

## Redox Behavior in Photochromic Polymers of the Thiazine Series

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### Synopsis

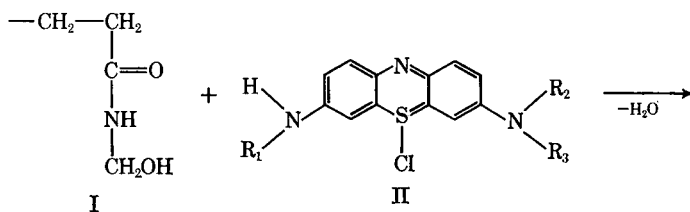
The photochromic redox behavior of the thiazine polymers prepared by the condensation reactions of the N-hydroxymethylacrylamido components of vinyl polymers with four thiazine compounds, i.e., thionine and asym-dimethyl-, trimethyl-, and monomethylthionine chloride, in combination with various electron-donating components, including hydroxyl, amino, and sulfhydryl groups and ferrous ion, were investigated.

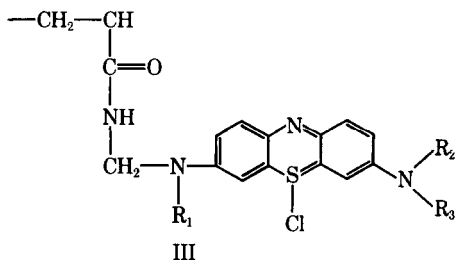
The reversible color fading (at ca. 600 m $\mu$ ) of the thiazine polymers under illumination in the solid state was found to be largely dependent upon the moisture content in the polymer. This, together with other evidence, suggests that water molecules adsorbed on the active groups in the polymer also participate in the reduction of the thiazine components. Polyvinyl alcohol, cellulose, and enzymes such as papain, when incorporated in the photochromic compositions, induce remarkable improvements of the photochromism, in both the sensitivity to light and the rate of color recovery in dark; the incorporation of the ferrous-ferri ion system into the polymers in the form of acrylates also improves photochromism remarkably, especially the rate of recovery.

### INTRODUCTION

In a previous paper<sup>1</sup> we presented the results of investigations on the photochromic behavior of N-acrylamidomethylthionine polymers and demonstrated that these polymers, when coupled with suitable electron-donating substances such as polyvinyl alcohol and ferrous ion, undergo, on light irradiation, reversible redox reactions which are accompanied by remarkable changes in absorbance around 600 m $\mu$ . From a practical standpoint, however, it is sometimes desirable that these polymers indicate photochromism fairly rapidly in the solid state, such as in films or fibers.

In this paper will be presented the results of an investigation of the effects of various electron-donating substances, especially polymers, on the photochromic behavior of the thiazine polymers synthesized as follows:





IIIa:  $R_1, R_2, R_3 = H$

IIIb:  $R_1 = H; R_2, R_3 = CH_3$

IIIc:  $R_1, R_2, R_3 = CH_3$

III d:  $R_1, R_2 = H, R_3 = CH_3$ ; or  $R_1 = CH_3, R_2, R_3 = H$

IIIa:  $R_1, R_2, R_3 = H$

IIIb:  $R_1 = H; R_2, R_3 = CH_3$

IIIc:  $R_1, R_2, R_3 = CH_3$

III d:  $R_1, R_2 = H, R_3 = CH_3$ ; or  $R_1 = CH_3, R_2, R_3 = H$

The thiazine polymers thus prepared (III) play the role of electron acceptors in the photosensitized redox reactions. As electron-donating substances, polymers containing the hydroxyl, amino, and sulfhydryl groups and ferrous ion are effective when coupled with the polymers (III). The incorporation of hydrophilic polymers containing hydroxyl groups, both natural and synthetic, such as polyvinyl alcohol and cellulose, and their comixtures with the ferrous-ferric ion system have been found very effective in the solid state.

Enzymes such as papain, urease, and glucose oxidase have also been tried and found to enhance the photochromism remarkably.

## EXPERIMENTAL

### Preparation of the Thiazine Polymers

Almost the same procedures as in the previous paper<sup>1</sup> were employed. In a typical procedure, to 10 ml of 5% aqueous solution of a N-hydroxymethylacrylamide (MAM)-acrylamide (AM) copolymer (1:5 by weight;  $[\eta]$  in water at 30°C, 1.2 dl/g) was added 0.05 g of thionine in 5 ml water. The mixture was heated at 90°C for 5 hr. The resulting violet-colored solution was precipitated in ethanol, followed by several repetitions of dissolution in water and subsequent precipitation in ethanol. The purified solution was then freeze-dried to give a fluffy violet polymer (polymer T). Redox titrations of this polymer in aqueous solution with titanium trichloride indicate that 89% of the thionine added reacted with the hydroxymethyl group of the polymer.

In another procedure by which copolymers containing ferrous-ferric ions in the forms of carboxylic acid salts were prepared, to 55 ml of a 10% aqueous solution of polyvinyl alcohol (DP, 500; 100% saponification) were

added 0.5 g acrylamide, 0.5 g acrylic acid, and 0.01 g potassium persulfate. The resulting solution was polymerized at 80°C for 4 hr with exclusion of air. The highly viscous solution thus prepared was precipitated in ethanol and then freeze-dried from water to provide a white powder. One gram of this powder was dissolved in 20 ml water. To this solution was added excess ferrous hydroxide freshly prepared and still wet, followed by 30 min of stirring at ambient temperature and subsequent filtration. Paraformaldehyde (0.2 g) was then added to the filtrate and the mixture was allowed to stand at room temperature with stirring. The pH value was maintained around 12 with sodium hydroxide addition. Paraformaldehyde was gradually dissolved during this procedure to effect the hydroxymethylation (methylolation) of the AM component in the polymer. After 1 hr, the reaction mixture was poured into ethanol to precipitate the hydroxymethylated polymer. This polymer was dissolved in 20 ml water, 0.05 g trimethylthionine chloride was added, and the mixture heated at 60°C for 5 hr, keeping the pH at 1 to 5. The reaction mixture was then precipitated in methanol, followed by purification with water-methanol reprecipitation. The purified polymer was freeze-dried from water to yield a blue-colored powder (polymer IIIc). The extent of the reaction was 92%, based on the thionine. It is preferable to store this polymer in aqueous solution since, in the solid state, it gradually becomes insoluble because of the condensation reaction of the hydroxymethyl groups in the polymer, with the resulting formation of crosslinkages.

Polymers IIIa, IIIb, and IIId were prepared in the same manner as polymer IIIc, using instead of trimethylthionine chloride the same quantity of thionine, *asym*-dimethylthionine chloride, and monomethylthionine chloride, respectively.

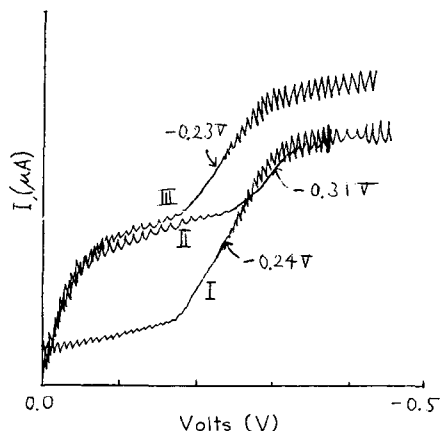


Fig. 1. Polarographic reduction waves of typical thiazine polymers with the dropping mercury electrode in an aqueous buffer (pH 5: 0.1M sodium acetate with the addition of acetic acid): curve I, monomethyl thionine chloride; curve II, polymer IIIa; curve III, polymer IIId. Polymers IIIa and IIId without incorporation of the ferrous-ferric ion system.

TABLE I  
Properties of Thiazine Polymers Prepared

Sample	Extent of reaction, % based on thionine added	Absorption max. in film state, $m\mu$	Polarographic half-wave potential, <sup>a</sup> V
Thionine	—	602 <sup>b</sup>	-0.30
Polymer IIIa	90	612	-0.31
<i>asym</i> -Dimethylthionine chloride	—	630 <sup>b</sup>	-0.30
Polymer IIIb	68	661	-0.22
Trimethylthionine chloride	—	650 <sup>b</sup>	-0.28
Polymer IIIc	92	619	-0.32
Monomethylthionine chloride	—	610 <sup>b</sup>	-0.24
Polymer IIId	74	617	-0.23

<sup>a</sup> pH 5 buffer with 0.1*N* sodium acetate and acetic acid.

<sup>b</sup> Aqueous solution.

Table I summarizes the properties of typical thiazine polymers and their model compounds. In Figure 1 are also indicated polarographic reduction waves of two polymers and a model compound.

### Preparation of Photochromic Compositions

When electron-donating polymers were required to be incorporated into the thiazine polymers prepared as above, these polymers, i.e., polyvinyl alcohol, enzymes, etc., were added to aqueous solutions of the thiazine polymers containing residual N-hydroxymethyl groups and, with suitable adjustment of pH value, the solutions were put on glass plates to homogeneous thickness or onto cellulosic substrates such as filter paper and textile fabric by dipping procedure and allowed to dry completely by the application of heat (30 min at 80°C). This procedure yielded films of ca. 0.05 mm thickness or coated paper or fabric, with the resulting formation of methylene bridges among the polymer molecules.

### Measurement of Photochromism

Illumination (ca. 80,000 lux) at a distance of 30 cm from a 500-watt tungsten lamp possessing the same spectral distribution as conventional electric light and without filters was employed for the solid samples, unless otherwise noted. As a handy measure of dark reactions, 50% recoveries in transmittance and reflectance were adopted for films and cellulose coatings, respectively, although the color recovery does not take place following the first kinetic order.

As can be seen from Table II, however, the photochromic behavior of thiazine polymers is strongly affected by the humidity of the atmosphere. In this table,  $E_{\max}^L$  and  $E_{\max}^D$  denote the absorbances at the absorption

maximum in the dark after and before irradiation, respectively. The temperature of the measurements was 20°C. The humidity was controlled by using pure water (100%) and saturated aqueous magnesium acetate (65%) or an air-conditioned room (65%).

TABLE II  
Effect of Moisture on Photochromism of Thiazine Polymers<sup>a</sup>

Polymer	Irradiation time, min	$E^L_{max}/D^D_{max}$	50% Recovery, min
Relative Humidity, 100%			
polymer IIIa	2	0.132	4
polymer IIIb	2	0.053	5
polymer IIIc	2	0.049	4
Relative Humidity 65%			
polymer IIIa	2	0.148	7
polymer IIIb	2	0.102	4
polymer IIIc	2	0.099	4
Relative Humidity 0% <sup>b</sup>			
polymer IIIa	2	0.156	23
polymer IIIb	2	0.101	20
polymer IIIc	2	0.098	11

<sup>a</sup> Substrate: cellulose filter paper.

<sup>b</sup> In phosphorus pentoxide desiccator.

The reproducibilities of the data presented here were fairly good for ca. 0.05 mm thickness films.

It is seen that the dark reactions, i.e., 50% recoveries, are especially affected by the moisture content in air. Hence, all experiments were carried out under the condition of 65% relative humidity.

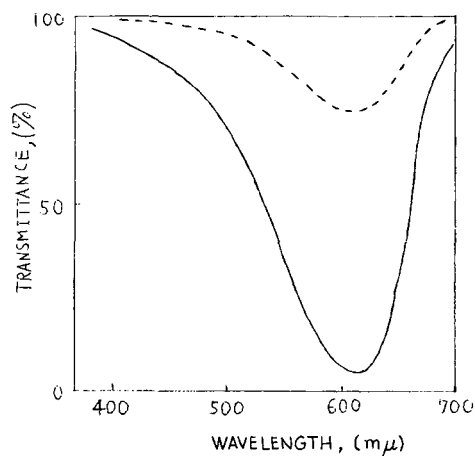


Fig. 2. Spectral change of polymer IIIa film in combination with 10% papain under illumination: solid and broken lines, transmission spectra before and immediately after 2-min illumination, respectively.

### Spectral Change with Irradiation

Figure 2 shows a typical change in transmission spectrum with irradiation. Figures 3 and 4 also show spectral changes in the case of addition of the coloring materials capable of reacting with thiazine polymers via methylene linkages.

Thus, in Figure 2 the color is changed from blue to colorless with irradiation, whereas in Figures 3 and 4 the color changes with irradiation are from violet to red and from green to yellow, respectively. Hence, in Figure 3 and in the curves I, I' in Figure 4, only the thiazine portion of the polymer

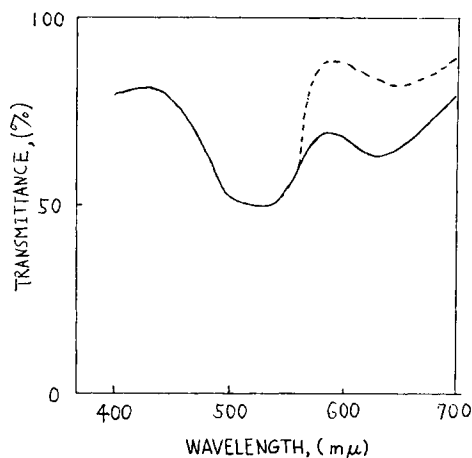


Fig. 3. Spectral change of polymer IIIc film in combination with 10% papain and a small quantity of tetraethylrhodamine under illumination: solid and broken lines, absorption spectra before and immediately after 2-min illumination, respectively.

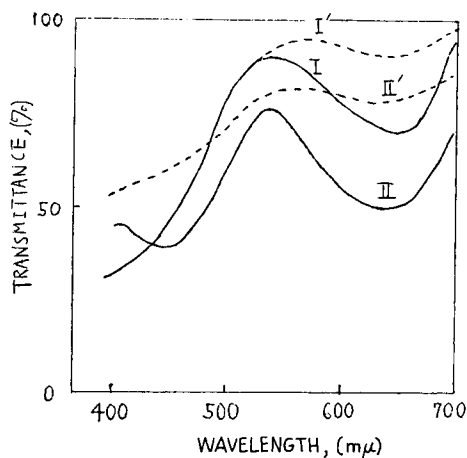


Fig. 4. Spectral change for polymer IIIc films in combination with 10% papain and 4-aminoazobenzene (I, I') and riboflavin 5'-phosphate (II, II') under illumination: solid and broken lines, absorption spectra before and immediately after 2-min illumination, respectively.

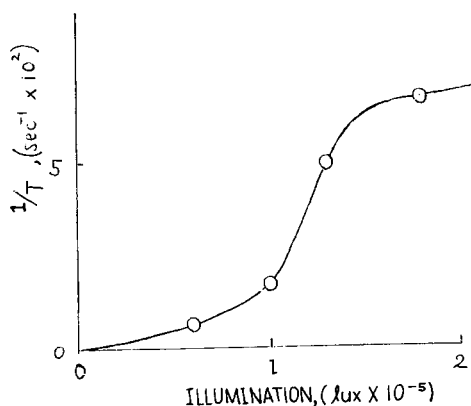


Fig. 5. Effect of illumination intensity on the reciprocal of the time ( $T$ ) required for complete decoloration of polymer IIIb.

is affected by illumination, thereby causing apparent changes in color; in the case of II,II' in Figure 4, both thiazine and riboflavin portions are affected, although color change was also observed.

#### Effect of Light Intensity

Figure 5 is an example of the effect of illumination intensity on the rate of color fading. The apparent saturation effect observed here might indicate, among others, that entropy effects are great in the solid state, although exact affirmation cannot be made because of the complexity of the reactions involved.

TABLE III  
Effect of Various Hydroxyl Groups on the Photochromic Behavior of Thiazine Polymers in Film State

Polymer	Hydroxyl group	Irradiation time, min	$E_{max}^L/E_{max}^D$	50% Recovery, min
Polymer T	None	10	1.000	—
Polymer IIIa <sup>a</sup>	polyvinyl alcohol grafted	5	colorless	60
Polymer IIIc <sup>a,b</sup> comixed with 10-fold cellulose diacetate	cellulosic hydroxyl	10	1.000	—
Polymer IIIc <sup>a,c</sup>	hydroxyethyl	10	1.000	—
Polymer IIIc coated onto cellulose filter paper (10%)	cellulosic hydroxyl and polyvinyl alcohol grafted	1	0.073	2

<sup>a</sup> Without incorporation of the ferrous-ferrie system.

<sup>b</sup> Acetone-soluble composition containing methyl acrylate as a comonomer component.

<sup>c</sup> Ethanol-soluble composition containing  $\beta$ -hydroxyethyl methacrylate as a comonomer component.

### Effect of the Incorporation of Hydroxyl Polymer

Table III shows the effects of the incorporation of various electron-donating hydroxyl-containing polymer components on the photochromic behavior of thiazine polymers. In this table, the third and fourth polymers were prepared from the copolymers of N-hydroxymethylacrylamide with methyl acrylate and  $\beta$ -hydroxyethyl methacrylate (1:20 by weight), respectively, followed by the acid-condensation reaction with equivalent trimethylthionine chloride.

Table IV indicates the photochromic properties of the thiazine polymers

TABLE IV  
Effect of Polyvinyl Alcohol (PVA) on Photochromic Behavior in Film States

Polymer	State	Irradiation time, min	$E^L_{\max}/E^D_{\max}$	50% Recovery, min
MAM-AM (1/7) copolymer	aqueous <sup>b</sup>	10 <sup>c</sup>	0.162	5
MAM-AM (1/7) copolymer + 10 fold PVA	film	5	colorless	60
Polymer IIIa <sup>a</sup>	film	5	colorless	60
Polymer IIIb <sup>a</sup>	film	5	colorless	60
Polymer IIIc <sup>a</sup>	film	5	colorless	60
Polymer IIId <sup>a</sup>	film	5	colorless	60

<sup>a</sup> Without the incorporation of the ferrous-feric system.

<sup>b</sup> 0.1M Phosphoric acid;  $1.8 \times 10^{-3}$  mole/l. ferrous sulfate.

<sup>c</sup> 100 Watt projection lamp.

in the presence of polyvinyl alcohol. Except for the first two polymers, polyvinyl alcohol was incorporated in the thiazine polymers in the form of grafting stems. In this case, the effect of variation in thionine derivative was not observed for film samples. This might indicate that, in the solid

TABLE V  
Effect of Cellulose Filter Paper as Substrate on Photochromic Behavior

Polymer	Irradiation time, min.	$E^L_{\max}/E^D_{\max}$	50% Recovery, min
Polymer IIIa	1	0.054	3
Polymer IIIb	1	0.082	1.5
Polymer IIIc	1	0.073	2
Polymer IIIId	1	0.085	2

state, factors other than oxidation potentials of the photo-reduced or complexed thionine components play more important roles on the rate of reactions concerned, as described above.

Table V also indicates the effect of cellulose paper as substrate on the photochromism of thiazine polymers. In these cases, the presence of ferrous-feric ions promotes both color fading and recovery.



**Effect of Incorporation of the Ferrous-Ferric Ion System**

Table VI shows the photochromic behavior of the thiazine polymers containing iron in the form of carboxylic acid salts. As compared with the results in Table IV, it is seen that both color fading and recovery are accelerated remarkably. Time effects on photochromism are indicated in Table VII.

TABLE VI  
Effect of Presence of the Ferrous-Ferric Ion System  
on Photochromic Behavior in Film States

Polymer	Irradiation time, min	$E^L_{max}/E^D_{max}$	50% Recovery, min
Polymer IIIa	2	0.111	15
Polymer IIIb	1	0.054	5
Polymer IIIc	2	0.001	15
Polymer IIId	2	0.153	15

TABLE VII  
Time Effects on Photochromic Behavior of  
10% Polymer T + 1% Ferrous Sulfate on Cellulose

	Immed- iately after	Days after sample preparation			
		10	30	60	90
Irradiation time required for complete decoloration, min	1	2	2	2	2
50% Recovery, min	5	10	10	10	10

**Effect of Incorporation of Enzyme**

Enzyme hydrolases such as papain and urease and oxidative enzymes such as glucose oxidase were incorporated into thiazine polymers and their photochromic behavior was investigated. The results obtained (Tables VIII, IX, and X) indicate that they considerably promote both color fading under illumination and color recovery in the dark.

TABLE VIII  
Effect of Papain Incorporated (10% Based on Polymer Weight)  
on Photochromism without incorporation of Ferrous-Ferric Ion System

Polymer	Irradiation time, min	$E^L_{max}/E^D_{max}$	50% Recovery, min
Polymer IIIa	2	0.103	30
Polymer IIIb	1	0.051	20
Polymer IIIc	1	0.154	20
Polymer IIId	1	0.038	15

TABLE IX  
Effect of Papain Incorporated (10% Based on Polymer Weight)  
on Photochromisms with Incorporation of Ferrous-Ferric Ion Systems

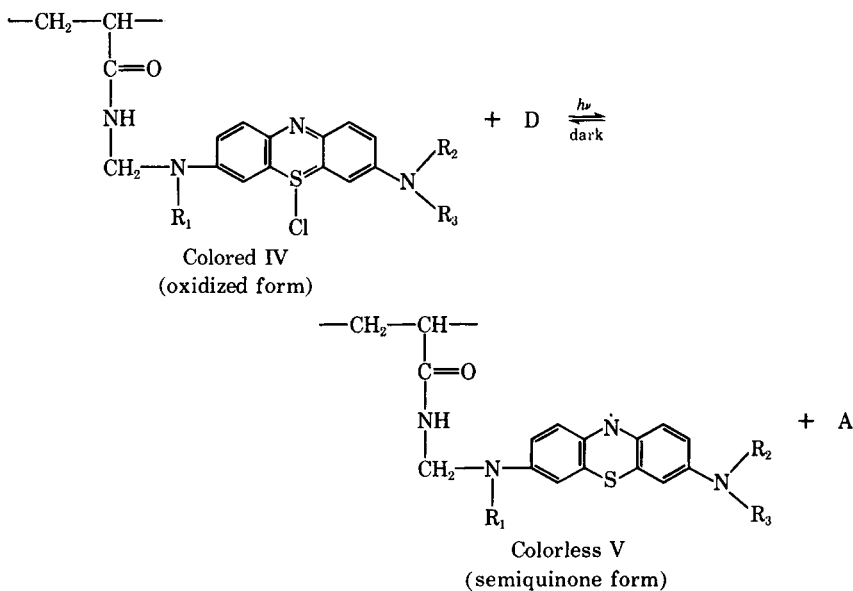
Polymer	Irradiation time, min	$E^L_{max}/E^D_{max}$	50% Recovery, min
Polymer IIIa	2	0.113	10
Polymer IIIb	2	0.058	10
Polymer IIIc	1	0.013	2
Polymer IIId	2	0.099	5

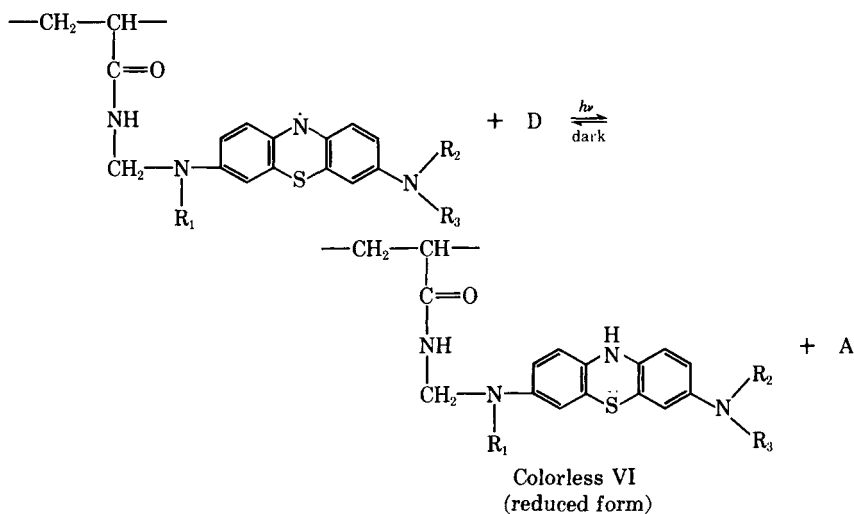
TABLE X  
Effect of Enzyme Incorporated (10% based on Polymer Weight)  
on Photochromisms without Incorporation of Ferrous-Ferric Ion System

Polymer	Enzyme	Irradiation time, min	$E^L_{max}/E^D_{max}$	50% Recovery, min
Polymer IIIId	Papain	1	0.038	15
Polymer IIIId	Urease	2	0.114	30
Polymer IIIId	Glucose oxidase	2	0.092	30

## DISCUSSION

As judged from Rabinowitch's pioneering work<sup>2,3</sup> on the thionine-iron system, from later mechanistic studies by Hardwick,<sup>4,5</sup> and from the results for the thionine polymer in our previous report,<sup>1</sup> etc., the photochromism, i.e., the reversible color fading of thiazine polymers by light is considered to be caused by reversible redox reactions as indicated below:





where D represents electron-donating components such as hydroxyl, amino, and sulfhydryl groups, ferrous ion, and possibly activated water molecule; and A represents electron-accepting components such as ferric ion, disulfide groups, and air oxygen.

The problem of the nature and action of D in the solid state is complicated and cannot be described simply. For instance, the photochromic effects are largely dependent upon the relative humidity of the atmosphere in which samples are placed, thereby upon the moisture contents in sample, as indicated in Table II. Since it is known that thionine and other thiazine compounds are activated in photoreduction by such active surfaces as silica gel and alumina<sup>6</sup> with water molecules adsorbed on them, it seems rational to consider the activation of the thiazine components by electron-donating polar groups in the presence of water molecules as well as the simple interpretation that the thiazine component merely oxidizes these polar groups and that the moisture in the polymer only aids mutual contacts of reactants. This interpretation is supported by the fact that less hydrophilic polymers containing thiazine components do not exhibit photochromism even though they contain appreciable amounts of hydroxyl groups (Table III). Therefore it is very likely that the polar groups in the polymer participate not only in redox reactions as electron donors in themselves, but also activate the thiazine component-water system, thereby leading to the photo-oxidation of the water molecules with the thiazine components to hydrogen peroxide.

Another important problem is the identity of A, i.e., the cause of the back reaction in the dark or under diminished light intensity. There is no question in the case of the ferrous-ferrous ion system and the sulfhydryl-disulfide system in enzymes. Thus, ferric ion or disulfide previously present in polymers or produced by the photo-oxidation readily oxidizes the reduced forms, especially VI, which is a strong reductant as judged from the polarographic half-wave potentials in Table I, back to the quinone type IV with regeneration of the characteristic color.

The presence of electron-donating groups such as hydroxyl and amino in

the polymer might also cause the formation of electron donor-acceptor type complexes with thiazine components under illumination, with the resulting disappearance of the thiazine color. The back reactions in these cases are, therefore, the return from these discolored states; the presence of a small amount of water promotes the back reaction by favoring the dissociation of these complexes.

These interpretations are supported by the fact that the photochromism of these materials is hardly observed in aqueous solutions, except when the ferrous-ferric system is used, but is remarkable in the solid state. The formation of hydrogen peroxide, if any, from water, as described above, would also promote the back reaction by oxidizing V and VI; and air oxygen is, of course, a strong candidate for the oxidation of V and VI.

Considering all these characteristics of the photochromic behavior of thiazine polymers, practical recipes are obtained by incorporating both organic electron-donating polymer components and the ferrous-ferric ion system. Thus, in polymer IIIa, containing both hydroxyl groups and the ferrous-ferric ion system in the form of PVA and acrylates, respectively, photochromism possibly takes place by the following mechanisms: (1) color fading on illumination caused by the hydroxyl group itself (reduction and complex formation) and spontaneous recovery in the dark; (2) color fading caused by the water molecules adsorbed on the hydroxyl groups and recovery via oxidation by the resulting hydrogen peroxide; (3) color fading by reduction with ferrous ion and recovery by oxidation with ferric ion thus produced or previously present; (4) color recovery in dark by oxidation with air oxygen.

As apparent in Table VII, due to the combination of these various effects the photochromic effects are maintained for long periods of time. In this case, the well-known photoreduction of ferric to ferrous ions, e.g., with alcoholic groups might also play a role in the persistency of the effect.

As regards the effect of the enzymes incorporated, clear conclusions cannot be drawn since their structures, both physical and chemical, are very complicated. In view of the preceding discussions, however, their physical conformations are considered also to play important roles, besides as mere electron donors, because of their sulfhydryl and amino groups, etc.

The fact that there is no appreciable variation in photochromic effect with the kind of thionine derivative might indicate that the predominant factor is the entropy condition of the reacting species, although the difference in oxidation potentials of these thiazine components is also not so remarkable.

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