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THE INFLUENCE OF OXYGEN ON THE FADING OF ORGANIC COLORANTS

J. S. Arney, A. J. Jacobs and R. Newman

Abstract—The feasibility of using an oxygen-free environment to retard the rate of fading of colorants has been explored. The factors by which the life expectancy of a variety of colorants would be multiplied in such an environment were determined by accelerated fading experiments. In general, the life expectancy of most colorants can be increased by such techniques, but a complete halt of the fading process has not been generally observed. In addition, some colorants were found to fade more quickly in an oxygen-free environment. However, it has also been found that at least 90% of the beneficial influence of an oxygen-free environment can be realized with as much as 0.2% oxygen (1% air) remaining in the environment of the colorant. Such an environment might be achieved and maintained at relatively little expense.

1. *INTRODUCTION*

THAT OXYGEN in our atmosphere can cause the deterioration of many organic materials found in museum objects has long been recognized[1], and the general nature of these oxidative processes has been reviewed by Feller.[2,3] The possibility of decreasing the rate of fading of organic colorants in museum objects by placing the objects in an oxygen-free environment has, from time to time, been suggested, and recent work by scientists in the conservation profession has made possible the construction of "microenvironmental" cases capable of maintaining an atmosphere of an inert gas with as low as 0.06% residual oxygen.[4,5] Nevertheless, the use of such cases for the storage or display of museum objects has not been widespread. This is so in part because of the expense involved in the construction and maintenance of such cases and in part because of the absence of quantitative information to indicate the degree of enhancement in the life expectancy of colorants under an inert gas environment.

The objectives of this project were to determine (1) how effective an oxygen-free environment is in decreasing fading rates of organic colorants and (2) how much oxygen must be removed from a display case before a significant decrease in the rate of fading is achieved. The results indicate that the fading of many organic colorants is not halted entirely by removal of oxygen and that the degree of enhancement of life expectancy varies from colorant to colorant. On the other hand, the results also suggest that for most organic colorants at least 90% of the beneficial influence of a completely oxygen-free environment can be achieved in a display case containing as much as 0.2% residual oxygen.

2. *BACKGROUND*

IT HAS LONG been known that the light-induced fading of many organic colorants can be inhibited by replacing the air surrounding the colorant with an oxygen-free gas.[1,6] However, a complete halt of the fading process under such conditions is generally not observed. In accounting for this non-zero rate of fading, it might seem reasonable to assume that chemical reactions are taking place that do not require oxygen. However, it is not possible to eliminate completely all of the oxygen from a container, and fading reported "in the absence of oxygen" might be a result of reactions with the residual oxygen. Thus, a practical question arises concerning how low a level of residual oxygen constitutes an "oxygen-free" environment.

Thomson has suggested that the oxidative degradation of most organic materials would show little or no decrease in rate of degradation until parts-per-million levels of oxygen were achieved.[7] Figure 1, curve A, illustrates the relationship between fading rate and oxygen concentration that might be observed if Thomson's prediction were to apply.

However, Giles has suggested that the rate of fading of most organic colorants should decrease linearly with a decrease in oxygen concentration[8], as shown in Figure 1, curve B. If curve B were to apply, then fading could be decreased by 90% with as much as 2% residual oxygen surrounding the colorant. On the other hand, if curve A were to apply, then extremely rigorous measures would be required to achieve a significant enhancement in the permanence of a colorant. Although display cases capable of maintaining such an environment have been constructed[4], the cost of construction and maintenance are prohibitive.

We have found only one report, published by Lasareff in 1912[9], quantitatively relating rates of fading to oxygen concentration. Lasareff reported that the fading rates of two cyanine dyes decreased linearly (curve B) with a decrease in oxygen concentration. Our research was undertaken to obtain additional data on rate versus oxygen-concentration relationships.

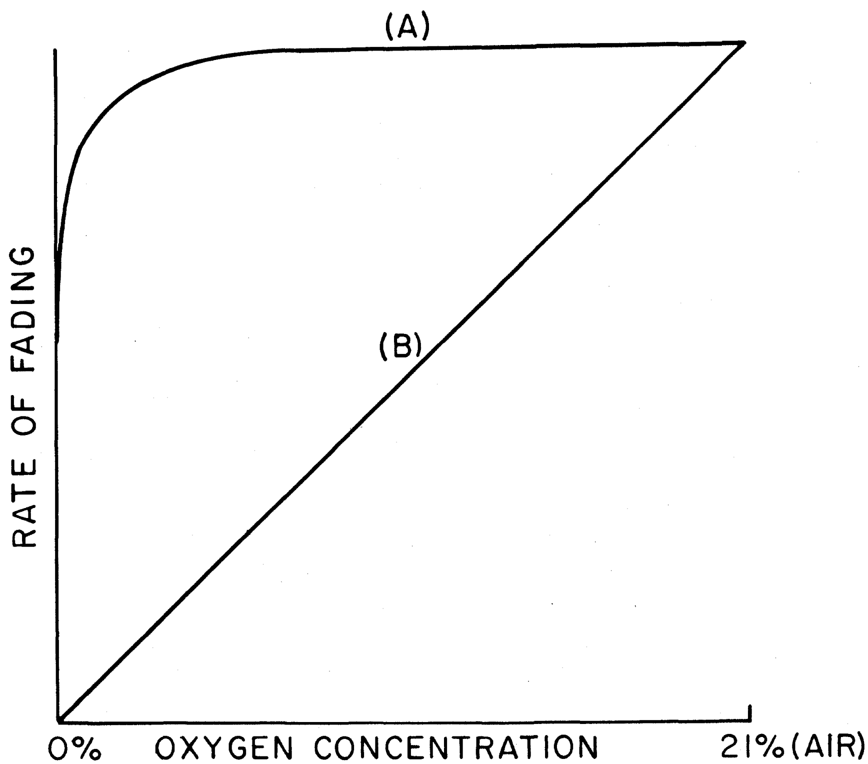

FIG. 1 Fading-Rate Versus Oxygen-Concentration Relationships Suggested by Thomson (Curve A)[8] and Giles (Curve B)[9].

3. *EXPERIMENTAL*

3.1 *Colorant Samples*

The colorant systems listed in Table I were selected for study from those on hand in our laboratory, and all were found to be particularly fugitive. Although these colorants represent only a small sample of the colorants one might encounter in museum objects, they include a variety of molecular types. Thus, we felt they would be representative of systems that one might wish to protect with an oxygen-free environment.

3.2 *Sample Preparation*

Rates of fading of the colorant systems listed in Table I were determined under various concentrations of oxygen ranging from 21% (an atmosphere of air) to 0% (nitrogen). Control of the oxygen concentration was achieved by sealing the test samples in pyrex glass tubes as shown in Figure 2. The tubes were evacuated, filled with dry air (R.H = 0%) and then evacuated to a pre-determined pressure. Dry nitrogen was then allowed to enter the tubes to bring the total pressure up to one atmosphere.

Oxygen concentrations are expressed relative to the concentration of oxygen in one atmosphere of air, as shown in equation 1,

$$\text{relative Oxygen concentration} = P/Pa \tag{1}$$

where P and Pa are the partial pressures of oxygen in the tube and in an atmosphere of air, respectively. The lowest oxygen concentration achieved in this project was $P/Pa = 0.0013$. The highest oxygen concentration examined was $P/Pa = 1.00$.

3.3 *Accelerated Fading*

The sealed pyrex tubes containing the colorant samples were exposed to a bank of G.E. Daylight fluorescent tubes (F48T12). The average intensity of light reaching the samples was 1×10^4 lux. Each sample was exposed for a known amount of time, and the total exposure for each sample, in terms of lux-hours, was calculated. Under the experimental conditions, the total light striking the samples undoubtedly included some ultraviolet radiation above 280 nm. No attempt was made to differentiate the influence of ultraviolet and visible light.

3.4 *Reflectance Measurements*

Reflectance measurements were made on the colorant samples before and after exposure to light. A Kollmorgen model D-1 "Color-Eye" reflectance spectrophotometer, modified for small area viewing, was used. Measurements were made relative to barium sulfate at the wavelength shown in Table I. The specular component of the reflected light was excluded in the measurement.

3.5 *Determination of Fading Rates*

Rates of fading were expressed as relative rate constants, k_r, defined in Equation 2.

$$k_r = \frac{\text{(RATE AT A GIVEN OXYGEN CONCENTRATION)}}{\text{(RATE AT } P/Pa = 1)} \tag{2}$$

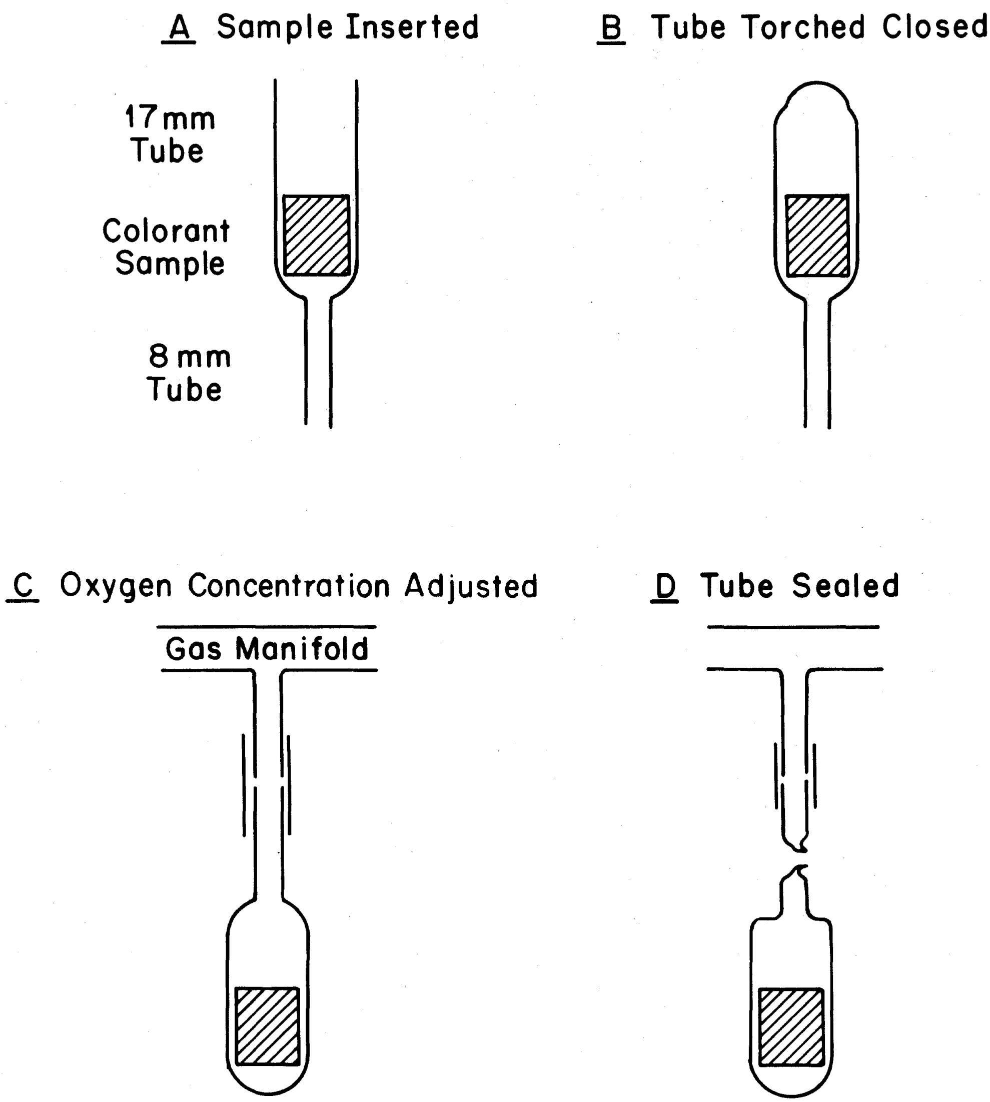

FIG. 2 Preparation of Sample Tubes with Atmospheres of Known Oxygen Concentration.

Values of k_r were obtained experimentally by dividing the time required for a colorant sample to fade an arbitrarily chosen amount by the time required to fade the same amount at the chosen oxygen concentration. Times were expressed in terms of lux-hours of exposure. Full discussions of this time-ratio method of kinetic analysis can be found in the references.[10,11]

The advantage of expressing the rate of fading in terms of k_r and the oxygen concentration in terms of P/Pa is that the influence of oxygen concentration on the fading of all of the colorants can be compared directly regardless of the lightfastness differences between the colorants. Thus, similarities and differences in the responses of colorants to changes in oxygen concentration can be seen easily.

3.6 *Reporting of Data*

From data obtained on k_r versus P/Pa, appropriate statistical regressions were performed to determine the value of k_r at P/Pa = 0 (zero oxygen concentration). Values of k_r at P/Pa = 0 are listed as i in Table II. Error limits are the 95% confidence intervals obtained from the regression calculations. Correlation coefficients, r^2, are also reported. In addition, the inverse, 1/i, is given in Table II. The value of 1/i is an estimate of the factor by which the life expectancy of the colorant in air would be multiplied if placed in an oxygen-free atmosphere.

4. *RESULTS*

VALUES of k_r were determined for the colorants listed in Table I under atmospheres with relative oxygen concentrations, P/Pa, ranging from 1.00 to 0.0013. The results of these experiments fell roughly into four experimental categories, as discussed below.

TABLE I

COLORANT SYSTEMS EXAMINED

No.	Commercial Name	System	Composition	Initial Reflectance[(a)]
1	Carmine	oil paint[b]	CI 75470	34% (560)
2	Felt Pen Green	felt marker[c]	acidic triphenylmethane	8.8% (640)
3	Geranium Lake	oil paint[b]	CI 45380	33% (540)
4	Alizarin	water color[d]	CI 58000	27% (520)
5	Gamboge	dye on paper[e]	CI Natural Yellow 24	37% (440)
6	ISO Blue #2	dye on wool[f]	CI 42740	4.2% (620)
7	ISO Blue #1	dye on wool[f]	CI 42735	5.6% (620)
8	Felt Pen Yellow	felt marker[c]	acidic triphenylmethane	25% (480)
9	Gamboge	water color[d]	CI Natural Yellow 24	26% (440)
10	Mauve	water color[d]	CI 42535	43% (560)
11	Felt Pen Red	felt marker[c]	acidic triphenylmethane	5.5% (520)
12	Carmine	water color[d]	CI 75470	45% (560)
13	Purpurin	dye on paper[e]	CI 75410	26% (480)
14	Carmine	dye on paper[e]	CI 75470	40% (560)
15	Alizarin	oil paint[b]	CI 58000	41% (520)
16	Vermillion Azo	oil paint[b]	azo pigment	49% (500)
17	Prussian Blue	oil paint[b]	CI Pigment Blue 27	45% (660)

[a]Reflectance before fading relative to $BaSO_4$ at the wavelength indicated.
[b]Oil paint mixed with flake white and applied to a glass slide with a spatula. Samples were dried two weeks at 20°C before exposure to light.
[c]Commercial felt marker ruled onto Strathmore 2 ply paper.
[d]Commercial water color brushed onto Strathmore 2 ply paper.
[e]Solution of dye applied to Whatman's #1 paper by immersion.
[f]Commercially dyed wool cloth used as ISO fading standard R105 (BS1006).

4.1 *Linear Rate Versus Oxygen Concentration*

Colorants #1 through #4 were found to fade at rates that varied linearly with oxygen concentration. The data for colorants #2 and #3, shown in Figure 3, are typical examples. A linear regression of k_r versus (P/Pa) allowed an estimate of the rate of fading in the absence of oxygen, and these rates are shown in Table II (A) as i. Colorant #2 appears to fade significantly (i > 0) in the absence of oxygen.

4.2 *Linear Rate Versus Square Root of Oxygen Concentration*

The rates of fading of colorants #5 through #11 did not decrease linearly with oxygen concentration but appeared to turn down sharply at the lower oxygen concentrations. Colorant #9, shown in Figure 3, is a typical example. It was found, empirically, that the rate of fading of colorants #5 through 11 varied linearly with the square root of the oxygen concentration, as shown in Figure 4 for colorants #8, #9, and #10. A linear regression of k_r versus $(P/Pa)^{1/2}$ allowed an estimate of the rate of fading of these colorants in the absence of oxygen, and these rates are shown in Table II (B) as i. Colorants #5 through #8 appear to fade significantly (i > 0) in the absence of oxygen.

TABLE II

SUMMARY OF DATA ON THE INFLUENCE OF OXYGEN CONCENTRATION ON THE FADING RATE OF COLORANTS

	(A) Linear Rate Versus Oxygen Concentration		
Colorant	*i*	r^2	*1/i*
1	.04 ± .10	.949	25
2	.48 ± .05	.968	2.1
3	.02 ± .05	.999	50
4	.08 ± .08	.961	13
	(B) Linear Rate Versus Square Root of Oxygen Concentration		
Colorant	*i*	r^2	*1/i*
5	.16 ± .04	.975	6.3
6	.34 ± .06	.980	2.9
7	.21 ± .07	.968	4.8
8	.36 ± .07	.938	2.8
9	.12 ± .08	.939	8.3
10	.04 ± .05	.974	25
11	.09 ± .08	.986	11
	(C) Poorly Correlated Data		
Colorant	*i*	r^2	*1/i*
12	.08 ± .03	.728	13
13	.14 ± .16	.592	7.1
14	.33 ± .24	.382	3.0
15	.32 ± .26	.815	3.1
	(D) Fading Accelerated by Absence of Oxygen		
Colorant	*i*		*1/i*
16	2.5		0.4
17	5.0		0.2

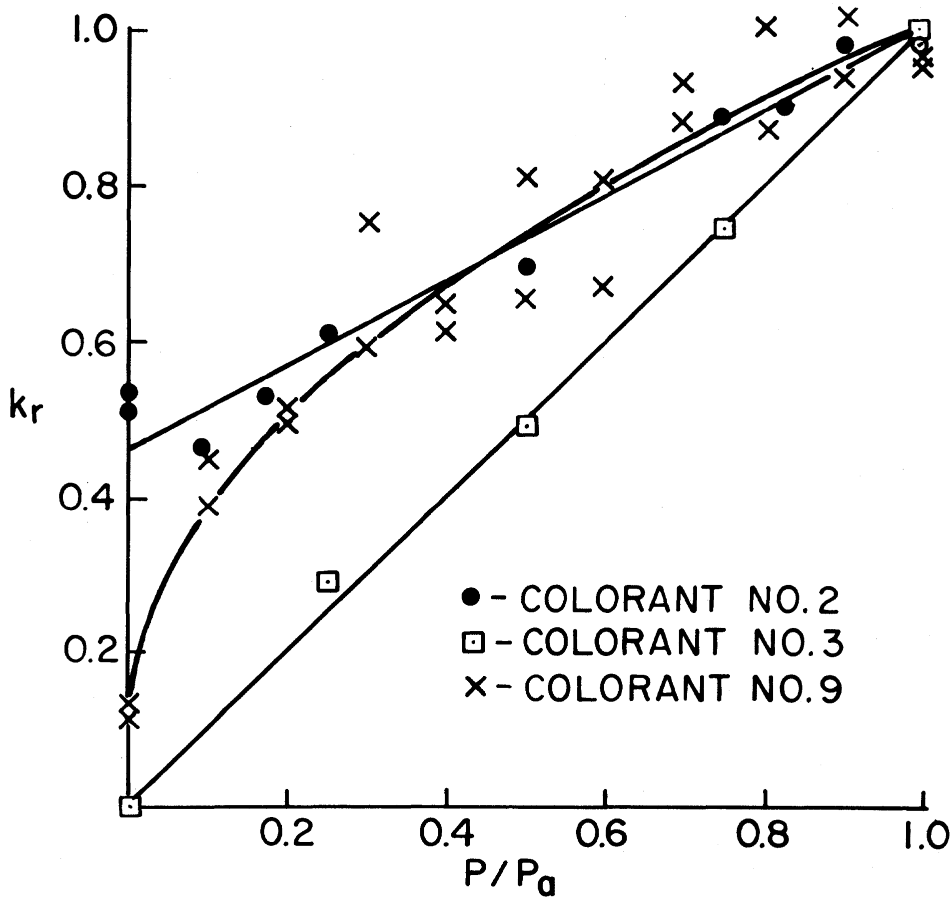

FIG. 3 Relative Fading Rate Versus Relative Oxygen Concentration for Colorants #2, #3, and #9.

4.3 *Experimentally Uncertain Data*

Colorants #12 through #15 were found to fade less rapidly in the absence of oxygen, but the values of k_r obtained were not of sufficient precision to allow an interpretation of the relationship between k_r and (P/Pa). Linear regressions of the data with respect to both (P/Pa) and $(P/Pa)^{1/2}$ were performed. The values of i and the 95% confidence intervals for i were roughly the same for both regressions. The values of i given in Table II (C) represent the values obtained from the regression that gave the highest correlation, r^2.

4.4 *Rate Increase with a Decrease in Oxygen Concentration*

Colorants #16 and #17 were found to fade more quickly at P/Pa = 0.0013 than at P/Pa = 1.00. Such behavior has been observed for a number of colorant systems[12,13,14], and extensive studies of these two colorants were not carried out.

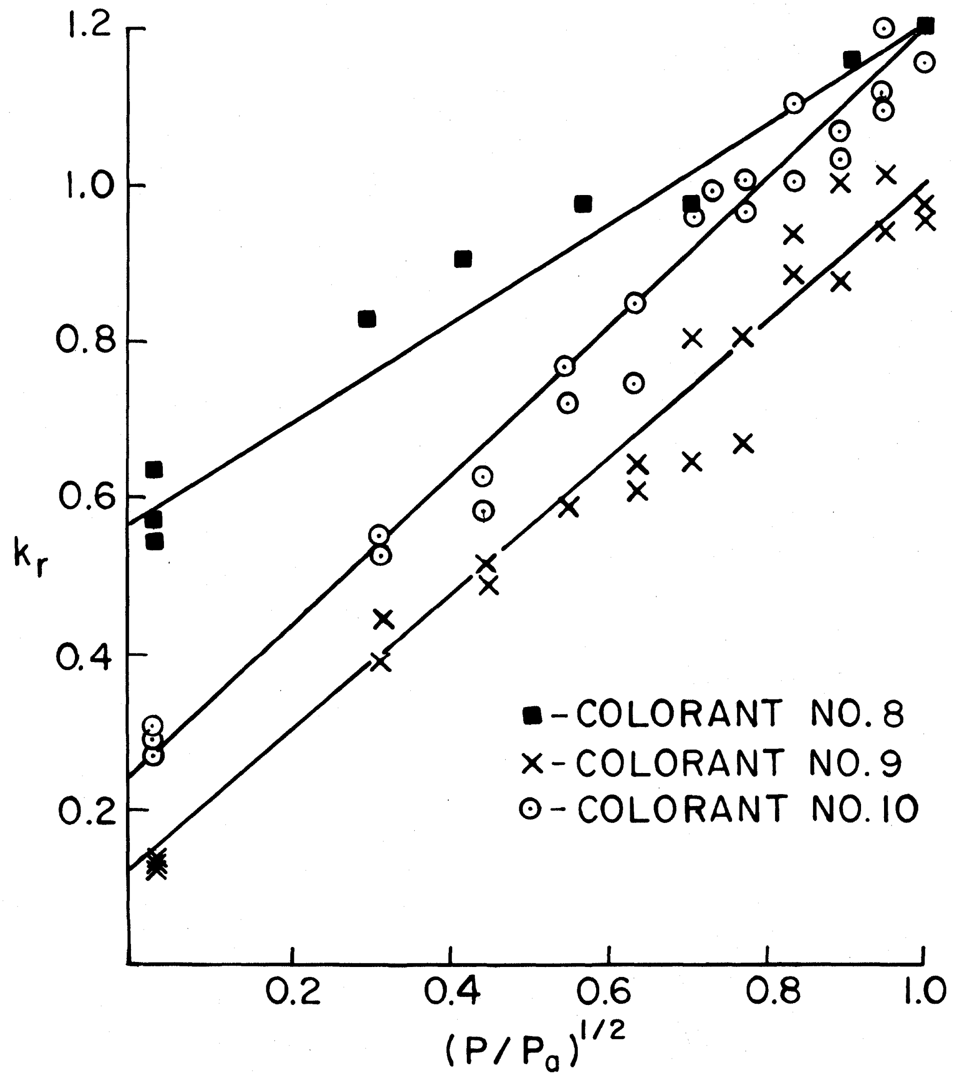

FIG. 4 Relative Fading Rate Versus the Square Root of the Relative Oxygen Concentration for Colorants #8, #9, and #10. (The data for colorants #8 and #10 have been shifted vertically by 0.2 rate units for clarity.)

5. *DISCUSSION AND CONCLUSIONS*

THE LINEAR RELATIONSHIP between fading rate and oxygen concentration observed for colorants #1 through #4 is in accord with the prediction of Giles[8] and the observations reported by Lasareff.[9] However, a nonlinear relationship between k_r and P/Pa was found to be the most common pattern of behavior. The down-turn in rate at lower oxygen concentrations, though less pronounced than expected, is nonetheless in general accord with the prediction of Thomson.[7] Furthermore, the square root of (P/Pa) was found to correlate linearly with the fading rate of colorants #5 through #11. This behavior suggests the occurrence of free-radical autoxidation reactions.[15,16]

The linear and square root relationships indicate that the beneficial influence of an oxygen-free environment can be obtained without the need to reduce the oxygen concentration to the parts-per-million level suggested by Thomson.[7] As much as 0.2% oxygen (equivalent to $P/Pa = 0.01$) would appear to give at least 90% of the effectiveness of a completely oxygen-free environment. Furthermore, a 0.2% oxygen concentration might be achieved easily in a practical situation at relatively little expense.[17]

From the data in Table II, one can estimate the practical benefit of an oxygen-free environment. The inverse of the relative rate at $P/Pa = 0$, ($1/i$ in Table II) is the factor by which the life expectancy of the colorant would be multiplied if displayed in the absence of oxygen. In general, a significant enhancement in life expectancy ($1/i > 10$) is not observed. Furthermore, colorants #16 and #17, as well as many others reported in the literature[12,13,14], fade more rapidly in the absence of oxygen. Thus, although an inexpensive display case might be constructed that is capable of achieving better than 90% of the efficiency of a truly oxygen-free environment, such a display case would be useful only if the colorants in an object have been identified, are known to be particularly fugitive, and are known to benefit significantly from an oxygen-free environment.

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