) [e)]	25.0	40	48–54 g/m^3	48 hours	insect repellent
Mixture of cyphenothrin and carbon dioxide (CPT) [f)]	23.0	40	48–54 g/m^3	4 hours	a pyrethroid insect repellent
Carbon dioxide, condition A (CO_2A)	25.0	not controlled (ca. 33)	60 v/v%	14 days	–
Carbon dioxide, condition B (CO_2B) [g)]	25.0	50	60 v/v%	14 days	insect repellent
Carbon dioxide, condition C (CO_2C)	25.0	<1	100%	14 days	–
Carbon dioxide, condition D (CO_2D)	25.0	>85	100%	14 days	–

ined: MI [10)], PO [11, 12)], EO [13)], SF [14, 15)], and CPT [16)]. CO_2 was also used [17–19)]. As MeBr remains in limited use in some areas and has been applied to some photographs, a MeBr-EO mixed fumigant (MBEO) was also tested.

2.3 Accelerated aging

Accelerated aging/deterioration tests were attempted in order to simulate long-term preservation. The tests were conducted according to ISO 18916 [8)]. Samples IJ and CP were stored at 60°C (because dyes may sublime at elevated temperatures) and 86%RH for 2 weeks, and Samples FB, RC, AP, CT, CS and GD at 70°C and 86%RH for 2 weeks [8)]. The incubation period is 15 days in ISO, but the incubation in this report was performed in 2 weeks due to the schedule.

2.4 Evaluation

For Samples IJ, CP, FB, RC, AP, and CT, the reflection density and the CIELab value were measured with a spectrophotometer (Spectrolino, GretagMacbeth), and the corresponding color differences were calculated. For transmitting Samples CS, GD, and NC, the transmission densities were measured with a densitometer (TR-924, Macbeth). The density measurements were performed under conditions optimized to the nature of each sample for maximizing the sensitivity to the variation: ISO visual density (*D*v) for Samples FB, RC, GD and NC, blue filtered density of Status A (*D*b) for Samples AP and CS, and red filtered density of Status A (*D*r) for Sample CT.

3. Results and Discussion

3.1 Influence of fumigation processes on photographic images (Stage ii)

CS fumigated with MBEO or MI exhibited a 4–6% increase in blue-filtered density (*D*b), although no change was observed as a result of the other fumigants. Fig. 2 shows the change in the transmission spectrum of CS before and after fumigation with MBEO or MI. For halogen-containing fumigants, the colloid silver chemically reacts with the halogen atom and the spectral properties are perturbed, resulting in an increased *D*b value. The change in transmission density before vs. after fumigation for the other transmitting samples was less than ± 1% (e.g. 0.58→0.58, 0.90→0.91 for GD; 0.97→0.97, 1.68→1.69 for NC). As CS is considered to be a very sensitive detector for substances that react with silver, potential effects of halogenous fumigants cannot be entirely ruled out, but they are certainly insignificant for MeBr and MI.

Fig. 3 shows the change in density before and after fumigation for AP and FB silver images. No significant density change was seen after fumigation for any fumigant, regardless of density level.

Table 5 shows the color differences before and after fumigation in yellow, magenta, cyan, and black patches of CP. Following CO_2B and EO treatments, a small but similar level of discoloration was observed for all colors. Although these results suggest some chemical influence on the dye images from these fumigants, the changes were well balanced and as noted below, practically

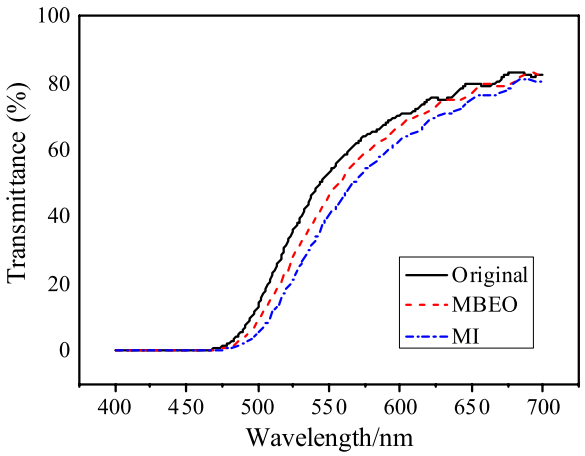

Fig. 2. UV/V is transmittance of CS before and after fumigation.

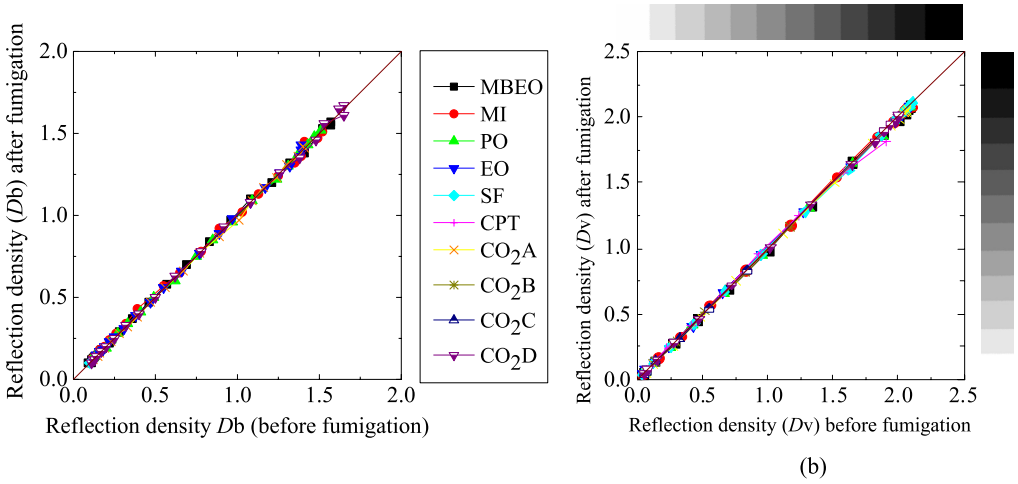

Fig. 3. Comparison of (a) AP and (b) FB with several other fumigants.

Table 5. Color difference of chromogenic print with fumigation.

Fumigant or treatment	Color difference of sample after first fumigation / after re-fumigation			
	Yellow ΔE	Magenta ΔE	Cyan ΔE	Black ΔE
MBEO	0.20 / –	0.51 / –	0.20 / –	0.24 / –
MI	0.76 / 0.73	0.34 / 0.54	0.32 / 0.29	0.27 / 0.40
PO	0.87 / 1.43	0.56 / 0.85	0.36 / 0.85	0.13 / 0.30
EO	0.67 / 0.69	0.58 / 0.55	0.67 / 0.65	0.16 / 0.15
SF	0.09 / 0.15	0.45 / 0.48	0.16 / 0.18	0.28 / 0.25
CPT	0.25 / 0.23	0.44 / 0.40	0.26 / 0.40	0.30 / 0.56
CO_2A	0.07 / –	0.30 / –	0.19 / –	0.15 / –
CO_2B	0.31 / 0.34	0.33 / 0.29	0.23 / 0.29	0.34 / 0.12
CO_2C	0.44 / –	0.74 / –	0.22 / –	0.35 / –
CO_2D	0.60 / –	0.52 / –	0.38 / –	0.19 / –

*For abbreviations, see Table 4.

insignificant. Following PO and MI treatments, the discoloration of yellow was somewhat larger than the other colors. After treatment with SF, MBEO, and CPT, the discoloration of magenta was larger. However, all of these changes are small relative to general visual recognition – few people can discern a color difference less than 0.6 even upon intense scrutiny, and in casual viewing, an acceptable color difference (taking into account various factors) is 1.2 [20].

3.2 Verification of image stability in long-term preservation (Stage vi)

Figs. 4 and 5 illustrate the influence of fumigation on AP and CT images after accelerated aging. For AP, a different trend was found for CPT as compared to the other fumigants in the low image density region, as indicated by the circled area in Fig. 4(b). Except for CPT, discoloration of the silver image after aging counterbalances the growing yellowness of the base paper, resulting in a suppressed density decrease after aging in this region. On the other hand, CPT might inhibit yellowing of the base paper and binder albumin. While the mechanism is uncertain, no effect on the silver image itself was also confirmed.

3.3 Influence of the re-fumigation processes on photographic images and long-term preservation (Stages iv, v)

Regular, repeated fumigation of resources is required for long-term preservation and should be applied after exposure to any out-of-museum-storage atmosphere. In order to evaluate the influence of re-fumigation on photographic images, a second fumigation treatment was carried out on the fumigated samples about one year after the first fumigation. The second treatment conditions (temperature, humidity, and fumigant concentration) were essentially identical to the ones described in section 2.1, although MBEO treatment could not be conducted because of legal prohibitions. For CO_2 treatment, the most popular CO_2B conditions were applied. In order to evaluate the influence on photographic images in long-term preservation, accelerated aging experiments were also applied to the twice-fumigated samples (Stage v).

Table 5 shows both the color differences before and after the first fumigation and re-fumigation in yellow, magenta, cyan, and black patches of CP. Fig. 6 shows the CS transmission density before and after re-fumigation and accelerated aging. No significant changes were detected following re-fumigation, unless the fumigant contained iodine, which causes chemical degradation of the colloidal silver and specific changes in the transmission density. The

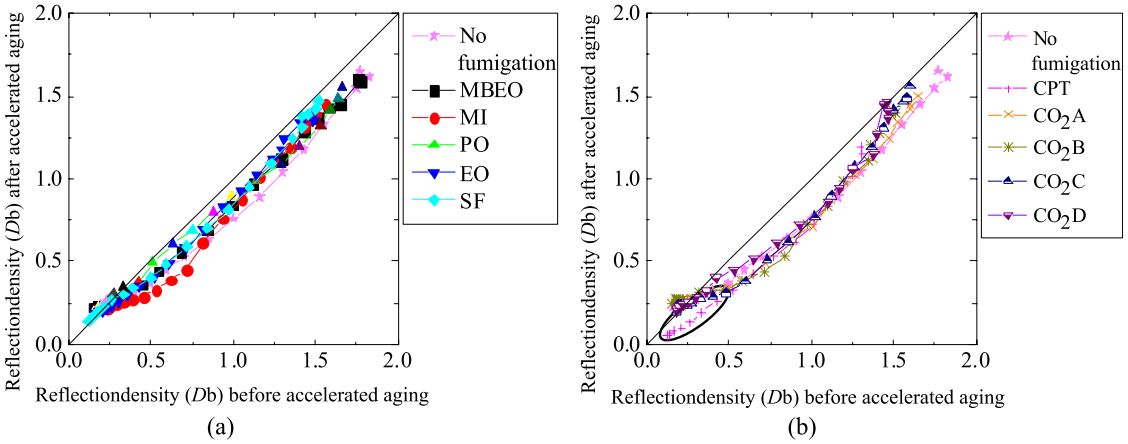

Fig. 4. Influence on AP with fumigation and with accelerated aging.

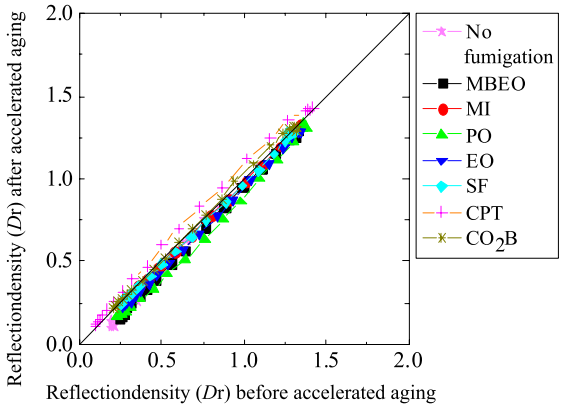

Fig. 5. Influence on CT with fumigation and with accelerated aging.

criteria specified in ISO 18916 indicate that the change in CS after accelerated aging must not exceed ±20% of the standard sample. Only MI exceeded this threshold. The sensitivity of CS is very high as a sensor. Thus, at least in a practical context, (except for MI) re-fumigation does not affect image stability for a wide variety of photographic images. In conclusion, upon treatment with each fumigant, all of the samples (other than CS fumigated with CPT) showed no significant difference in both density and color. Furthermore, fumigation did not affect the long term stability of the images upon accelerated aging. For the first time, significant practical data has been acquired for works museums actually handle.

The same experiments were conducted on gelatin dry plates (GD) and nitrocellulose films (NC) that were produced more than 50 years ago. The storage environment and other details of these samples are unknown. The samples showed no significant changes after fumigation for all of the fumigants examined. The GD sample was then stored under the accelerated aging conditions, and no significant changes were observed (the accelerated aging test was not conducted for the NC sample because of the risk of spontaneous combustion). These results are consistent with the results found for the more modern samples. The older samples may be protected from the fumigants by some degradation due to age (influence of hardened gelatin, exhaust/pollution in the atmosphere, etc), although this has not yet been proven. At the very least, these results strongly suggest that fumigation of old works having an uncertain storage history does not affect image quality, though further studies with other old photographs using other photographic techniques is of course recommended (and ongoing).

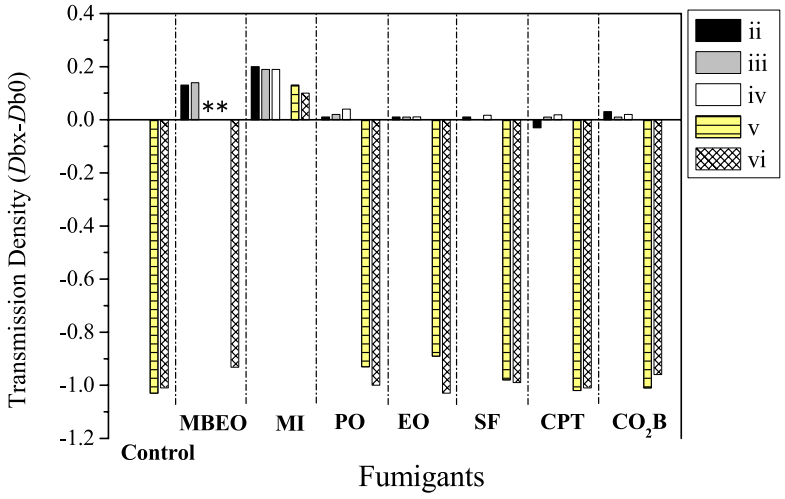

Fig. 6. CS density at all experimental stages with various fumigants (The control sample was examined after aging (Stage iii), after accelerated aging (Stage vi) and after aging followed by accelerated aging (Stage v) without any fumigant applied at any point.) Initial density *D*b0 = 3.23.
*Not tested because fumigant was commercially discontinued.

4. Conclusion and Future Studies

The effects of the primary fumigants currently being used and/or recognized as useful for the preservation of cultural properties were examined, specifically the effect on image quality of photographs processed using the primary photographic techniques. Negligible changes in density and color were observed, and thus, it can be concluded that fumigation does not affect the images. No effect on image quality for long-term preservation following fumigation was also confirmed, and residue from the fumigant is negligible or, at least, does not affect stability. These residue tests will be the subject of a future publication. Re-fumigation treatment has little effect on images processed using the major photographic techniques, at least using the appropriate fumigants and procedures. No apparent problem was found upon repeated fumigation, at least using an interval of one year. Over such a time, residual fumigant on the photographs completely diffuses into the atmosphere, and hence, any influence of the residue was found to be negligible. Of course, it is necessary to devote some attention to the selection of fumigant because there are chemicals which cause significant density deterioration (such as CPT in the low density range), and colloid silver reacts with halogens.

When considering these results, the following should be kept in mind: (1) the samples used in this study were generally modern (and hence, rather durable) photographic materials – classical photographs may contain more sensitive materials; (2) image deterioration takes place due to a wide variety of causes, including an oxidative/reductive storage environment and residual chemicals from photographic processing; and (3) residues from fumigants and/or photographic processes may act synergistically resulting in severe effects on image quality. Combinations of fumigants (including ones not tested here) should be carefully examined, as well as photographic materials prepared with techniques not tested in this study.

The recent total ban of methyl bromide has increased the number of museums using Integrated Pest Management (IPM), which requires daily action, instead of occasional fumigation to control insects and fungi.[21] In order to avoid insect damage, two storage conditions are known to be effective: (1) low oxygen concentration (0.1% or less), and/or (2) low temperature (from –30°C to –20°C) [22–24]. The former method may have the additional benefit of preventing oxidative degradation of images. However, the latter method must be re-examined for use with the storage of photographs due to the possibility of microscopic damages (e.g. the effect on a gelatin layer) caused by the freezing.

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