THE FADING OF ARTISTS' COLORANTS BY EXPOSURE TO ATMOSPHERIC NITRIC ACID

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Abstract—Experiments show that atmospheric nitric acid vapor is capable of inducing fading and color shifts in a variety of important artists' colorants. Seventy-nine samples were exposed to 12 and 40ppb nitric acid in air at 22°C and 50% RH in two consecutive experiments, each of 12 weeks duration. About half (27 from 52) of the colorants applied to paper showed sensitivity to nitric acid and most (22 from 27) of the Japanese dyed silk cloths showed some reactivity toward nitric acid at the higher concentration. At a concentration of 12ppb for 12 weeks, the nitric acid dose (concentration multiplied by duration of exposure) employed in this study is equivalent to the dose inside an unprotected museum in central Los Angeles over a seven-year period.

1 Introduction

The threat imposed by the intrusion of gaseous pollutants from the outdoor atmosphere is a problem of increasing concern to those responsible for museum collections. The concentration of air pollutants found in museums has been reviewed by several authors [1, 2], and it is clear that measures to protect museum collections from damage need to be taken. These measures may include the use of air filtration equipment to reduce pollutant concentration levels, as well as construction of display cases or frames to protect sensitive objects.

To determine when control measures are needed, it is essential that the chemical identity of sensitive museum materials, as well as that of the damaging pollutants, be established. Currently, there is substantial evidence that a large number of pigments, including natural organic colorants and modern watercolors, are quite sensitive to ozone [3–6].

In addition to ozone, other oxidizing gases are present in urban areas, including a variety of nitrogen oxides. Prolonged exposure to an atmosphere containing oxides of nitrogen has been reported to cause the deterioration of materials including dyes, textile fibers, plastics, rubber and metals [7–17]. In several of these studies, the identity of the damaging agent has not been explicitly determined because of the coexistence of various nitrogenous pollutants in the atmosphere.

The fading of natural and synthetic artists' colorants induced by nitrogen dioxide (NO_2) was investigated in a previous experiment [18]. Nitric acid (HNO_3) and other pollutants were removed, so that the effect of nitrogen dioxide alone could be determined. NO_2 was found to cause only minor fading, so it is suspected that another pollutant, such as nitric acid, may have caused the damage attributed to the oxides of nitrogen in some past studies.

The object of this study is to assess the fading hazard to works of art from nitric acid at concentrations found in indoor atmospheres. Indoor and outdoor pollutant monitoring was conducted in five museums and art galleries in the Los Angeles area to determine the relative concentrations of nitric acid in outdoor and indoor air [19]. Average indoor nitric acid concentrations of up to 0·42ppb were measured in a museum that lacked any pollutant removal system. Typical nitric acid values between 0·04 and 0·06ppb were measured in museums fitted with activated carbon air filtration systems, showing that nitric acid concentration can be reduced. In contrast, the ambient concentration of NO_2 in other museums typically ranged between 4 and 60ppb [20]. Unlike NO_2, the removal of HNO_3 from building atmospheres is relatively easy and inexpensive. It is important, therefore, to ascertain the hazard posed by each pollutant so that reasonable measures can be taken to protect museum collections.

2 Experimental

Samples that duplicated those used in previous NO_2 and ozone exposure studies [5, 6, 18] were created so that comparisons could be drawn

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between the relative effects of the various pollutants. The 79 samples can be divided into three distinct classes:

1. traditional natural organic colorants on paper;
2. Japanese dyed silk cloths;
3. modern synthetic organic and inorganic colorants on paper.

Table 1 Natural organic colorants tested on paper

Weld lake	Natural yellow 2
Curcumin	Natural yellow 3
Saffron	Natural yellow 6
Quercitron lake	Natural yellow 9
Persian berries lake	Natural yellow 14
Gamboge	Natural yellow 24
Cochineal lake	Natural red 4
Madder lake	Natural red 9
Lac lake	Natural red 25
Litmus	Natural red 28
Dragon's blood	Natural red 31
Indigo	Natural blue 1
Van Dyke brown	Natural brown 8
Sepia	Natural brown 9
Bitumen	Natural black 6
Indian yellow	—
Aigami	(dayflower blue)

The natural organic colorants, listed in Table 1, were prepared from pigment samples obtained from the Forbes collection of the Fogg Museum at Harvard University as well as other sources, and had previously been authenticated [5]. As described earlier [5, 18], samples were prepared by grinding dry pigments until fine with a mortar and pestle. Methanol suspensions of the colorants were then applied with an airbrush through a 1cm-diameter mask onto 2·5 × 5cm pieces of Arches hot-pressed watercolor paper in an effort to achieve approximately 40% reflectance at the wavelength of minimum reflectance.

The samples of silk cloth dyed using traditional Japanese colorants were supplied with information on the identities of the plant sources and mordants used [18]. For the exposure test, pieces of silk cloth were cut into approximately 2·5cm^2 squares and sewn onto watercolor paper for mounting in the exposure chamber. These samples are listed in Table 2.

Table 2 Natural colorant/mordant combinations tested on silk cloths

Color	Natural dye	Mordant
Yellow:	*Enju* (Japanese pagoda tree)	Al
	Kariyasu (Arthraxon hispidus)	Al
	Kariyasu (Arthraxon hispidus)	Cu
	Kihada (Japanese yellow wood)	Al
	Kuchi nashi (jasmine)	Al
	Ukon (turmeric)	Al
	Ukon (turmeric)	Ethanoic acid
	Woren (Coptis japonica)	None
	Yamahaji (Rhus succedanea)	Al
	Yama-momo (Myrica rubra)	Al
	Zumi (Malus toringo)	Al
	Shiō (orpiment, As_2S_3)	None
Red:	*Seiyo akane* (Western madder)	Al
	Akane (Japanese madder)	Al
	Enji (cochineal)	Sn
	Shiko (lac)	Al
	Suo (Caesalpinia sappan L.)	Al
	Beni (safflower) (orange)	None
	Beni (safflower) (red)	None
Blue:	*Ai* (indigo) light blue	None
	Ai (indigo) medium blue	None
	Ai (indigo) dark blue	None
	Ai (indigo) very dark blue	None
Green:	*Ai + enju*	Al
	Ai + kariyasu	Al
	Ai + kihada	Al
Violet:	*Shikon (Lithospermum)*	Al

The synthetic organic and inorganic colorants on paper listed in Tables 3 and 4 were also selected. Dry pigment samples were prepared in the same manner as the natural organic colorants, except that the watercolors were prepared in a methanol/water mixture for airbrushing. Iron ink samples prepared by Whitmore [18, 21] were added to the sample set, along with a sample of the American Association of Textile Chemists and Colorists (AATCC) NO_2 fading standard no. 1 (Disperse blue 3 on cellulose acetate), included to determine whether this NO_2 fading test is also sensitive to HNO_3. In addition, pigment samples that were intended for analysis by mass spectrometry in a separate reaction product study were included [22]. These are listed in Table 5.

Color change was used to determine the amount of damage to each sample over the course of the experiment. A Diano MatchScan II spectrophotometer which measured diffuse reflectance spectra was used for color measure-

Table 3 Synthetic organic colorants tested on paper

*Colorant name**	*Manufacturer*	*Composition*
Arylide yellow G	Binney & Smith	Monoazo (PY1)
Arylide yellow 10G	Binney & Smith	Monoazo (PY3)
Paliogen yellow	BASF	Anthraquinone (PY108)
Toluidine red	BASF	Naphthol (PR3)
Bright red (wc)	Winsor & Newton	Monoazo (PY1) + naphthol (PR4)
Scarlet lake (wc)	Winsor & Newton	Monoazo (PR10)
Rose carthame (wc)	Winsor & Newton	Monoazo (PR10) + xanthene (PR90)
Alizarin crimson	Winsor & Newton	Anthraquinone (PR83)
Alizarin crimson (wc)	Winsor & Newton	
Thioindigo violet	BASF	Thioindigoid (PR88)
Naphthol	Binney & Smith	Naphthol (PR188)
Permanent magenta (wc)	Winsor & Newton	Quinacridone (PV19)
Dioxazine purple	BASF	Dioxazine (PV23)
Mauve (wc)	Winsor & Newton	Triphenylmethane lake (of BV14) + phthalocyanine (PB15)
Phthalocyanine blue	Binney & Smith	Phthalocyanine (PB15)
Prussian blue	Binney & Smith	Ferric ferrocyanide (PB27)
Paliogen blue	BASF	Indanthrone (PB60)
Phthalocyanine green	Binney & Smith	Phthalocyanine (PG7)
Aniline black	BASF	Azine (PBk1)

*Pigments were in dry powder form unless designated as watercolor (wc).

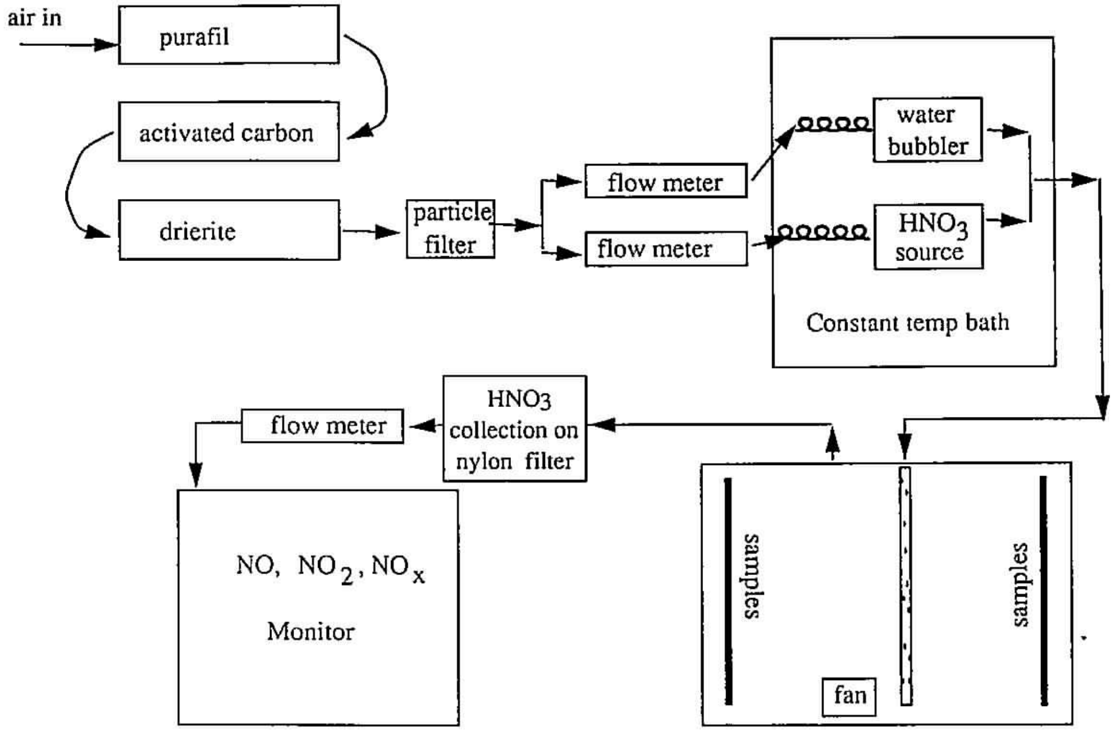


Figure 1 Nitric acid exposure apparatus.

Table 4 Synthetic inorganic colorants tested on paper

*Colorant name**	*Manufacturer*	*Composition*
Chrome yellow (wc)	Winsor & Newton	Lead chromate (PY34)
Aureolin (wc)	Winsor & Newton	Potassium cobaltinitrite (PY40)
Cadmium yellow medium	Binney & Smith	Cadmium sulfide (PY37)
Manganese violet	Binney & Smith	Manganese ammonium pyrophosphate (PV16)
Vermilion (wc)	Winsor & Newton	Mercuric sulfide (PR106)
Orpiment	Forbes collection	Arsenic trisulfide (PY39, CI77086)
Realgar	Ransome collection	Arsenic disulfide (PY39, CI 77085)

*Pigments were in dry powder form unless designated as watercolor (wc).

Table 5 Additional samples

Colorant name	*Manufacturer*	*Composition*
Watercolor paper	Arches	
NO_2 test cloth	AATCC	Disperse blue 3 on cellulose acetate
Turmeric	Frontier H & S	
Alizarin crimson on filter paper*	Winsor & Newton, Whatman	Anthraquinone (PR83)
Iron inks:		
Iron ink I	Caltech	Iron gallotannate
Iron ink II	Caltech	Iron tannate
Samples for mass spectrometry†:		
Alizarin	Aldrich	Anthraquinone
Alizarin crimson (dry)	Winsor & Newton	Anthraquinone (PR83)
Indigo, synthetic	Aldrich	Indigotin, vat blue 1
Thioindigo violet	BASF	Thioindigoid (PR88)
Basic fuchsin	Aldrich	Triphenylmethane (BV14)
Pararosaniline base	Aldrich	Triphenylmethane
Quinacridone red	Binney & Smith	Quinacridone (PV19)
Acridone	Aldrich	Acridone
Prussian blue	Binney & Smith	Ferric ferrocyanide (PB27)
Chrome yellow (watercolor)	Winsor & Newton	Lead chromate (PY34)

*Sample on Whatman 41 filter paper instead of watercolor paper.
†Samples applied to Teflon filters in addition to watercolor paper; intended for reaction products analysis reported elsewhere [22].

ments. Reflectance spectra were measured for all the samples immediately prior to placing them in the exposure chamber. Samples were periodically withdrawn for examination and color changes were determined by comparing the reflectance spectra of the exposed samples to the initial reflectance spectra. Care was taken to ensure that subsequent measurements were made at the same location on each sample.

Reflectance spectra for the samples were made at 2nm intervals from 380 to 700nm. The instrument reported tristimulus values (X, Y, Z), and the Commission Internationale de l'Eclairage (CIE) color difference (ΔE, from the CIE 1976 L*a*b* formula) was calculated for CIE illuminant C [23]. Munsell color notations were subsequently computed from the tristimulus values [24]. The value of ΔE gives the magnitude of the total color change of a sample between measurements and is one means of comparing the effect of nitric acid on various samples.

The HNO_3 exposure apparatus is illustrated in Figure 1. The air entering the system was passed through a series of filters to remove any existing pollutants and moisture. Filter media consisted of Purafil (potassium permanganate-impregnated alumina pellets), activated carbon, Drierite desiccant and a particle filter. The purified, dry air was split into two streams; one stream passed through a distilled water bubbler to saturate that stream with water vapor and the other passed over a HNO_3 permeation tube (VICI Metronics). The flow rates of the two air streams and the temperature of the permeation tube were regulated so that the humidity and concentration of HNO_3 entering the chamber could be controlled. The air entering the exposure chamber was tested for HNO_3, NO and NO_2 content using HNO_3 removal on a nylon filter followed by analysis using a chemiluminescent nitrogen oxides monitor (Thermo Electron Corp. model 14B/E) to verify that levels of other nitrogenous species (i.e., NO and NO_2) were negligible compared to that of HNO_3.

The samples were held against the walls of the exposure chamber, facing inward, by aluminium holders coated with Teflon to minimize the reaction of HNO_3 with the holders. Similarly, all exposed surfaces in the chamber were lined with Teflon to reduce loss of HNO_3 in the box. The air in the chamber was mixed using a Teflon fan-blade powered by a magnetically coupled external motor. The temperature and relative humidity (RH) inside the chamber were monitored with a thermohygrometer and maintained at 22°C and 50% RH respectively. The chamber was sealed and samples were kept in the dark. The chamber dimensions were 30 × 30 × 25cm.

The HNO_3 concentration leaving the chamber was continuously monitored by collecting HNO_3 on nylon filters (Gelman, Nylasorb) that were analyzed by ion chromatography [19]. The HNO_3 concentration supplied to the chamber was periodically checked by placing a nylon filter in the air stream at the entrance to the chamber. Nylon filter material was also sewn onto watercolor paper and placed inside the chamber to determine the HNO_3 deposition flux to the samples. The nylon filters used are known to bind and retain HNO_3 [19, 25]. Analysis of Whatman filter paper samples by ion chromatography was also used to measure the HNO_3 deposition flux to paper surfaces during the experiment. Whatman filter paper had to be used for this purpose because the nitrate levels present in the watercolor paper were not equal to zero.

The samples were exposed to nitric acid in two stages. During the first 12 weeks of exposure, nitric acid levels were kept at the relatively low level of 12ppb. For purposes of comparison, that concentration is approximately ten times higher than the average outdoor HNO_3 concentration in the Los Angeles atmosphere but less than the short-term peaks, which have reached 20ppb [26, 27]. Samples were withdrawn from the chamber for reflectance measurements after one, two, three, four, six, eight and 12 weeks of exposure. At the end of the first 12 weeks, the level of nitric acid was increased approximately threefold, the experimental apparatus was serviced and the calibration of the spectrophotometer was confirmed. All reflectance spectra values were re-measured at week 14, and a second 12-week exposure experiment was begun at that point. Minor color differences were observed for some samples between the end of stage one in week 12 and the beginning of the second stage in week 14. During stage two, the samples were again withdrawn for reflectance measurements after one, two, four, six, eight and 12 weeks of exposure.

3 Results

Rapid loss of nitric acid occured on surfaces inside the exposure chamber such that, in stage one, when 110ppb of nitric acid were supplied to the chamber inlet, a standing concentration of 12ppb HNO_3 was measured inside the stirred volume of the chamber. The actual nitric acid deposition flux to surfaces inside the chamber was from $0{\cdot}03$ to $0{\cdot}07 \mu g\, m^{-2} s^{-1}$. This was approximately ten times the flux measured at Sepulveda House in central Los Angeles during the museum study, which ranged from $0{\cdot}002$ to $0{\cdot}006 \mu g\, m^{-2} s^{-1}$ [19]. The nitric acid dose (concentration multiplied by duration of exposure) employed in stage one is equivalent to the magnitude of the dose experienced inside an unprotected museum like Sepulveda House over a seven-year period or during 50 years in a museum fitted with an air-conditioning system which includes activated carbon filters [19].

During the second 12-week exposure period, concentrations were increased approximately threefold, with 320ppb HNO_3 supplied to the exposure chamber. Nitric acid concentrations of approximately 40ppb were measured within the chamber. The average flux to nylon surfaces inside the chamber was $0{\cdot}14 \mu g\ m^{-2}\ s^{-1}$.

Twelve of 78 samples experienced noticeable fading after the initial 12 weeks of exposure, and 49 of 79 samples showed some degree of fading after the second 12-week period with higher nitric acid levels. Color values in the Munsell system were calculated for each sample at periodic intervals, allowing easy interpretation of the color change in terms of hue, value (lightness) and chroma (saturation). It is estimated that a human observer can discern a change in color corresponding to a hue difference of 0·5, a value difference of 0·1 or a chroma difference of 0·4 [24].

A more useful quantity for comparing the observed color change between different colorants is the ΔE value, or total color difference, which provides an approximate indication of the magnitude of the total color change undergone by a sample. The colorants have been grouped into somewhat arbitrary categories based on the extent of color change after exposure to nitric acid for 24 weeks. These are 'very reactive' ($\Delta E > 8$), 'moderately reactive' ($\Delta E = 2$–8), 'borderline' cases where ΔE is less than 2 but clearly showing a monotonic increase in ΔE over time, and 'resistant'. Typically, a ΔE value of less than 0·5 represents an imperceptible difference, and a ΔE of less than 1 is considered a good color match.

3.1 *AATCC standard of fading*

A sample of the American Association of Textile Chemists and Colorists (AATCC) NO_2 fading test cloth was included in this experiment for comparison with previous studies. Since the NO_2 levels present (1–5ppb) would cause negligible fading of the test strip [18], fading of the test strip was due to nitric acid. Exposure to nitric acid caused a large color change in the AATCC

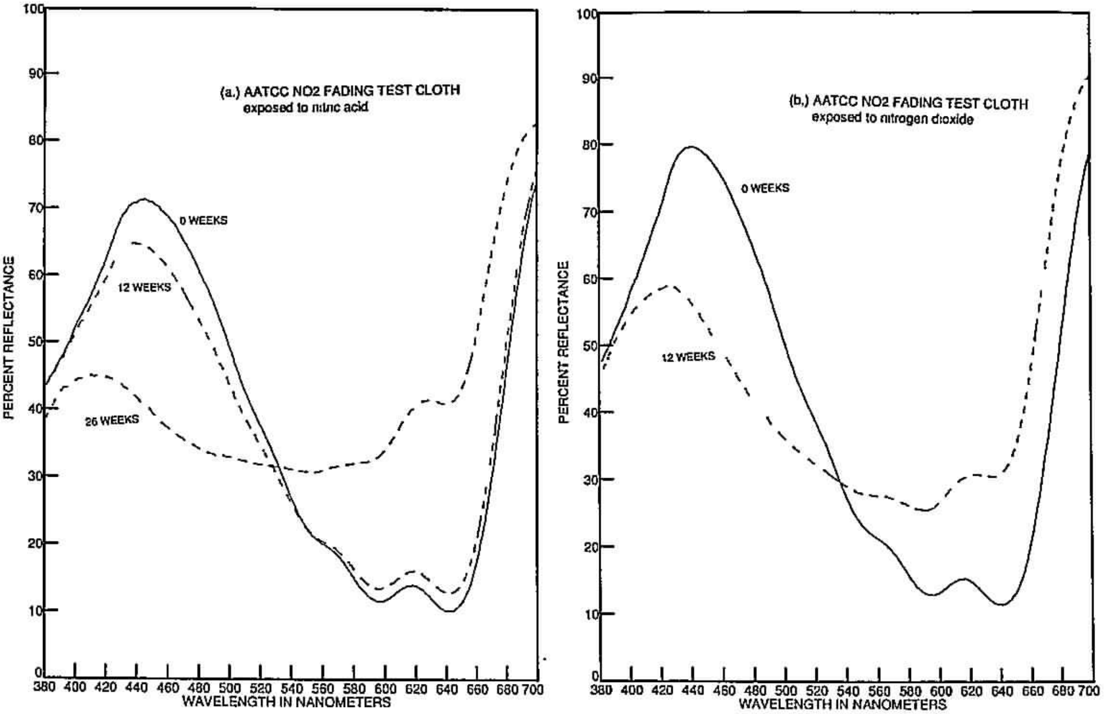


Figure 2 Reflectance spectra of the AATCC NO_2 fading test cloth (Disperse blue 3 on cellulose acetate). (a) Before (solid line) and after a 12-week exposure to 12ppb HNO_3 followed by exposure to 40ppb nitric acid at 22°C and 50% RH for 12 weeks. (b) Before and after exposure to 500ppb NO_2 at 24°C, 50% RH for 12 weeks.

Table 6 *Color changes observed in AATCC NO_2 fading test cloth*

Sample	*Week*	*CIE tristimulus values*			*Munsell color notation*	*Color difference ΔE*
		X	*Y*	*Z*		
NO_2 test cloth	0	25·98	25·73	78·22	4·72PB 5·61/11·65	—
	12	25·80	25·12	70·58	5·32PB 5·55/10·55	5·21
	14	25·80	24·98	68·27	5·52PB 5·54/10·19	—
	26	35·64	33·08	45·88	7·85P 6·25/ 3·48	34·25

fading test cloth, as indicated in Table 6 by the ΔE value of 5·2 after 12 weeks of exposure to 12ppb HNO_3 and a ΔE of 34·3 after a further 12 weeks of exposure to 40ppb HNO_3. This can be compared to the magnitude of color change, ΔE 26·34, shown by the cloth when exposed to 500ppb NO_2 for 12 weeks.

Figure 2a shows the reflectance spectra of the AATCC fading test cloth over the course of exposure. The nature of the color change is displayed by a decrease in reflectance at the blue end of the visible spectrum (450nm) and an increase in reflectance in the red (620nm), accompanied by a sharp decrease in the chroma of the sample. This is similar to the change shown by the sample of AATCC fading test cloth exposed to 500ppb NO_2 for 12 weeks (Figure 2b). The conclusion is that the AATCC NO_2 fading test is not specific for NO_2 exposure, but instead responds to both NO_2 and HNO_3.

3.2 Colorants on paper

Two plain samples of Arches hot-pressed watercolor paper were included in the HNO_3 exposure experiment. They showed no significant color change even at the higher HNO_3 concentration used in stage two, with ΔE values of 0·8 and 0·3.

The colorant systems on watercolor paper have been divided into categories according to their reactivity to nitric acid, as discussed previously. The color measurements of samples before and after each exposure period are listed in Tables 7–9 for samples deemed very reactive, moderately reactive and borderline. It should be noted that the second ΔE value represents a color change beyond that reported during the first 12 weeks.

Figure 3 shows the observed color change, ΔE, over time for the most reactive colorants on paper. The NO_2 test ribbon is included for comparison. The most reactive sample, pararosaniline base, underwent most of its color change in the first week of exposure. The sample will have been depleted of most of the initial colorant and then remained stable during the rest of the experiment. Looking at the time-dependence of the color changes to the samples on paper, several samples (e.g., litmus and alizarin) showed most color change early in the experiment and had successively smaller color

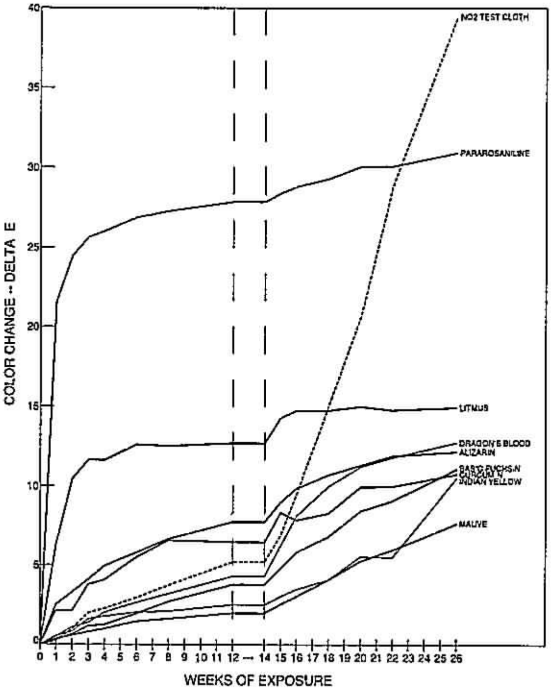


Figure 3 *Observed color change, ΔE, over time for the most reactive colorants on paper exposed to 12ppb HNO_3 during weeks 0 through 12 and 40ppb HNO_3 during weeks 14 through 26. The AATCC NO_2 fading test cloth is included for comparison.*

Table 7 Color changes of colorants very reactive toward nitric acid

Sample	*Week*	*CIE tristimulus values*			*Munsell color notation*		*Color difference ΔE*
		X	*Y*	*Z*			
Pararosaniline base	0	43·56	32·86	52·78	1·04RP	6·24/9·67	—
	12	22·20	19·69	26·14	2·14RP	4·99/3·55	27·83
	14	20·96	18·85	25·35	1·13RP	4·90/3·20	—
	26	20·05	18·57	24·45	0·67RP	4·86/2·48	3·08
Litmus	0	64·29	65·11	78·19	6·21P	8·33/0·53	—
	12	75·45	73·42	73·87	1·92YR	8·75/2·43	12·70
	14	74·31	72·60	74·50	1·63YR	8·71/2·26	—
	26	77·14	75·19	74·94	2·59YR	8·84/2·44	2·21
Dragon's blood	0	61·87	57·16	41·57	4·06YR	7·89/5·10	—
	12	62·98	59·52	41·21	6·29YR	8·02/5·02	4·30
	14	63·45	59·74	42·45	5·70YR	8·04/4·93	—
	26	65·52	64·21	40·91	9·62YR	8·28/5·16	8·43
Alizarin	0	56·17	52·77	19·62	9·28YR	7·63/8·31	—
	12	61·76	59·44	19·88	0·64Y	8·02/8·91	7·76
	14	62·41	60·51	20·74	0·94Y	8·08/8·73	—
	26	65·82	64·75	21·09	1·71Y	8·31/9·00	4·39
Basic fuchsin	0	65·88	57·54	75·08	2·42RP	7·91/5·88	—
	12	64·46	57·98	75·94	1·51RP	7·94/5·04	3·78
	14	63·65	57·52	76·27	0·87RP	7·91/4·94	—
	26	64·30	60·90	77·10	0·88RP	8·10/3·35	7·27
Curcumin	0	73·34	76·71	26·76	4·43Y	8·91/8·44	—
	12	74·27	77·96	31·96	4·60Y	8·97/7·45	6·48
	14	74·41	78·21	32·82	4·67Y	8·98/7·30	—
	26	75·39	79·36	36·83	4·78Y	9·03/6·67	4·26
Turmeric*	14	69·36	73·59	20·22	5·20Y	8·76/9·59	—
	26	71·46	75·95	28·26	5·37Y	8·87/7·89	11·27
Indian yellow	0	75·00	78·57	40·63	4·53Y	9·00/5·95	—
	12	75·47	79·03	43·18	4·54Y	9·02/5·59	2·52
	14	75·62	79·46	44·35	4·81Y	9·04/5·43	—
	26	77·88	82·54	54·31	6·35Y	9·18/4·24	7·97
Mauve (wc)	0	43·20	37·91	68·24	4·04P	6·63/7·01	—
	12	43·21	38·46	68·07	3·59P	6·67/6·61	1·99
	14	43·21	38·67	68·60	3·19P	6·69/6·54	—
	26	42·87	39·84	66·57	1·94P	6·77/5·38	5·66
Alizarin crimson on Whatman filter paper	0	50·81	42·70	45·57	9·29RP	6·97/6·30	—
	12	52·74	44·80	46·54	0·37R	7·12/6·06	2·25
	14	52·47	44·65	46·43	0·39R	7·11/6·00	—
	26	56·90	49·75	49·05	3·36R	7·44/5·36	5·24

*New sample made. Started exposure on week 14.

changes as time passed, again suggesting significant depletion of the initial colorant. Others, such as Indian yellow, mauve and basic fuchsin, changed progressively throughout the exposure period and had not ceased changing at the end of the second 12 weeks. The same is true for most of the moderately reactive colorants shown in Figure 4. For many of the slowly reacting colorants in the moderately reactive group, increasing the concentration of HNO_3 during the second stage of the experiment increased the rate of color change.

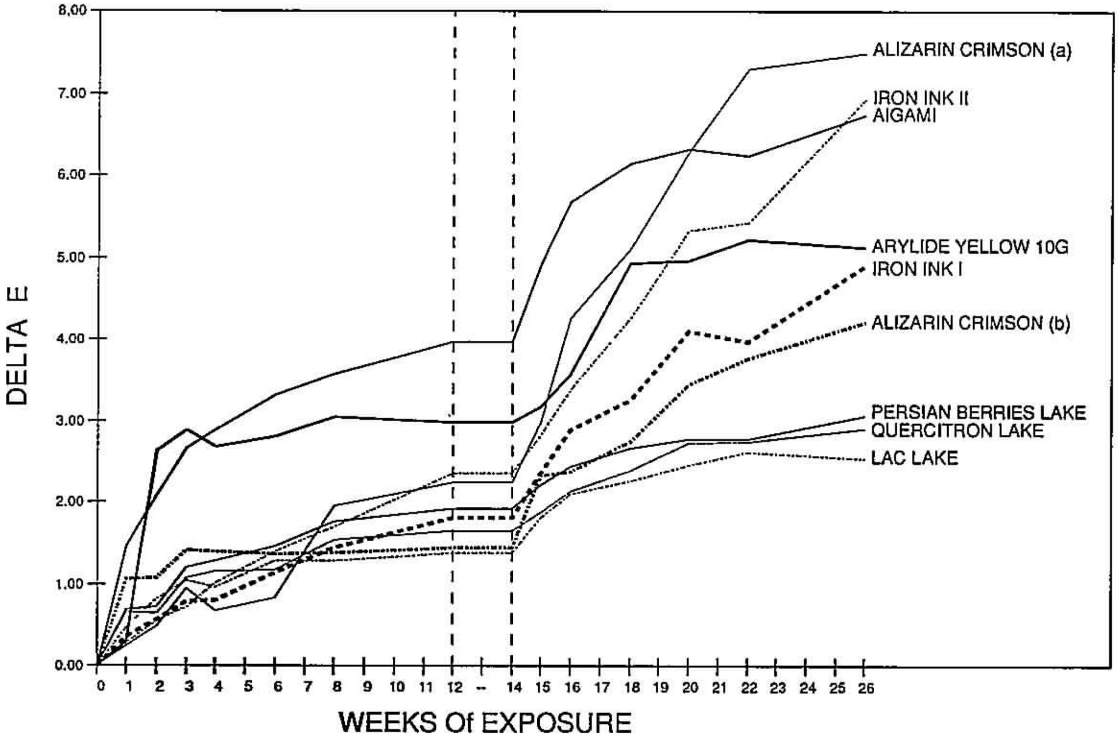


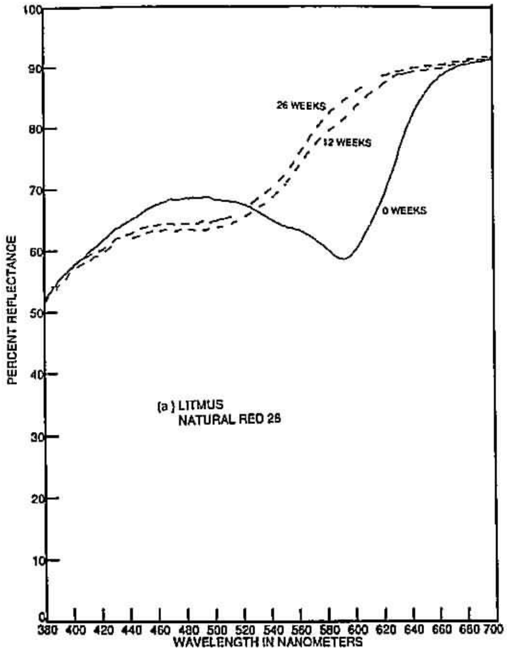
Figure 4 Observed color change, ΔE, over time for moderately reactive colorants on paper exposed to 12ppb HNO_3 during weeks 0 through 12 and 40ppb HNO_3 during weeks 14 through 26.

The ozone-induced fading of natural colorants typically proceeds via destruction of the chromophore, yielding colorless reaction products and hence a faded sample of the same hue. In contrast, many of the color changes produced by nitric acid exposure involve a shift in hue, suggesting the production of colored reaction products. This is shown, for example, among the natural colorant systems that displayed the largest degree of color change, including litmus, dragon's blood, Indian yellow and *aigami*. Their reflectance spectra are shown in Figures 5a–d.

As a counter example, curcumin (the coloring agent in turmeric) faded via loss of chroma without a change in hue, suggesting oxidation products analogous to those formed upon reaction with ozone [22, 28]. A sample of ground turmeric added during stage two of the exposure experiment behaved in the same manner as curcumin (Figure 5e).

Table 10 provides a comparison of the color change (ΔE) observed for colorants exposed to 12ppb of nitric acid in this study with the color change when exposed to either 500ppb of NO_2 or 400ppb of ozone in previous 12-week exposure experiments [3–6, 18, 28–31]. In stage one of the present experiment, as well as in the NO_2 and O_3 experiments, the pollutant concentration used approximated the peak short-term levels observed outdoors in Los Angeles, and was set at about ten times the long-term average atmospheric level in southern California. Thus the comparison in Table 10 represents the relative risk of damage from various pollutants.

For the natural organic colorants, litmus, Indian yellow and *aigami*, nitric acid-induced fading or color change was more rapid than that induced by ozone, while for the remaining natural colorants ambient ozone levels would pose the greater threat. In the case of the synthetic organics, most pigments, other than arylide yellow 10G and the mauve watercolor sample, are fairly stable toward nitric acid exposure, with alizarin crimson showing borderline sensitivity. Reflectance spectra for these samples are shown in Figures 5f–h.


(a) LITMUS
NATURAL RED 28
26 WEEKS
12 WEEKS
0 WEEKS
PERCENT REFLECTANCE
WAVELENGTH IN NANOMETERS
0
10
20
30
40
50
60
70
80
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620
640
660
680
700

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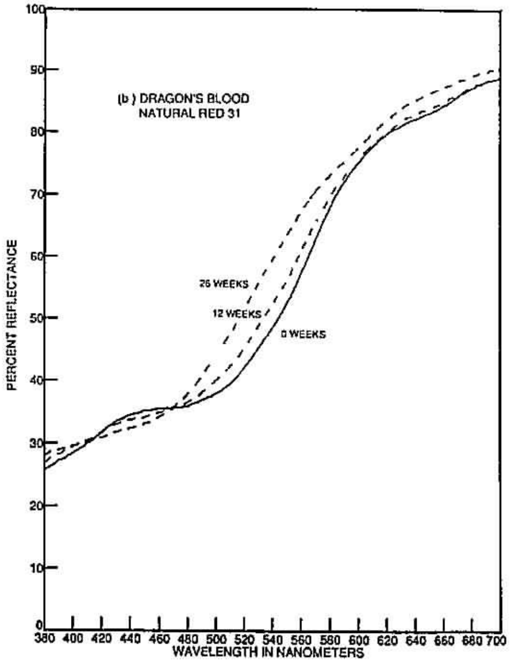
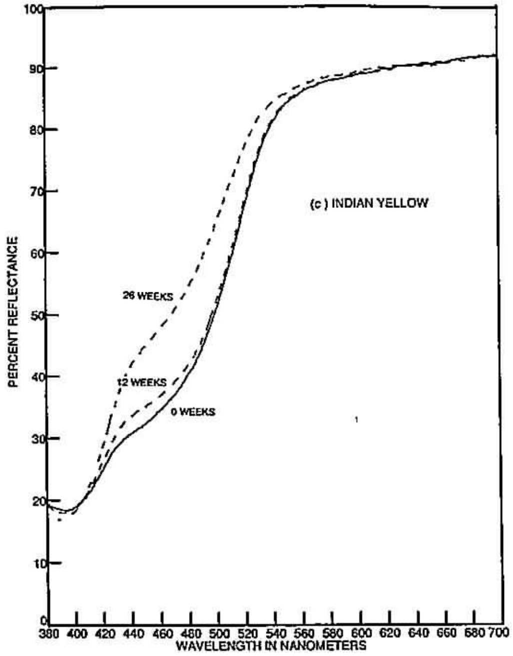

(b) DRAGON'S BLOOD
NATURAL RED 31
26 WEEKS
12 WEEKS
0 WEEKS
PERCENT REFLECTANCE
WAVELENGTH IN NANOMETERS
0
10
20
30
40
50
60
70
80
90
100
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700

b


(c) INDIAN YELLOW
26 WEEKS
12 WEEKS
0 WEEKS
PERCENT REFLECTANCE
WAVELENGTH IN NANOMETERS
0
10
20
30
40
50
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70
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90
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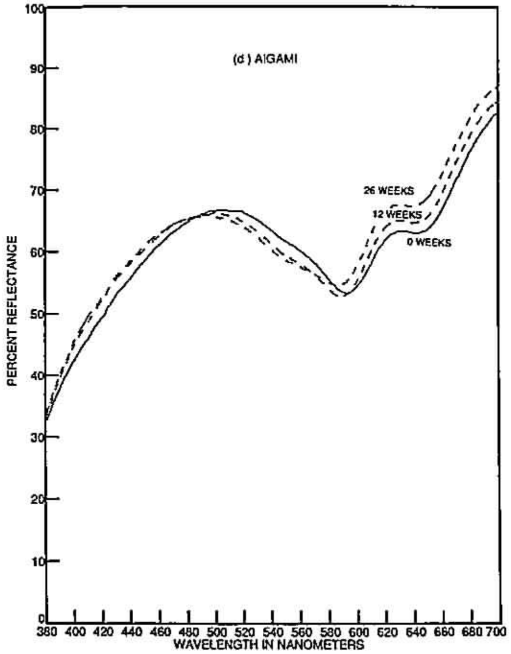
(d) AIGAMI
26 WEEKS
12 WEEKS
0 WEEKS
PERCENT REFLECTANCE
WAVELENGTH IN NANOMETERS
0
10
20
30
40
50
60
70
80
90
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380
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640
660
680
700

d

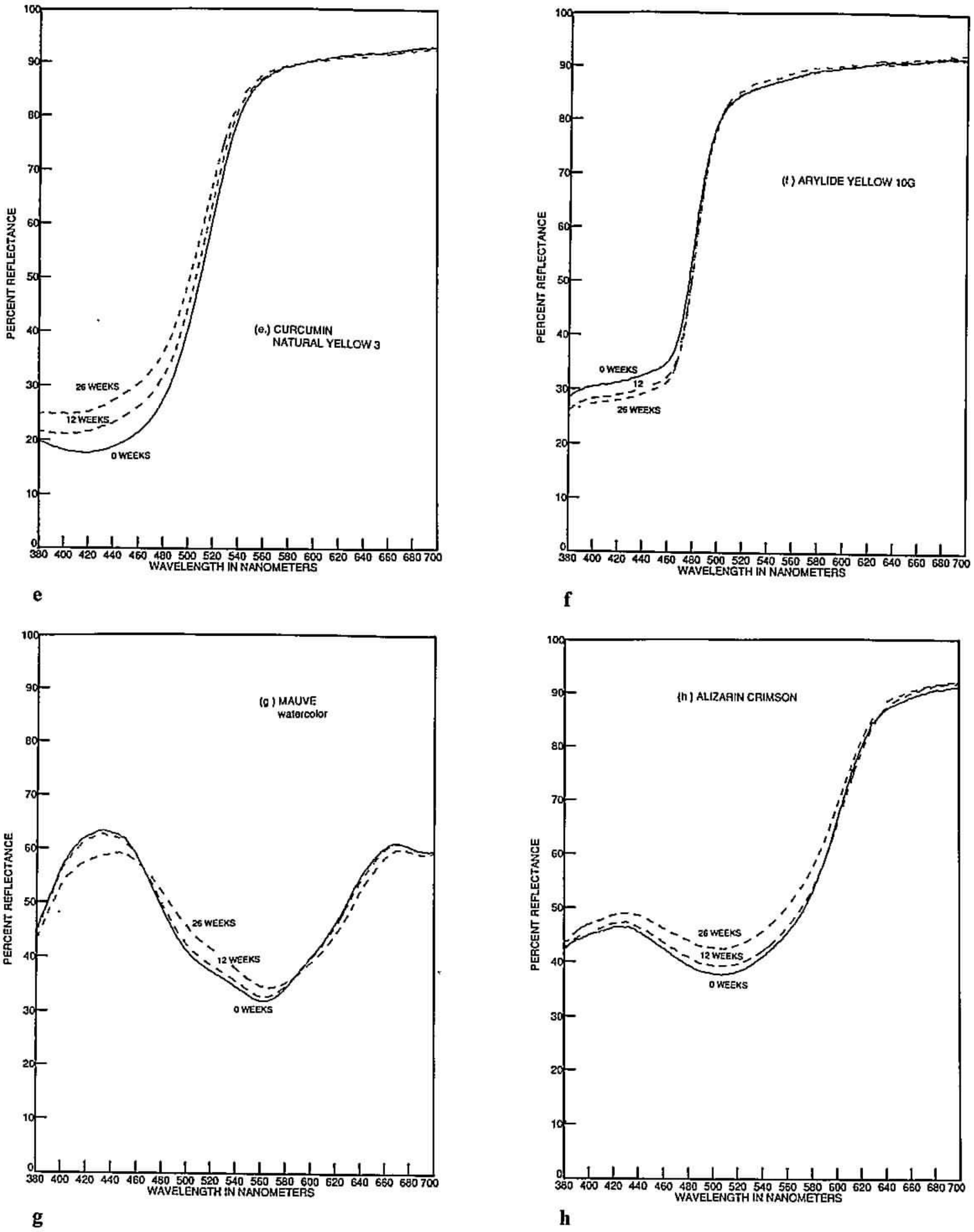

Figure 5 Reflectance spectra of colorants on paper exposed to 12ppb HNO_3 for 12 weeks followed by 40ppb HNO_3 for 12 weeks. (a) Litmus, (b) dragon's blood, (c) Indian yellow, (d) aigami, *(e) curcumin, (f) arylide yellow 10G, (g) mauve watercolor, (h) alizarin crimson.*

Table 8 Color changes of colorants moderately reactive toward nitric acid

Sample	*Week*	*CIE tristimulus values*			*Munsell color notation*		*Color difference ΔE*
		X	*Y*	*Z*			
Iron ink I	0	28·83	29·08	27·55	0·92Y	5·92/1·40	—
	12	30·47	30·89	29·91	1·59Y	6·07/1·25	1·81
	14	30·23	30·66	29·73	1·68Y	6·05/1·24	—
	26	33·69	34·30	32·97	2·32Y	6·35/1·30	3·10
Iron ink II	0	8·53	8·58	9·25	9·04YR	3·42/0·44	—
	12	9·65	9·75	10·28	0·99Y	3·63/0·52	2·36
	14	9·60	9·70	10·17	1·13Y	3·63/0·55	—
	26	11·83	11·99	11·75	2·52Y	4·00/0·85	4·57
Aigami	0	57·62	61·13	69·58	5·38G	8·11/0·87	—
	12	57·98	60·16	71·52	6·44BG	8·06/0·46	3·98
	14	58·11	60·49	72·06	6·67BG	8·08/0·55	—
	26	59·19	60·42	71·94	2·43PB	8·07/0·15	2·77
Arylide yellow 10G	0	77·04	85·29	47·36	0·73GY	9·30/5·50	—
	12	76·50	85·16	44·56	0·81GY	9·29/5·90	2·98
	14	76·76	85·47	45·34	0·92GY	9·31/5·82	—
	26	76·75	85·72	43·60	0·91GY	9·32/6·11	2·14
Alizarin crimson*	0	57·82	49·85	50·92	1·39R	7·45/5·79	—
	12	58·13	50·59	52·32	1·23R	7·49/5·51	1·45
	14	58·27	50·87	53·11	0·94R	7·51/5·42	—
	26	60·95	53·98	55·09	2·52R	7·70/5·05	2·77
Quercitron lake	0	70·35	72·40	51·72	3·22Y	8·70/3·72	—
	12	69·66	71·83	52·88	3·46Y	8·67/3·48	1·65
	14	70·16	72·37	53·63	3·50Y	8·70/3·43	—
	26	69·62	71·99	54·55	3·82Y	8·68/3·24	1·26
Persian berries lake	0	76·28	80·54	57·74	6·39Y	9·09/3·59	—
	12	76·48	80·83	60·11	6·89Y	9·10/3·31	1·92
	14	76·66	81·05	60·37	6·97Y	9·11/3·30	—
	26	76·99	81·31	61·89	7·01Y	9·12/3·14	1·15
Lac lake	0	56·23	50·49	52·86	2·02R	7·49/4·50	—
	12	57·44	51·71	53·00	3·19R	7·56/4·46	1·38
	14	57·93	52·33	54·18	2·88R	7·60/4·36	—
	26	58·69	53·19	54·09	3·95R	7·65/4·29	1·16

*Same dry pigment as alizarin crimson sample applied to Whatman filter paper in Table 7. This sample applied to watercolor paper.

The mauve watercolor contains the lake of a triphenylmethane dye. Other triphenylmethane compounds included in the study, basic fuchsin and pararosaniline base, also showed large color changes in the presence of nitric acid. Alizarin crimson is known to be extremely ozone fugitive, and is sensitive to NO_2 as well as HNO_3. Arylide yellow 10G changed when exposed to HNO_3, with an increase in chroma and a decrease in the reflectance of blue light. It was not sensitive to NO_2 exposure.

Orpiment and realgar were the only inorganic colorants tested that were affected by exposure to HNO_3 even at borderline levels. Previously both had been found to react in the presence of NO_2 [18]. Both samples of iron ink showed moderate color changes when exposed either to HNO_3 or to NO_2, and were still changing at the end of the exposure period.

Color difference values for some of the colorants considered to exhibit borderline color changes are shown in Figure 6. While none of

Table 9 Samples showing borderline color changes when exposed to nitric acid

Sample	*Week*	*CIE tristimulus values*			*Munsell color notation*		*Color difference ΔE*
		X	*Y*	*Z*			
Orpiment	0	80·93	85·48	70·07	8·17Y	9·31/2·60	—
	12	81·16	85·51	71·49	7·87Y	9·31/2·45	1·17
	14	81·59	85·94	72·79	8·08Y	9·33/2·35	—
	26	82·43	86·69	74·50	7·93Y	9·36/2·24	0·87
Gamboge	0	81·54	85·10	76·14	6·65Y	9·29/1·96	—
	12	81·47	84·96	77·57	6·84Y	9·28/1·81	1·18
	14	82·15	85·64	78·83	6·91Y	9·31/1·76	—
	26	82·88	86·42	80·14	7·14Y	9·35/1·70	0·52
Cochineal lake	0	60·87	53·07	55·79	0·56R	7·65/5·53	—
	12	60·09	52·55	56·07	0·03R	7·62/5·41	0·99
	14	60·69	52·99	56·45	0·05R	7·64/5·48	—
	26	60·88	53·49	57·15	0·10R	7·67/5·29	0·90
Weld lake	0	83·68	86·77	85·04	6·79Y	9·36/1·33	—
	12	84·09	86·98	86·86	6·41Y	9·37/1·21	1·18
	14	84·12	87·10	87·09	6·86Y	9·38/1·19	—
	26	84·71	87·65	88·19	6·79Y	9·40/1·15	0·45
Prussian blue	0	32·15	36·01	61·52	8·37B	6·49/5·41	—
	12	32·06	36·05	62·49	8·35B	6·49/5·62	0·92
	14	31·78	35·72	62·64	8·50B	6·46/5·74	—
	26	31·68	35·68	62·18	8·30B	6·46/5·68	0·43
Realgar	0	71·36	69·21	42·11	8·89YR	8·54/5·56	—
	12	70·79	68·45	42·19	8·63YR	8·50/5·51	0·95
	14	71·24	68·93	42·32	8·69YR	8·53/5·53	—
	26	71·65	69·27	42·67	8·60BR	8·54/5·53	0·23
Indigo, synthetic	0	37·91	39·61	53·04	0·12PB	6·76/1·97	—
	12	37·68	39·40	52·66	9·91B	6·74/1·94	0·20
	14	38·62	40·37	53·94	9·98B	6·81/1·96	—
	26	38·93	40·77	53·75	9·09B	6·84/1·79	0·77
Indigo	0	48·63	50·52	60·03	5·94BG	7·49/0·46	—
	12	48·47	50·41	60·05	6·59BG	7·48/0·50	0·19
	14	48·61	50·57	60·33	6·99BG	7·49/0·52	—
	26	49·44	51·51	60·61	2·59BG	7·55/0·49	0·95
Bitumen	0	54·98	55·30	48·70	0·20Y	7·78/2·29	—
	12	54·81	55·17	49·13	0·20Y	7·77/2·20	0·58
	14	54·28	54·67	48·56	0·32Y	7·74/2·21	—
	26	53·60	53·99	48·00	0·34Y	7·70/2·19	0·41

these showed color changes greater than a ΔE value of 2 during the course of this study, some, such as indigo (both natural and synthetic), displayed a steady color change over time and would have crossed that threshold during a more extended experiment.

3.3 *Natural colorants on silk*

The nitric acid fading behavior of the various silk cloth samples is not a good indicator of the relative stability of a particular colorant due to variations in the depth of shade of the dyed materials. It was possible, however, to establish some measure of the stability of Japanese silk cloths dyed with traditional colorants and procedures. A number of silk cloths dyed with natural colorants showed color changes upon exposure to nitric acid. *Enju, kariyasu* (with a

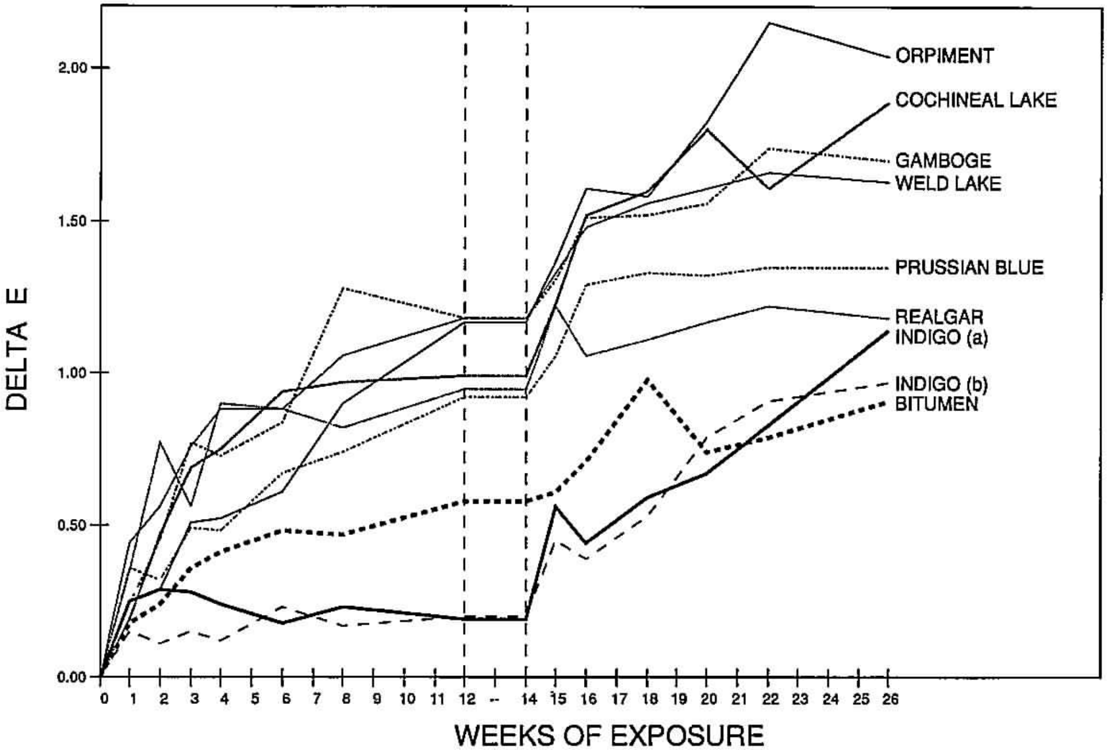

Figure 6 Observed color change, ΔE, over time for borderline reactive colorants on paper exposed to 12ppb HNO_3 during weeks 0 through 12 and 40ppb HNO_3 during weeks 14 through 26.

copper-containing mordant), *beni, ukon, akane, yama-momo, ai + enju* and *ai + kariyasu* were the most reactive and their color changes over time are shown in Figure 7.

In Table 11, ΔE values for the dyed silk cloths are compared to the results of the previous NO_2 fading study [18]. *Beni*, while sensitive to HNO_3, was not nearly so sensitive to NO_2. Most of the other samples found to be sensitive to HNO_3 were also sensitive to NO_2. A few samples that were reactive with NO_2 were not affected by HNO_3 in this study.

4 Discussion

Extrapolation of the results of these experiments to lower nitric acid concentration exposures delivered over longer periods of time is useful when trying to estimate effects that might be observed within museums where nitric acid levels are lower. In the case of the ozone-induced fading of alizarin crimson pigment samples, it has been shown that the extent of fading is directly related to the pollutant dose (concentration multiplied by duration of exposure) [32]. If that is also the case for nitric acid exposures, then linear extrapolation of the present results to equivalent doses delivered over different exposure times would be possible.

Data from Figures 3 and 4 can be used to examine this scaling hypothesis as it relates to nitric acid exposures. The total dose delivered during the first stage of the experiment (12 weeks × 12ppb HNO_3) is about the same as that delivered during the first four weeks of the second stage of the exposure (four weeks × 40ppb HNO_3). For many colorants that show a nearly linear rate of fading in both the first and the second 12 weeks of the experiment (e.g., mauve, basic fuchsin, Indian yellow, dragon's blood, alizarin crimson and the iron inks), the color changes (ΔE) over the first 12 weeks and over the following four weeks are approximately equal. The linear scaling hypothesis would be expected

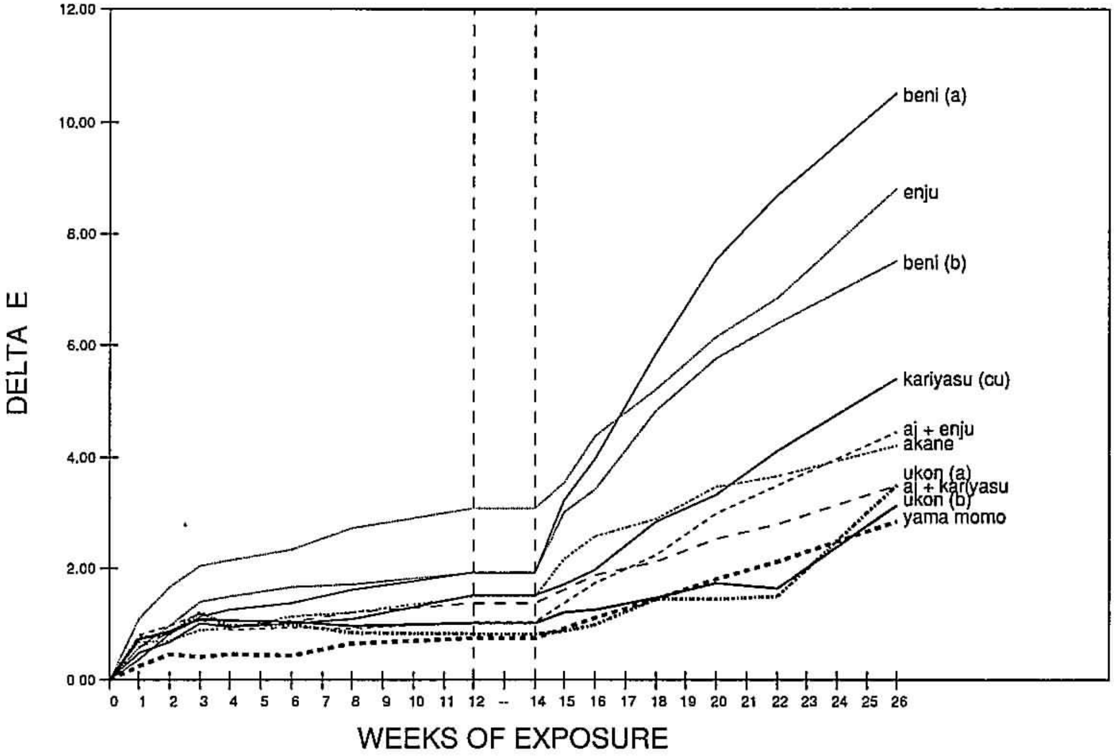

Figure 7 Observed color change, ΔE, over time for silk cloths dyed with traditional Japanese colorants exposed to 12ppb HNO_3 during weeks 0 through 12 and 40ppb HNO_3 during weeks 14 through 26.

to work well for such samples. The risk posed to such colorants when exposed to nitric acid in indoor atmospheres can be assessed. The nitric acid dose administered in the lower concentration, stage one experiment (12ppb for 12 weeks) could be experienced by a sample outdoors in central Los Angeles or in similar urban settings in a period of two and a half years and could be accumulated in seven years inside an unprotected museum in Los Angeles, such as the Sepulveda House [19]. A second set of colorants can be identified (e.g., litmus or pararosaniline base) that exhibit non-linear changes in ΔE over time (in some cases due to colorant depletion), and results for such colorants cannot be extrapolated as easily to account for altered exposure conditions.

Triphenylmethane colorants were found to be most susceptible to damage from atmospheric nitric acid. Closely related colorants not tested in this study could be expected to be similarly sensitive to nitric acid, including brilliant green, crystal violet, methyl green and pararosaniline chloride. Other colorants, such as dragon's blood, Indian yellow, curcumin (also turmeric), litmus, alizarin crimson and iron ink, suffered noticeable damage as a result of exposure to nitric acid vapor at concentrations similar to those found in urban atmospheres.

A comparison of the relative sensitivity of colorants to NO_2, ozone and nitric acid is shown in Tables 10 and 11. It was found that nitric acid-induced fading posed a more serious threat than that induced by ozone or NO_2 for litmus, Indian yellow, arylide yellow 10G, pararosaniline base and the Japanese silk cloth dye, *beni.* Ambient ozone levels, however, pose a greater threat for most of the other colorants tested, although a few of the natural organic colorants (e.g., quercitron lake, gamboge and *aigami*) as well as some natural colorants on silk cloths (e.g., *enju, yamamomo, zumi* and *shiō*) and the iron inks were most sensitive to nitrogen dioxide fading.

Procedures for the control of indoor nitric acid

Table 10 Comparison of color change (ΔE) of samples on paper exposed to different pollutants

Colorant name	*HNO_3*[a]	*NO_2*[b]	*Ozone*[c]
Natural organic colorants:			
Weld lake	1·2	0·9	3·4
Curcumin	6·5	14·5	41·8
Saffron	0·6	2·7	6·3
Quercitron lake	1·7	3·2	2·1
Persian berries lake	1·9	3·5	6·8
Gamboge	1·2	4·4	3·6
Cochineal lake	1·0	3·7	4·6
Madder lake	0·5	0·7	10·0
Lac lake	1·4	4·9	6·9
Litmus	12·7	1·0	2·7
Dragon's blood	4·3	7·6	17·2
Indigo	0·2	2·8	14·2
Van Dyke brown	0·5	0·5	1·6
Sepia	0·3	1·5	1·3
Bitumen	0·6	0·6	3·8
Indian yellow	2·5	0·6	2·0
Aigami	4·0	5·2	2·5
Synthetic organic colorants:			
Arylide yellow G	0·4	0·2	0·9[d]
Arylide yellow 10G	3·0	0·4	1·1[d]
Paliogen yellow	0·6	0·4	—
Toluidine red	0·3	0·7	2·4[d]
Bright red (wc)	0·5	0·4	no fading[e]
Scarlet lake (wc)	0·5	0·7	no fading[e]
Rose carthame (wc)	0·2	1·0	no fading[e]
Alizarin crimson	1·5	2·9	48·4[f]
Alizarin crimson (wc)	0·7	—	11·3[f]
Thioindigo violet	0·2	0·7	0·8[d]
Naphthol	0·6	0·5	1·7[d]
Permanent magenta (wc)	0·3	0·8	no fading[e]
Dioxazine purple	0·5	1·6	3·0[d]
Mauve (wc)	2·0	4·6	faded[e]
Phthalocyanine blue	0·3	1·1	7·2[d]
Prussian blue	0·9	1·0	2·1
Paliogen blue	0·3	2·6	—
Phthalocyanine green	0·2	0·5	—
Aniline black	0·7	0·5	—
Alizarin	7·8	—	16·8[f]
Indigo, synthetic	0·2	—	14·2
Basic fuchsin	3·8	—	7·0[d]
Pararosaniline base	27·8	—	no reaction[g]
Quinacridone red	0·5	—	0·6[d]
Acridone	0·3	—	—
Inorganic colorants:			
Chrome yellow (wc)	0·2	0·6	no fading[e]
Aureolin (wc)	0·2	0·3	—
Cadmium yellow medium	0·3	0·4	—
Manganese violet	0·4	0·8	1·4[d]
Vermilion (wc)	0·2	0·5	—
Orpiment	1·2	5·7	20·0
Realgar	1·0	10·6	21·2[d]
Inks:			
Iron ink I	1·8	5·8	3·7[d]
Iron ink II	2·4	7·4	3·1[d]

(a) This study, 12ppb nitric acid at 22°C, 50% RH for 12 weeks.
(b) Previous study [18], 500ppb NO_2 at 24°C, 50% RH for 12 weeks.
(c) Previous studies [5, 6], 400ppb ozone at 22°C, 50% RH for 12 weeks unless otherwise noted.
(d) Unpublished results for samples exposed to 400ppb ozone at 22°C, 50% RH for 12 weeks.
(e) Previous study [3], 300ppb ozone at 22°C, 50% RH for 90 days.
(f) Previous study [29], 356ppb ozone at 22°C, 49·5% RH for 95 days.
(g) Previous study [30], 10ppm ozone pulled through colorants on Teflon filters for 96 hours.

concentrations in museums are similar to those described previously for ozone control [32, 33]. These include nitric acid removal via activated carbon air-filtration [19] or other types of acid gas absorption or washing systems [34], use of reduced ventilation rates, enclosure within display cases, and protection behind glass or varnish layers.

In previous studies, we have shown how building ventilation systems can be redesigned to lower the indoor concentrations of ozone and airborne particles [32, 35]. Similar steps can be taken to reduce indoor nitric acid levels. Several ventilation strategies can be used either alone or in combination. The first step is to control air infiltration rates through the installation of a mechanical ventilation system in those cases where none exists. Air exchange rates can then be adjusted to minimize pollutant infiltration from outdoors provided that there are no overwhelming sources of air pollutants within the museum. As a further step, pollutant removal systems can be built into the ventilation system. Activated carbon filters placed in the outdoor air intake duct or in both the outdoor and recirculated air ducts of the ventilation system are particularly effective. This is because such filters will not only remove nitric acid but also the ozone contained in outdoor air which may react with NO_2 to produce additional nitric acid [36, 37]. Existing systems which employ an alkaline water wash for NO_2 and SO_2 pollutant removal should also remove nitric acid.

Table 11 Comparison of color change (ΔE) of silk cloths exposed to different pollutants

Colorant name	*HNO_3*		*NO_2*[c]	*Ozone*[d]
	Low[a]	*High*[b]		
Enju	3·1	5·8	7·8	1·3
Kariyasu (Al)	0·6	1·1	0·6	1·1
Kariyasu (Cu)	1·5	3·9	1·5	1·8
Kihada	0·7	0·9	0·4	1·6
Kuchi nashi	0·5	0·6	2·5	5·0
Ukon (Al)	1·0	2·1	1·4	1·9
Ukon (acetic acid)	0·8	2·7	1·2	1·5
Woren	1·0	1·5	1·2	1·0
Yamahaji	0·6	0·7	1·7	2·1
Yama-momo	0·8	2·1	3·2	2·2
Zumi	0·7	1·1	3·1	2·4
Shiō	0·4	0·4	3·3	1·3
Seiyo akane	0·5	1·4	1·0	1·1
Akane	1·5	2·7	2·1	4·4
Enji	0·2	1·0	0·7	0·8
Shiko	1·2	1·2	1·6	1·7
Suo	1·3	0·5	1·8	1·1
Beni (orange)	1·9	5·6	0·5	1·1
Beni (red)	1·9	8·6	—	0·6
Ai (light blue)	0·2	0·3	2·0	1·0
Ai (med. blue)	1·0	1·0	—	3·8
Ai (dark blue)	0·6	0·4	—	3·4
Ai (very dark blue)	0·3	0·7	—	2·2
Ai + enju	1·0	3·4	3·6	4·1
Ai + kariyasu	1·3	2·1	1·1	7·7
Ai + kihada	0·8	1·5	1·9	13·0
Shikon	0·6	0·5	2·0	5·2

(a) This study, 12ppb nitric acid at 22°C, 50% RH for 12 weeks.
(b) This study, 40ppb nitric acid at 22°C, 50% RH for 12 weeks.
(c) Previous study [18], 500ppb NO_2 at 24°C, 50% RH for 12 weeks.
(d) Previous study [6], 400ppb ozone at 22°C, 50% RH for 12 weeks.

Modifications to the ventilation system of a museum can be costly and are not always practicable. It may, however, be possible to protect sensitive objects by using display cases which will reduce the effective air exchange rate in the vicinity of an object, thus allowing an extended time for nitric acid depletion by reaction with nearby surfaces within the display case and preventing the easy replenishment of the HNO_3 that has been lost to the interior of the display case.

Framing under glass, in the case of watercolors and paintings, can also serve as protection against attack from atmospheric pollutants including nitric acid. A frame acts as a very tight, small display case, and thus should contain a negligible amount of HNO_3. Ozone exposure experiments conducted on an alizarin crimson pigment sample applied to watercolor paper and then framed under glass showed that pollutant intrusion was prevented, at least in the short term [32].

In summary, a wide range of control measures exists, many of which are both simple and inexpensive. With careful planning, it should be possible to protect most museum collections from damage due to atmospheric nitric acid.

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Suppliers

Arches 140lb. hot pressed water color paper: The Art Store, 7200 W. Beverly Blvd, Los Angeles, CA 90036, USA.

Purafil: Purafil, Inc., P.O. Box 80434, Atlanta, GA 30366, USA.

Drierite desiccant: W. A. Hammond Drierite Co., P.O. Box 460, Xenia, OH 45385, USA.

Nitric acid (HNO_3) permeation tube: VICI Metronics, 2991 Corvin Drive, Santa Clara, CA 95051, USA.

Nitrogen oxides monitor: Thermo Electron Corp., 8 West Forge Parkway, Franklin, MA 02038, USA.

Nylasorb nylon filters: Gelman Sciences, 600 South Wagner Road, Ann Arbor, MI 48106, USA.

Whatman filter paper: Whatman Lab Sales, P.O. Box 1359, Hillsboro, OR 97123, USA.

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Résumé—L'expérience montre que l'acide nitrique atmosphérique est susceptible de provoquer des pâlissements ou des changements de couleurs dans un grand nombre de colorants utilisés par les artistes. Soixante-dix-neuf échantillons ont été exposés à 12 et 40ppb d'acide nitrique dans de l'air à 22°C et 50% HR, au cours de deux expériences successives de 12 semaines chacune. Environ la moitié (27 sur 52) des colorants appliqués sur papier ont montré une sensibilité à l'acide nitrique, et une majorité (22 sur 27) des vêtements japonais en soie teinte ont manifesté une réactivité à l'acide nitrique à la concentration la plus élevée. Avec une concentration de 12ppb sur 12 semaines, la dose totale d'acide nitrique (concentration multipliée par la durée d'exposition) employée pour cette étude est équivalente à celle reçue à l'intérieur d'un musée de Los Angeles pendant une période de sept ans.

Zusammenfassung—Experimente zeigen, daß atmosphärische Salpetersäuredämpfe in der Lage sind, eine Reihe wichtiger Künstlerfarben auszubleichen und ihre Farbe zu verändern. Hierzu wurden in zwei aufeinanderfolgenden Versuchen 79 Proben einem Salpetersäuregehalt von 12 und 40ppb in Luft bei 22°C und 50% relativer Feuchte ausgesetzt. Ungefähr die Hälfte (27 von 52) der auf Papier aufgebrachten Farbstoffe zeigte sich gegenüber Salpetersäure empfindlich. Die meisten der auf japanische Seide aufgezogenen Farbstoffe (22 von 27) erwiesen sich gegenüber Salpetersäure in der höheren Konzentration reaktiv. Eine Salpetersäurekonzentration von 12ppb über 12 Wochen entspricht der Salpetersäuredosis (Dosis = Konzentration mal Expositionsdauer), die der im Innenraum eines Museums ohne besondere Schutzmaßnahemn im Stadtkern von Los Angeles über einen Zeitraum von sieben Jahren entspricht.