

Organic Solid Photochromism by Photoreduction Mechanism: Thionine-Reductant System

HIROYOSHI KAMOGAWA, SEIICHI KATSUTA, and MASATO
NANASAWA, *Department of Applied Chemistry, Yamanashi University,
Kofu, Japan 400*

Synopsis

Reversible color fading of various kinds of papers coated with thionine-reductant compositions with irradiation by visible light were investigated. Water-repellent papers, when coated with aqueous compositions containing thionine, triethanolamine, and PVA, indicated the most rapid reversible color-fading (photochromism); the color-fading rate occurred in decreasing order: thionine, azure C, azure B, and methylene blue. Infrared spectral changes around 1600 cm^{-1} with irradiation corresponded exactly to visible spectral changes, denoting that the photoredox reaction of thionine occurs even in the solid PVA matrix.

INTRODUCTION

Thiazine dyes, such as thionine in aqueous solutions, undergo reversible color fading by visible light in the presence of a suitable reductant such as ferrous ion.¹ Thionine and its *N*-methyl derivatives, together with a suitable reductant such as triethanolamine (TEA), when linked to vinyl polymer backbones as pendants, indicate reversible photocolor fading in the solid state.²⁻⁴

Simple addition of thionines and reductants to a matrix polymer is sufficient for some purposes, especially when a moisture-sensitive system is admitted. In the present study we used a system consisting of thionine and a reductant in solid PVA matrix. A systematic study of reversible color fading of the films deposited on substrate papers by visible light has been done.

RESULTS AND DISCUSSION

Infrared-Spectral Change with Color Fading by Visible Light

A PVA film containing thionine and triethanolamine (TEA) was irradiated by visible light from a 500-W tungsten lamp. A large difference around 1600 cm^{-1} in infrared spectrum (IR), which could be attributed to the change in the quinoid structure of thionine,⁵ was recognized between IRs before (blue-colored; abs peak, 610 nm) and immediately after irradiation (colorless) (Fig. 1). The IR change around 1600 cm^{-1} corresponds exactly to the visible spectral change, the complete recovery of color (visible spectrum) also affording the complete recovery of the IR spectrum.

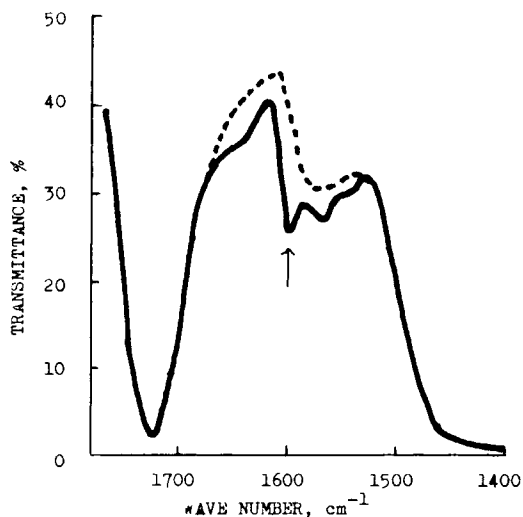


Fig. 1. IR-spectral change of a PVA film containing 2% of thionine and 20% of TEA by 5-min irradiation at a distance of 30 cm from the lamp. (—) Before irradiation and after complete recovery (dark-blue colored); (---) immediately after 5-min irradiation (colorless).

Effect of the Kind of Thiazine Dyes

Figure 2 indicates a typical change in absorption spectrum for the thionine-reducant system in PVA matrix deposited on a paper with water-repellent coating (Tomoegawa, for bottle label use; paper T). The blue color (abs max, 610 nm) of the paper with an absorbance of approximately 1.0 faded rapidly with visible irradiation. The irradiated paper, when stored in a desiccator at constant rel-

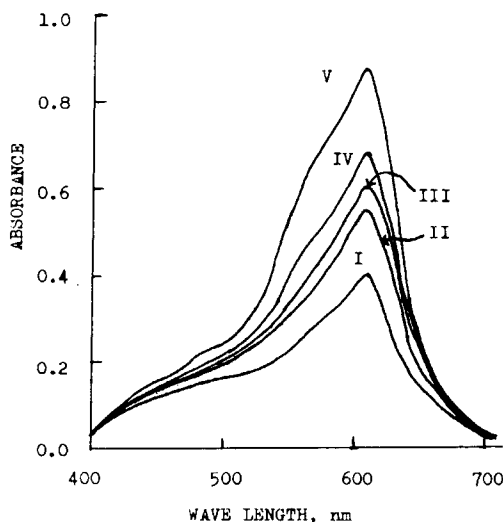


Fig. 2. Photochromic spectral change of paper T coated with a PVA containing 1% of thionine and 10% of TEA (58% RH). (I) Immediately after 10-s irradiation at a distance of 30 cm from the lamp; (II, III, IV) curves obtained at 15, 30, and 60 min after irradiation, respectively; (V) before irradiation and after complete recovery.

TABLE I
Effect of Kind of Thionines^a

Thionines	Abs Peak (nm)	A/A ₀ at RH (%) ^b		
		84	58	30
Thionine	610	0.46 (45) ^c	0.46 (45)	0.48 (45)
Azure C	610	0.64 (43)	0.68 (80)	0.71 (130)
Azure B	650	0.67 (40)	0.68 (100)	0.82 (100)
Methylene blue	665	0.75 (58)	0.79 (70)	0.80 (80)

^a Paper T coated with a solution consisting of 0.01 g of dye, 0.1 g of TEA, 1.0 g of PVA, and 10 mL of water was used.

^b A = Absorbance at abs max immediately after 10-s irradiation at a distance of 30 cm from a 500-W tungsten lamp. A₀ = absorbance before irradiation.

^c Figures in parentheses indicate 50% recovery times zero (min) at 20°C.

ative humidity (RH), gradually recovered its original color. The recovery was complete except for exposure to an extremely intense light.

In Table I are given the results obtained with various thiazine dyes. Although both color fading and especially recovery rates, are affected by RH, as in the case of pendant polymers,⁴ the light sensitivity at each RH is decreased with each replacement of the amino hydrogens of thionine by the methyl group, which corresponds to the bathochromic effect of the *N*-methyl group to afford higher values of absorption maximum. Since the *N*-methyl substituent also decreases the dark oxidation potential of thionine,⁶ higher dark oxidation potentials might afford higher color-fading rates. An analogous result was also obtained in the case of the photoreduction of viologen dications in solid polymer matrices.⁷

Effect of the Kind of Reductant

Table II indicates the results obtained by changing the kind of reductant. Both light (color fading) and dark (recovery) reactions are remarkably rapid for TEA as compared with others, although all experiments indicated complete reversibility.

TABLE II
Effect of Kind of Reductant^a

Reductant	A/A ₀ at RH (%) ^b		
	84	58	30
EDTA	0.80 (160) ^c	0.83 (200)	0.85 (210)
EDTA—diNH ₄ ⁺ salt	0.84 (70)	0.86 (100)	0.87 (150)
EDTA—diNa ⁺ salt	0.82 (75)	0.85 (100)	0.89 (120)
H ₂ NCH ₂ CH ₂ OH	0.96 (60)	0.96 (110)	0.98 (120)
HN(CH ₂ CH ₂ OH) ₂	0.80 (60)	0.81 (90)	0.86 (120)
N(CH ₂ CH ₂ OH) ₃	0.46 (45)	0.46 (45)	0.48 (45)

^a Paper T coated with a solution consisting of 0.01 g of thionine, 0.1 g of a reductant, 1.0 g of PVA, and 10 mL of water was used.

^b The same as in Table I.

^c Figures in parentheses indicate 50% recovery times (min) at 20°C.

TABLE III
Effect of Amount of TEA^a

TEA (g)	Irradiation time (s)	A/A_0 at RH (%) ^b		
		84	58	30
0	10	1.00	1.00	1.00
	5 ^c	0.62	—	—
	20 ^c	0.20	—	—
	40 ^c	0.16	—	—
0.01	10	0.70 (60) ^d	0.72 (90)	0.77 (150)
	20	0.53 (105)	0.55 (90)	0.58 (120)
	30	0.37 (105)	0.30 (130)	0.39 (240)
0.05	10	0.68 (60)	—	0.66 (80)
	20	0.53 (55)	0.52 (120)	0.58 (60)
	30	0.17 (75)	0.23 (240)	0.24 (90)
0.10	10	0.46 (45)	0.46 (45)	0.48 (45)
	20	0.24 (35)	0.25 (40)	0.28 (45)
	5 ^c	0.13	—	—
0.50	10	0.20 (20)	0.19 (20)	0.19 (20)
	20	0.18 (20)	0.14 (33)	0.15 (35)

^a Paper T coated with a solution consisting of 0.01 g of thionine, TEA, 1.0 g of PVA, and 10 ml of water was used.

^b A = absorbance at abs max (610 nm) immediately after irradiation at a distance of 30 cm from a 500 W tungsten lamp, unless otherwise noted.

^c Distance from the lamp = 3 cm.

^d Figures in parentheses indicate 50% recovery times (min) at 20°C.

Effect of the Concentration of TEA

The larger the TEA concentration and the longer the irradiation time, the stronger the color fading (Table III). Since the coatings have light-inactive absorbances (exceeding 0.1) around abs peaks, it is impossible to obtain a value of A/A_0 below 0.1. However, at values of A/A_0 below 0.2, papers are nearly colorless.

Effect of Irradiation Intensity

Table IV indicates that the smaller the distance from the lamp, i.e., the more intense the irradiation, the stronger the color-developing. Too high intensities

TABLE IV
Effect of Irradiation Intensity^a

Distance from lamp (cm)	A/A_0 at RH (%) ^b		
	84	58	30
30	0.69 (60) ^c	0.70 (90)	0.75 (120)
10	0.24 (80)	0.24 (110)	0.25 (160)
3	0.13 (75) ^d	0.12 (120) ^d	0.16 (150) ^d

^a Paper T coated with a solution consisting of 0.01 g of thionine, 0.1 g of TEA, 1.0 g of PVA, and 10 mL of water was used.

^b A = absorbance immediately after 5-s irradiation.

^c Figures in parentheses indicate 50% recovery times (min) at 20°C.

^d Recovery is not complete.

TABLE V
Repeating Characteristics^a

TEA (g)	Repeating number	Final absorbance recovery (%)	Recovery procedure
0.01	3	100	After irradiation, sample left standing at 58% RH for a couple of days (procedure I)
0.10	4	100	
0.50	4	100	
0.10	3	100 (100) ^b	After irradiation, sample treated with steam, followed by standing at 58% RH for a couple of hours (procedure II)
	5	97 (100) ^b	
	6	94 (100) ^b	
	7	— (100) ^b	
	8	91	
	10	83	

^a Paper T coated with a solution of 0.01 g of thionine, TEA, 1.0 g of PVA, and 10 mL of water and kept at 58% RH was irradiated at a distance of 30 cm for 10 s.

^b For film treated as in procedure I.

cause loss of reversibility, presumably due to deformations caused by a large amount of heat generated.

Repeating Characteristics

Table V indicates the results obtained by repeating the irradiation of the coated paper or film and subsequent recovery in the dark. The coated paper is inferior to a simple film in repeating characteristics, although an absorbance recovery exceeding 90% practically leaves no residual images. Accordingly, regardless of the form of sample and recovery operation, several repetitions should be assured under practical conditions.

Effect of coating substrate

The kind of substrate paper used for coating affects the light sensitivity profoundly (Table VI). Thus, papers nos. 1, 2, and 3, with water-repellent properties, afford the highest light-sensitivities, whereas nos. 4, 5, 6, and 8, with hydrophilic properties, afford low sensitivities.

Discussion

These results indicate the following features of this type of redox photochromism:

1. As for the substrate for coating the photoredox compositions (Table VI), hydrophobic sheets such as polyester (no. 2) or papers to which a hydrophobic coating was applied (nos. 1 and 3) are preferable from the viewpoint of high light sensitivity. Too high hydrophobicities, however, render the satisfactory coating of the aqueous composition difficult, yielding inferior results (no. 7). This phenomenon indicates that such coatings exist as separate films independent of the substrate without any interactions in both physical and chemical senses. The fact that films made of these compositions without substrates give the best results (Table V) supports this interpretation. The presence of interactions

TABLE VI
 Effect of Coating Substrate^a

No.	Substrate paper	A/A ₀ ^b	50% recovery ^c	Remark
1	paper T	0.26	45 min	
2	polyester sheet	0.22	1-3 h	
3	tracing papers, precoated	0.27	1-3 h	
4	tracing paper	0.76	1-3 h	
5	paper without coating	0.74	1-3 h	
6	baryta paper	0.85	1-3 h	inactive peak at 480 nm
7	silicone-coated paper	0.69	1-3 h	
8	precoated paper ^d	0.74	1-3 h	inactive peak at 520 nm

^a Papers were coated with a solution consisting of 0.3 g of thionine, 3 g of TEA, 30 g of PVA, and 300 mL of water.

^b Irradiation was carried out for 20 s at a distance of 30 cm from the lamp. A, A₀: for 610-nm peak.

^c At 20-30% RH and 10-15°C.

^d Unknown composition.

between coating components and substrate papers is indicated in the appearances of new inactive absorption peaks (no. 6 and 8, Table VI).

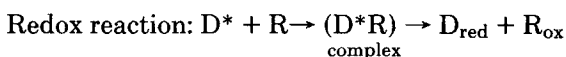
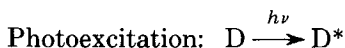
2. Thionine, presumably having the highest oxidation potential of the dyes employed, indicates the highest light sensitivity (Table I).

3. Triethanolamine (TEA) as reductant provides the most light-sensitive compositions (Table II). It also provides tough films and higher color recovery rates, presumably playing an excellent role as a plasticizer.

4. Polyvinyl alcohol (PVA), used as matrix, can also play the role of reductant (Table III), but its contribution may be minor as compared with TEA.

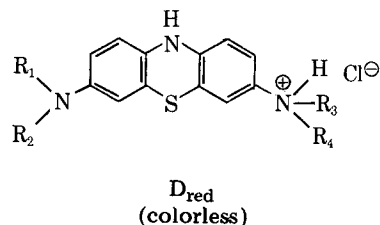
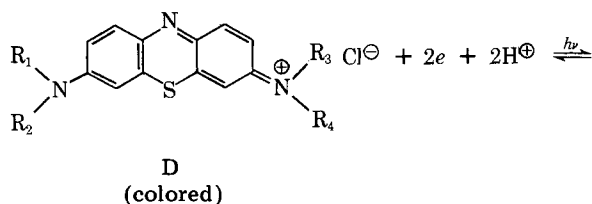
5. Moisture included in the coatings may also act as a plasticizer, which is demonstrated in higher color recovery rates at higher RHs. Higher half-recovery rates at higher TEA concentrations (Table III) may be caused by the plasticizing effect of both TEA itself and the moisture absorbed by hygroscopic TEA. The increase in the degree of mobility of each reaction component in solid matrix by plasticization with either water or TEA should be reflected more explicitly in the dark reaction governed by the thermal motion of each component.

All results described above, together with those so far reported,²⁻⁴ indicate the following mechanism of the reversible color fading of the solid thionine-reductant system.



where D = thionine dye, R = reductant such as TEA, D_{red} = reduction product of D (leucothionines), and R_{ox}: oxidation product of R.

Thus, it is considered that, for thionines, the well-known redox reaction takes place even in the solid PVA matrix:



EXPERIMENTAL

Preparation of Coating Composition

In a typical example, 0.01 g of thionine was dissolved in 5 mL of hot water. To the resulting solution was added a solution of 1 g of PVA (Iwai Chem. Co., DP 500) in 5 mL of water and the mixture was stirred at 50–70°C for 30 min. Upon cooling below 50°C, 0.1 g of TEA was added and stirring was continued further for 30 min to afford a dark-blue coating composition.

Coating on Substrate

Several kinds of paper and films with or without water-repellent precoatings were employed as substrate (Table VI). A coating composition was applied to a substrate by means of a coater so as to afford a dry absorbance of approximate unity at the absorption peak around 600–700 nm. The coated substrate was then dried at room temperature or below 90°C.

Storage in a Constant RH Atmosphere

Coated substrates were stored in a desiccator at constant RH except for irradiation or measurements of absorption spectra.

Sat. Solution in Desiccator	RH (%) ⁸
KBr	84 (20°C)
NaBr	58 (20°C)
NaCl	30 (16°C)

Irradiation

A Toshiba 500-W reflector lamp (tungsten) was used as light source.

Measurements of Absorption Spectra

Coated substrates were placed in a cell compartment of a Hitachi 200-10 spectrophotometer fitted with a reflection attachment. Absorption spectra were then measured against the substrate coated with PVA solution without dye and reductant.

Measurement of IR Spectra

Films made of coating compositions by evaporation of solvent on mercury were subjected to IR measurements by means of a Hitachi 215 IR spectrophotometer.

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