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Spectral Sensitization Improved by Some Fog Inhibitors

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The spectral-sensitization of an AgCl emulsion was investigated in the presence of some fog inhibitors. It was found that the sensitivity of spectral-sensitized emulsions could be increased or decreased by these inhibitors according to the order of addition of the compounds. On the basis of spectral measurements, one reason could be the influence of these compounds on the aggregation behavior of the cyanine dyes. When it was beneficial to the formation of dye J-aggregates, sensitization took place; and when it was beneficial to the formation of dye H-aggregates, desensitization appeared. ESR experiments show that the addition of inhibitors can decrease the number and accelerate the decay of dye positive holes. The desensitization, caused by the recombination of dye positive holes with photoelectrons and/or latent image centers, was reduced in the presence of these fog inhibitors, leading to an increase in sensitivity of the emulsion.

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Introduction

A lot of photographic fog inhibitors such as hydroxytetraazaindene (TAI) and some thiolic compounds, showed sensitizing effect when introduced into silver halide emulsions and carried through the digestion process.[1–6] Many investigations on the mechanism of the sensitizing effect have been carried out and several have been proposed: (a) decrease of the adsorption of sensitizing dye,[7] (b) effects on the aggregation of dye at the silver halide grains,[8] and (c) depression of desensitization due to dye.[9,10]

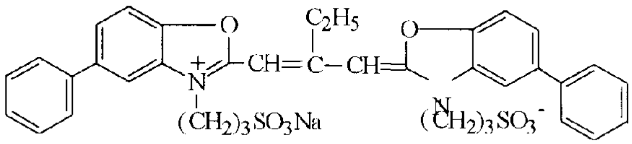
Sensitizing dyes could bring about desensitization because of the recombination of dye positive holes with photoelectrons and/or with image centers.[11,12] Tani[9] concluded that the interaction of TAI with emulsion grains increases the fraction of the photoelectrons captured by the sensitivity centers of sulfur sensitization and decreases the mobility of dye positive holes in dye aggregates and, accordingly, depresses the dye desensitization. The sensitization, despite desorption of dyes caused by TAI, was attributed to the changes in the states of the dye aggregate and/or of the emulsion grains. However, Shapiro et al.[10] explained the depression of dye desensitization by TAI with an "isolation theory." He thought that TAI first adsorbed at the surfaces of silver halide grains and then sensitizing dye adsorbed at the layer of TAI on the surfaces. Therefore an isolation layer formed between the dye and the grain surface, leading to the decrease of the recombination of positive holes with electrons.

We recently observed the sensitization in unsensitized and sulfur-sensitized silver chloride emulsion by TAI and some thiolic antifoggants,[5,6] which is somewhat different from that in silver bromide emulsions.[13] In this report, relationships between the photographic properties and dye aggregates at silver chloride grains were investigated with respect to the method of addition of some inhibitors in relation to sensitizing dye. The formation of dye positive holes at the presence of TAI was studied by ESR measurement. On this basis, the mechanism of sensitization by inhibitor in spectral-sensitized emulsion can be discussed.

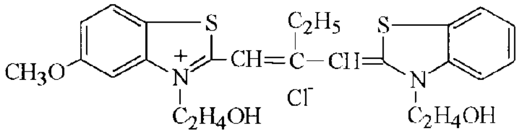
Experimental

The molecular structures of the sensitizing dyes used in this report are as follows:

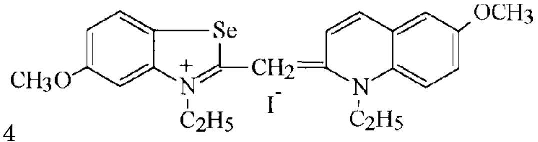
Dye 1



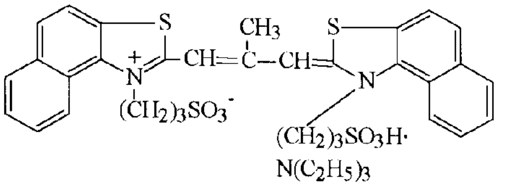
Dye 2



Dye 3



Dye 4



Structures of the inhibitors are shown in Table I.

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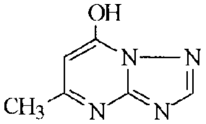
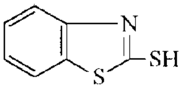
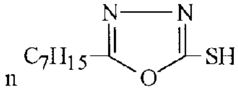
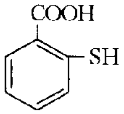
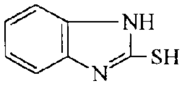
TABLE I. Name, Structure, and Abbreviation of the Antifoggants

Name	Structure	Abbreviation
4-Hydroxy-6-methyl-1, 3, 3a,7-triazaindolizine		TAI
2-Mercaptobenzothiazole		MBT
2-Mercapto-5-heptyl-1,3,4-oxadiazole		MHO
2-Mercaptobenzoic acid		MB
2-Mercaptobenzimidazole		MBM

The photoemulsion comprised cubic silver chloride grains similar to that previously used.[13] After sulfur-sensitization, the emulsion was digested at 45°C with the additions of sensitizing dye and inhibitor. The modes of addition were as follows: (a) dye before inhibitor, (b) simultaneously, and (c) dye after inhibitor. The amount of dye used was 1.16×10^{-4} mol/molAgCl and the amount of TAI was 3 mmol/mol AgCl, unless otherwise stated. After the digestion, the emulsion was coated on the films and dried. Then the coatings were exposed for 1 s at color temperature 5500 K and developed with D-11 developer for 1 min at 20°C. Photographic sensitivity was expressed as the reciprocal of the amount of exposure required to give 0.85 optical density above fog.

The dielectric loss measurements were performed at 25°C in the frequency range between 30Hz and 30 KHz, by using Ando Electric type TRS-10C, as in an earlier paper.[11] Measurement of microwave photoconductivity was performed at 25°C to obtain the photoelectron lifetimes in emulsion grains. This technique is the same as described by Kaneda.[14] Absorption spectra of the sensitizing dye solution and reflection spectra of the coated spectral-sensitized AgCl emulsion were recorded with a Hitachi 340 ultraviolet-visible spectrometer.

ESR signals of dye adsorbed on silver chloride grains were obtained using a Varian E-109 ESR spectrometer with X-band and magnetic field modulation of 100 KHz. Silver chloride grains, which were prepared as described in a former paper,[13] dye solution, and TAI were put into an air-tight vessel with agitation for 2.5 h at 25°C. Then the grains were separated by centrifuging and dried by means of vacuum freeze drying. The obtained grains were put into a quartz tube and exposed to a xenon lamp for 5 s prior to ESR measurement.

Results and Discussion

Photographic Properties. Figure 1 shows photographic characteristic curves of emulsions with different orders of addition of Dye 1 and TAI. From Fig. 1, it could be found that different adding order of TAI and dye resulted in different sensitizing effect. Only when TAI was added after dye would sensitization occur. Except for MB, similar effects with other inhibitors also took place, as shown in the results given in Table II. In addition to the effect on the sensitivity, it was found that fog of emulsion in the presence of inhibitors was decreased whatever the order of addition of inhibitor and dye.

TABLE II. Relative Sensitivity of Emulsion Affected by the Adding Order of Dyes and Fog Inhibitors.

Inhibitor	Amounts of inhibitors (mmol/mol AgCl)	Dye	Relative sensitivity A*	B*	C*
TAI	3	Dye 1	1.82	0.69	0.59
TAI	3	Dye 2	1.66	1.05	0.98
TAI	3	Dye 3	1.04	0.97	0.91
TAI	3	Dye 4	1.06	0.82	0.76
MHO	0.45	Dye 1	1.19	0.68	0.57
MB	2.76	Dye 1	1.22	—	—
MBT	0.54	Dye 1	1.12	0.95	0.93
MBM	3	Dye 1	1.10	0.44	0.32

*A, B, and C, respectively, represent inhibitors, added after, before, and simultaneously with dye.

When digestions were performed with TAI added after Dye 1, the results obtained are shown in Fig. 2 and Fig. 3. Figure 2 shows the sensitivity of emulsion with the digestion with various levels of dye in the absence and presence of TAI. Under the condition of the present experiments, the sensitivity increased with the increasing amount of dye added and also a sensitizing effect existed in the presence of TAI. The influence of the amount of TAI on the sensitizing effect is shown in Fig. 3. The results indicate that the degree of the sensitizing effect depended upon amount of TAI added, with optimum effect obtained on addition of ca. 4 mmol/mol AgCl. These experiments indicated that the optimum level was determined by several factors, including dye, amount of dye, and choice of inhibitor.

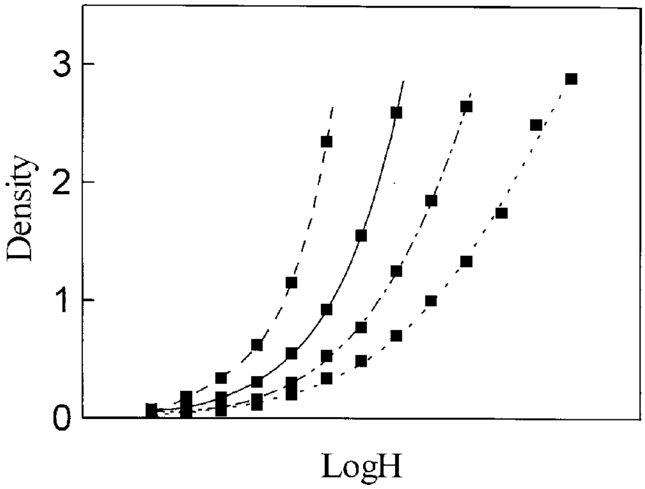


Figure 1. Photographic characteristic curves of emulsions with different ading orders of Dye 1 and TAI. The additions are: only dye added (solid line); TAI added after dye (dashed line); TAI added before dye (– • – •); and TAI and dye added at the same time (dotted line).

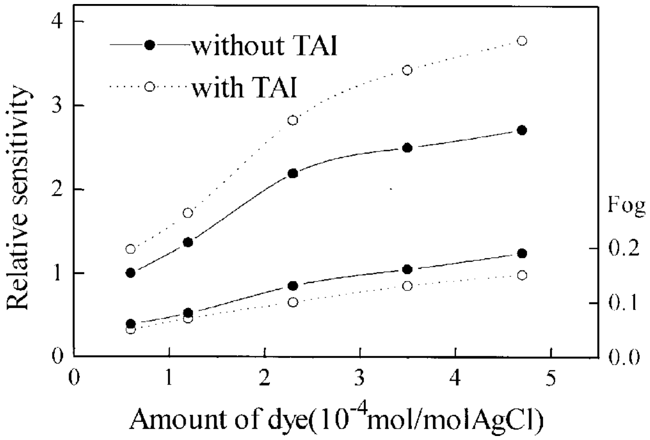


Figure 2. Effect of TAI on sensitivity of spectral-sensitized emulsion in which various amounts of Dye 1 were added.

TABLE III. Electron Lifetimes τ_1 and τ_2 Affected by TAI

	no TAI	TAI
τ_1(ns)	11.2	14.4
τ_2(ns)	33	41.2

Electronic Properties. When fog inhibitor was added to unsensitized or sulfur-sensitized silver halide emulsions, the electronic properties would be changed, e.g., decrease of ionic conductivity and/or increase of photoelectron lifetime, leading to the sensitiztion.[1,5,15] The results shown in Fig. 4 and Fig. 5 prove that inhibitors also have the same effects on the electronic properties of spectral-sensitized emulsion grains. Figure 4 indicated that in the presence of TAI, whatever the order of addition, the dielectric loss peak frequency (fmax) was reduced. Namely, the ionic conductivity of the emulsion was decreased.

From the logarithmic plot of the microwave photoconductivity, signal intensity as shown in Fig. 5, it can be seen that there exist two decay components with first-order kinetics. The photoelectron lifetimes (τ_1 and τ_2) of emulsion are listed in Table III. These results suggest that the photoelectron lifetimes increase in the presence of TAI. Similar results to Fig. 4 and Table III can also be obtained

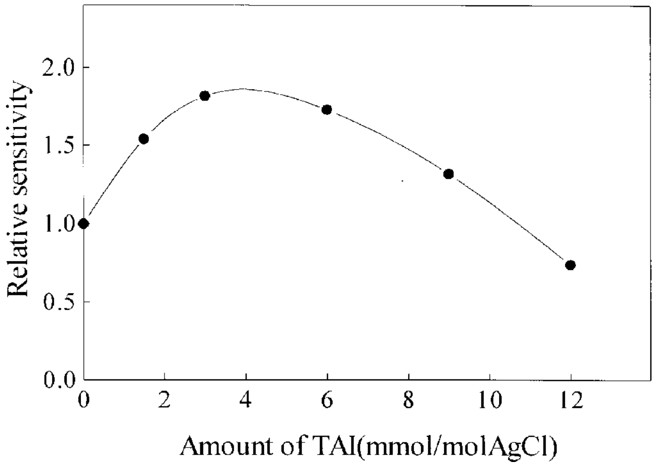


Figure 3. Sensitivity of spectral-sensitized emulsion with various amounts of TAI. The amount of Dye 1 is 0.116 mmol/mol AgCl; which was added before TAI.

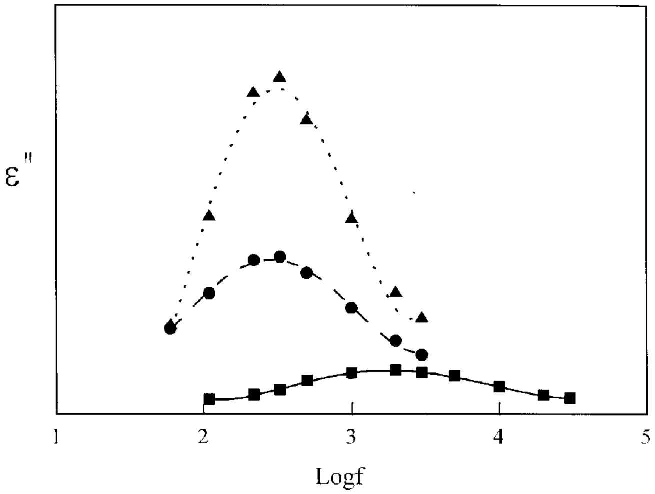


Figure 4. Effect of TAI on dielectric loss of spectral-sensitized AgCl emulsion. The amounts of TAI and Dye 1 were 6.67 and 0.116 mmol/mol AgCl, respectively. The additions of TAI and Dye 1 are: only dye added (solid line): TAI added after dye (dotted line); TAI added before dye (dashed line).

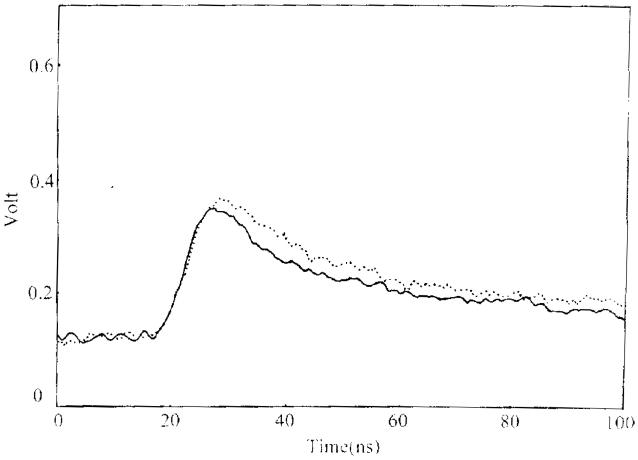


Figure 5. Microwave photoconductivity for Dye 1 spectrally sensitized AgCl emulsion with (dotted line) and without TAI (solid line).

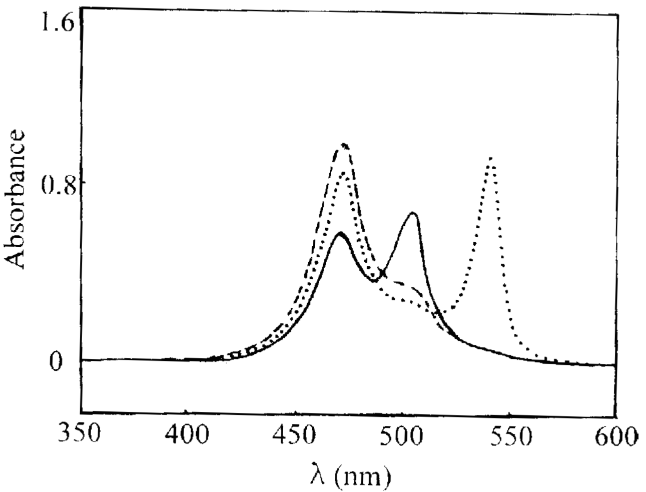


Figure 6. Absorption spectra of aqueous sensitizing Dye 1 solution. Concentration of solution is: 1.3 (solid line); 5.2 (dashed line); and 10.4 (dotted line) mmol/L.

using other inhibitors. From the above results, we conclude that these compounds should bring about supersensitization.[9,15]

Influences on the Aggregation of Dye. To elucidate the different photographic properties in relation to the order of addition of sensitizing dye and inhibitor, the absorption spectra of dye solution and reflection spectra for spectral-sensitized emulsions were investigated. It is known that concentration of the dye is a variable affecting its aggregation and absorption spectrum. Figure 6 shows absorption spectra of the sensitizing Dye 1 in solution. Monomer of the dye exists and the maximum of absorption (M-absorption band) is at 504 nm when concentration of dye is 1.3×10^{-3} mol/L. H-aggregation appears and the maximum of absorption (H-absorption band) is at 474 nm when concentration of dye is 5.2×10^{-3} mol/L. And J-aggregation occurs and the maximum of absorption is at 548 nm when concentration of dye reaches 1.04×10^{-2} mol/L.

Apart from influences of concentration of dye and temperature[16] on the dye aggregation, it is also reported that solvent as well as dye anion, added organic and inorganic salts, and polyanion matrices are variables.[17] In this experiment, results indicate that TAI also has an effect on the aggregation of the dyes as shown in Fig. 7. With Dye 1 and Dye 4, the presence of TAI is beneficial to the formation of J-aggregate, and with Dye 2 and Dye 3, TAI can lead to the disbanding of H-aggregate and the formation of monomer. These phenomena become more pronounced with the increasing concentration of TAI in the solution.

Figure 8 shows the reflection spectra of spectral-sensitized emulsions with different order of addition of TAI in relation to sensitizing Dye 1. From the figure, monomer absorption (at 506 nm) and J-aggregate absorption (at 548) could be easily seen when TAI was added after dye. However, when TAI was added before the dye or at the same time as the dye, two J-aggregate absorptions (at 544 and

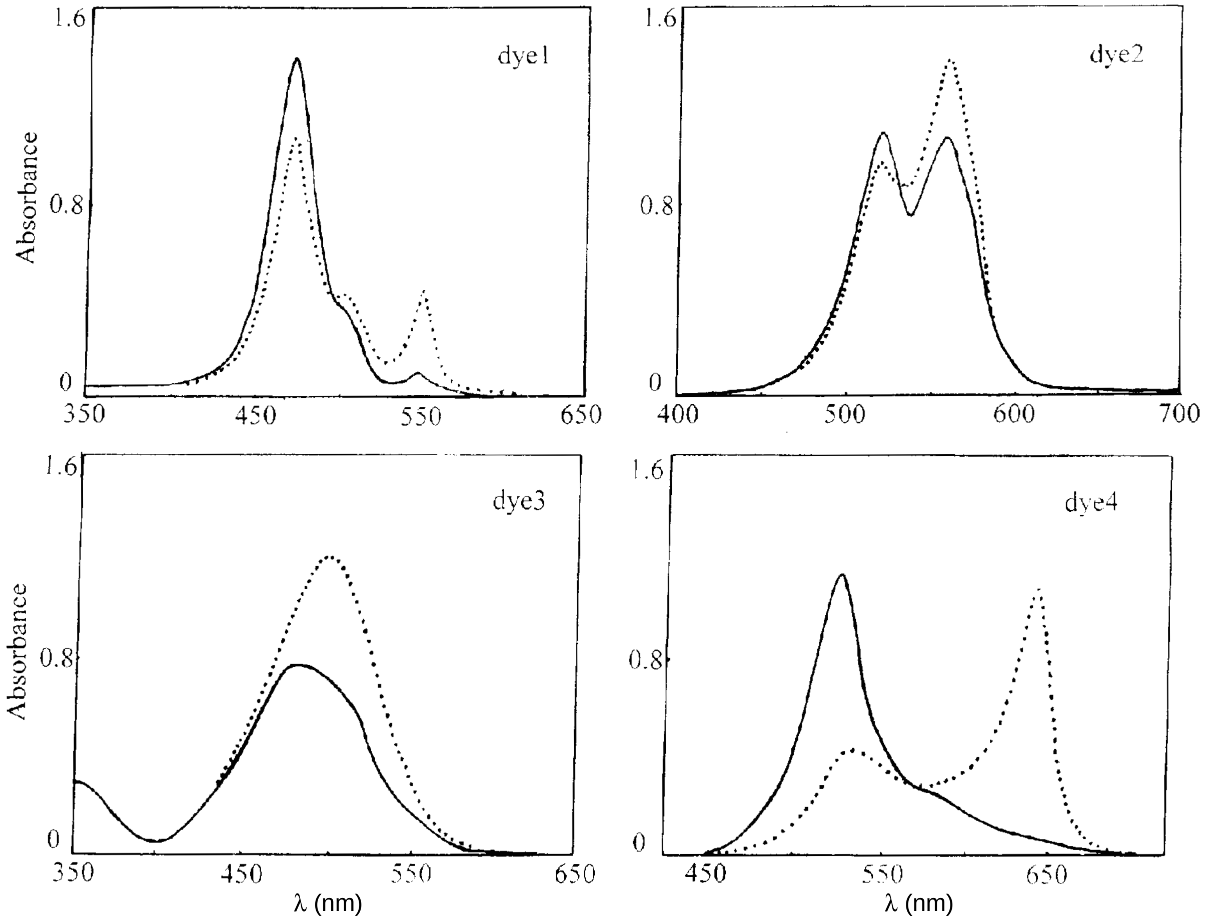


Figure 7. Absorption spectra of aqueous sensitizing dyes solution with (dotted line) and without TAI.

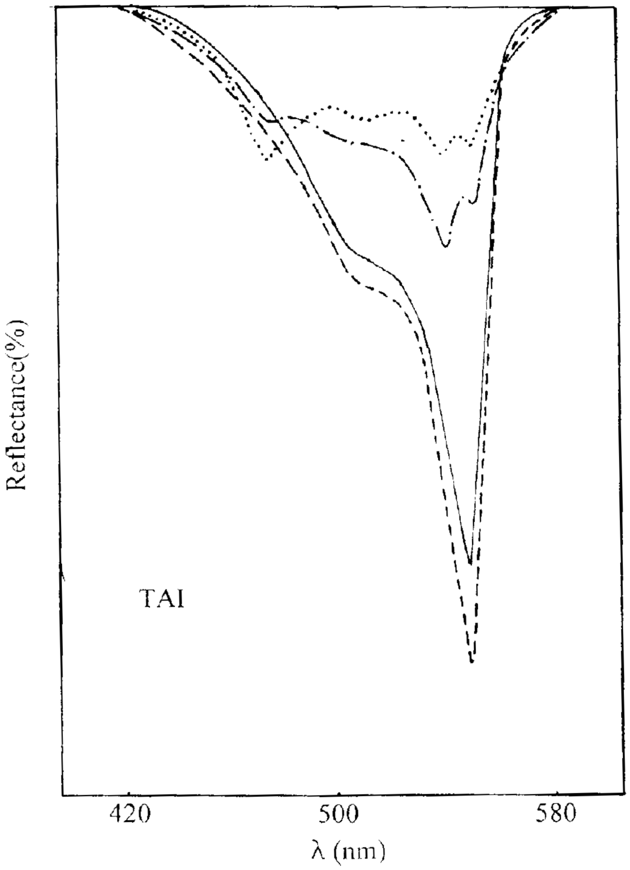


Figure 8. Effects of the order of addition of TAI and Dye 1 on the reflection spectra of AgCl emulsion. The orders of addition of TAI and Dye 1 are similar to that in Fig. 1: only dye added (solid line); TAI added after dye (dashed line); TAI added before dye (– • – •); TAI and dye added at the same time (dotted line).

552 nm) appeared and the absorptions were much weaker than with TAI added after dye. Also, the H-aggregate absorption (at 473 nm) appears instead. When MBT and MHO were used, it was found that similar changes in J-aggregation took place. When MBM was added at the same time as or before the dye, the J-aggregate disappeared and only H-band and M-band were observed: when MB was added before dye or simultaneously, there was only the H-band, as shown in Fig. 9.

Instead of Dye 1, other dyes were used under experimental conditions the same as in Fig. 8. It could be seen that J-aggregates for Dye 2, Dye 3, and Dye 4 were not formed, but the effects of TAI on the absorption spectra of these dyes were less than with Dye 1, as shown in Fig. 10.

ESR Spectroscopy. Measurements of ESR spectra were made at room temperature. Experiments indicated that only dyed AgCl power gave ESR signals on exposure to light. All of the light-induced ESR signals of dyes adsorbed on silver chloride grains were structureless at g = 2.004, as shown in Fig. 11. The intensity of this ESR signal increased with the increasing of exposure time until greater than 3 min. Moreover, intensities of ESR signal increased with increasing amount of dye, which indicates that more dye positive holes are formed with increasing amount of dye. The ESR signals were observed for Dye 1 and Dye 4 but not for Dye 2 and Dye 3. It is possible that the highest occupied levels of Dye 2 and Dye 3 were not high enough for electron transfer to AgCl.[18]

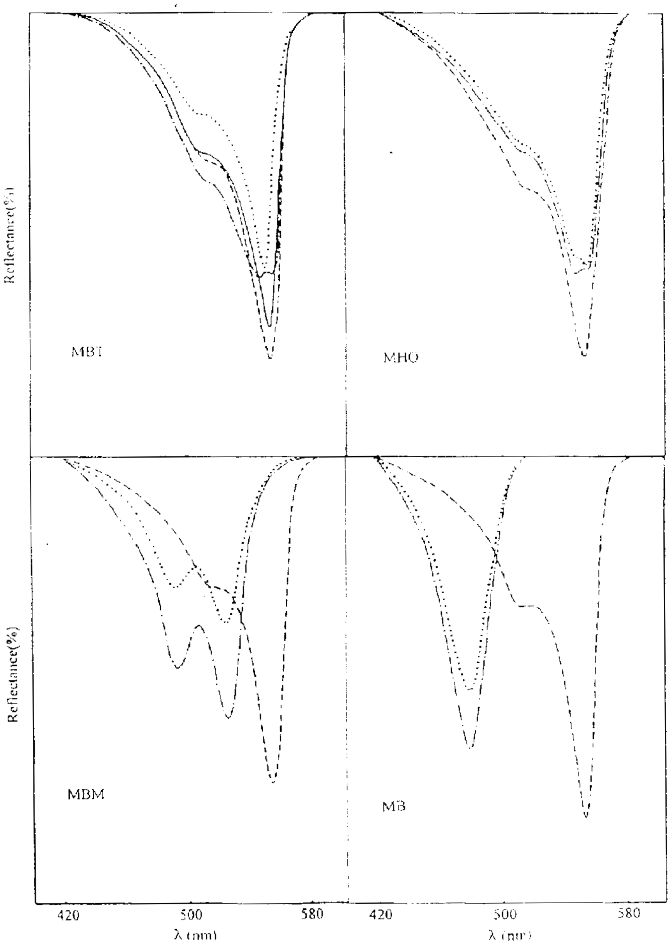


Figure 9. Same as Fig. 8, except for inhibitors.

TABLE IV. Intensity of ESR Signal Affected by Inhibitors

Inhibitor	Amount of inhibitor mol/mol AgCl	Intensity of ESR signal Dye 1	Dye 4
—	—	65.5	101
TAI	0.37	35.5	45.5
MB	0.36	34	64.5
MBT	0.33	27	58
MBM	0.37	31.5	62.5

It was reported[9] that the addition of TAI to the emulsion causes the decrease in relative peak height and increase in maximum slope linewidth of the ESR signals. However, our experiments indicated that intensity of ESR signals obviously decreases in the presence of inhibitors, as shown in Table IV. Intensities of ESR signals of dye adsorbed grains with various amounts of TAI are shown in Fig. 12. As shown in the figure, intensity of the ESR signals decreases with increasing amount of TAI adsorbed. Thus desensitization by dye can be reduced with increasing amount of TAI.

Decay of the ESR signal in the presence of TAI is shown in Fig. 13. This decay in all examined specimens is a second-order reaction, and in the presence of TAI it is faster than in the absence of TAI.

It was demonstrated[19] that dye positive holes are trapped by supersensitizers to form another kind of more stable positive hole, which could decrease the possibility of recombination between positive hole and photoelectron. On

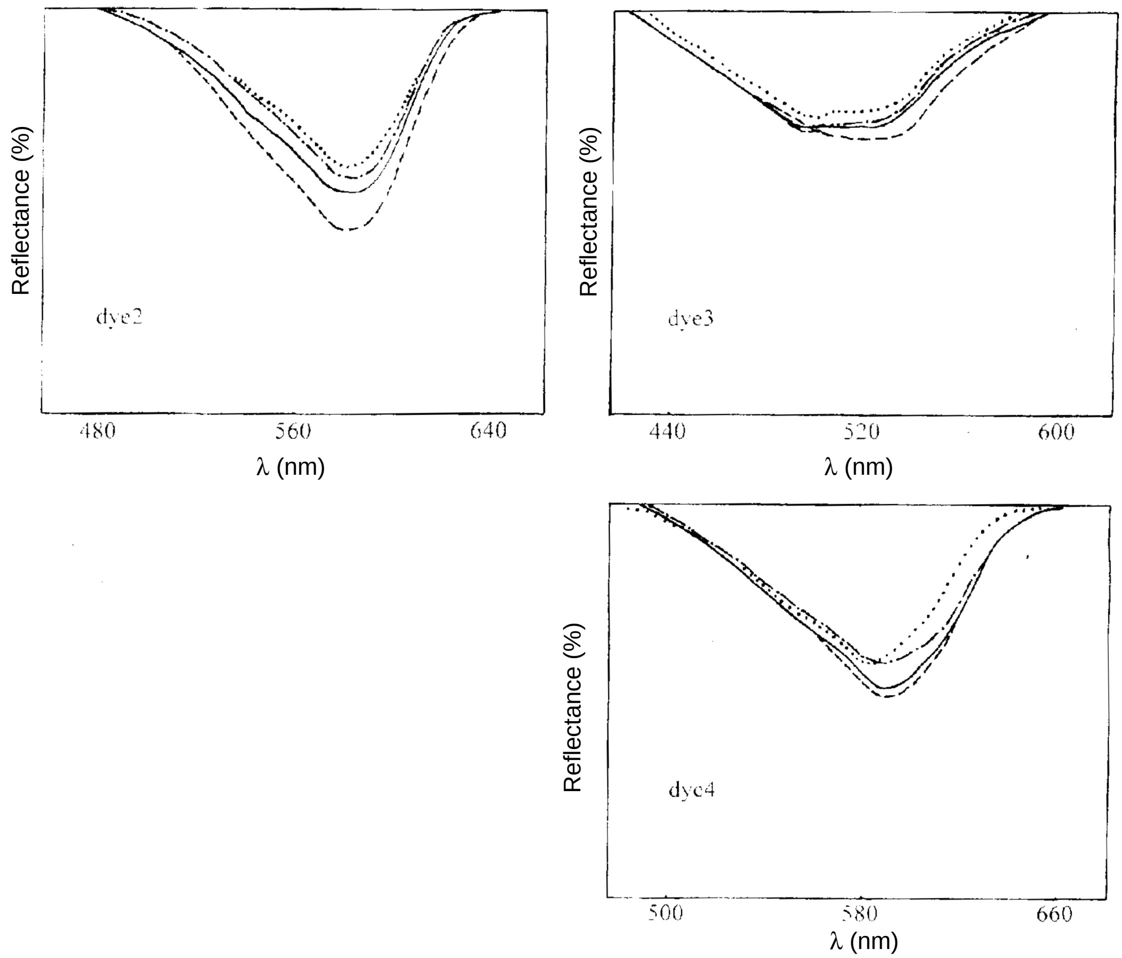


Figure 10. Same as Fig. 8, except for dyes.

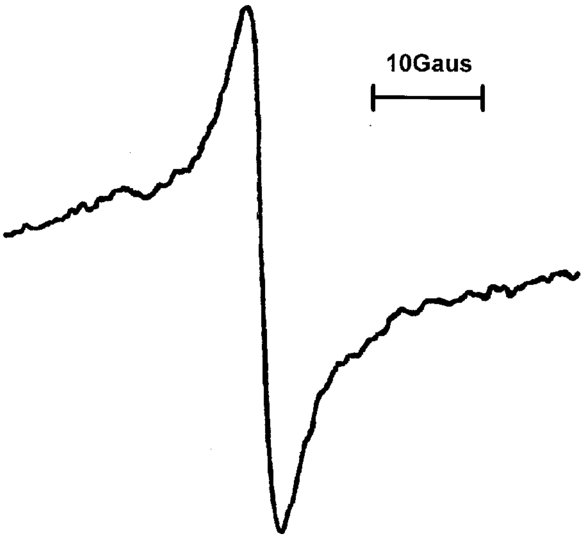


Figure 11. Typical light-induced ESR signals of dye absorbed on AgCl grains.

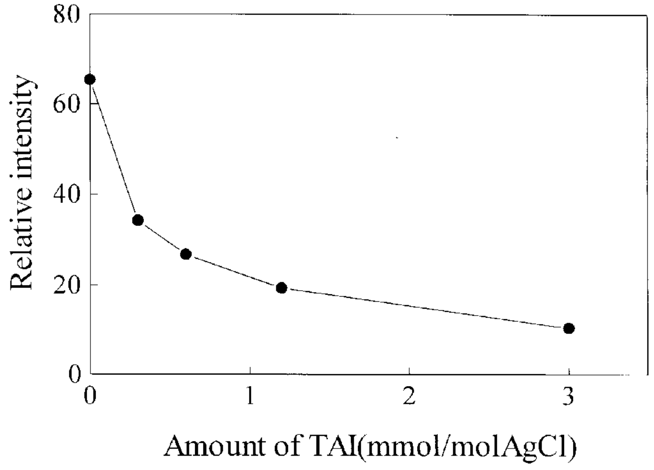


Figure 12. Intensity of ESR signal of Dye 1 absorbed on AgCl grains with various amounts of TAI.

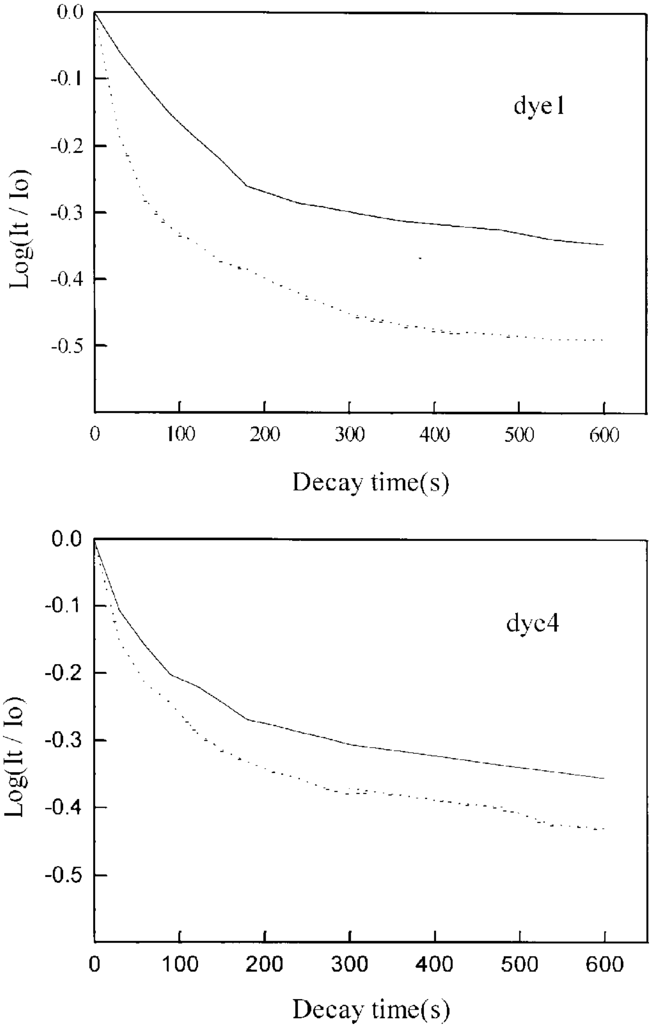


Figure 13. Decay of ESR signal affected by TAI. The amount of TAI added is 3 mmol/mol.

the contrary, our results suggest that TAI decreases the number of dye positive holes and makes the dye positive holes even more unstable. It is known that most of the adsorption of TAI on silver halide grain is by chemisorption.[5] Thus, it is possible an interaction exists between TAI and dye. Moreover, TAI is a compound with weak electron donating properties.[20] Therefore, it could be reasonably proposed that dye positive holes are trapped by TAI anions, $\text{Dye}^+ + \text{TAI}^-$ – Dye • TAI, leading to the above results.

General Discussion

Our results show that the sensitivity of spectral-sensitized AgCl emulsion could be increased by further digestion with fog inhibitors. With different order of addition of inhibitor in relation to dye, there are different sensitizing effects and distinctive dye aggregate absorptions. Accordingly, we consider that the sensitization by TAI has something to do with the effects of TAI on the dye aggregates on the AgX grains as well as on the optical absorption of the aggregates.

It is know that monomers, J-aggregates and H-aggregates of sensitizing dye, all have effects in photographic emulsion, but the effects are different. Among these, J-aggregate is the most effective and H-aggregate is, on the contrary, the most ineffective and unfavorable to photographic response. Based on the results obtained as shown in Table II and Figs. 8 and 9, the sensitizing effect is brought about when the addition of inhibitor benefits the spectral absorption of dye, especially that of the J-aggregate. A desensitizing effect took place when inhibitor addition benefits the formation of H-aggregates. Thus, it is demonstrated that sensitization by inhibitors mainly resulted from J-aggregate enhanced formation.

In aqueous dye solution, enhanced J-aggregate absorption could be ascribed to the interaction of TAI with dye. In the emulsion, enhanced absorption also may be caused by the competitive adsorption between TAI and sensitizing dye on the surface of silver halide grains.

Comparison of adsorption isotherms of TAI and some sensitizing dyes suggest that the adsorption of the sensitizing dyes on the silver halide grains is stronger than that of TAI.[21] So when TAI first adsorbs at the surface of silver halide grains, it is possible that sensitizing dye removes some TAI molecules from silver halide grains in order to be adsorbed at the same sites on the grain surfaces. Then we suppose that the adsorbed dye molecules are somewhat disordered and mainly form H-aggregates. When dye molecules adsorb before TAI, they can adsorb on grains in good order and form J-aggregates. Therefore after adsorption of TAI molecules, the dye molecules on grains are already neatly arranged and may even become more uniform and stable in the case of interaction of TAI with dye molecules, hence displaying stronger light absorption. Similar reasons are behind the changes in the adsorption spectra of emulsions incorporating other inhibitors.

Cooper[22] observed that the bromide salt of pseudoisocyanine, at low temperature and appropriate concentrations and in a solvent of 1:1 mixture of ethylene glycol and water, forms two-bands in the long wavelength region. It doubtlessly is the absorption of two different J-aggregates according to the present experiments. Daltrozzo et al.[17] also found a similar phenomenon only for the bromide salt of the dye. In addition Shapiro[10] reported a similar result for spectral-sensitized emulsion, to which TAI was added before dye, as described here. But Shapiro did not offer a reason for the formation of two different J-aggregates, which in our opinion, may be the result of competitive adsorption between TAI and dye.

From their ESR spectroscopic experiments, Siegel et al.[23,24] suggested that sensitizing dyes are reduced in the act of spectral sensitization. However, it is more generally considered that the dyes are oxidized. The induced dye positive holes lead to desensitization because of recombination, which can be classified as two types: one is the recombination of dye positive holes with free electrons; and the other is the reaction of dye positive holes with latent image centers.

It is said that J-aggregate formation has a significant influence on the behavior of dye positive holes. Gilman[25] proposed that one of the major sources of spectral sensitizing inefficiency by dyes in the J-aggregate is photoelectron-hole recombination, which is enhanced by the highly ordered nature of J-aggregated dye molecules. It is known that there is an energetic difference between the dye molecules at the ends of the aggregate and those at the middle of the aggregate. The growth of J-aggregates leads to decrease in the rate of electron transfer in spectral sensitization and an increase in the rates of the recombination of photoelectrons and dye positive holes, but also to the decrease in the rate of recombination of latent image centers with dye positive holes, because the rate of the latent image fading decreases with the decrease in the rate of the positive hole injection.[26] Moreover, research suggests that the growth of J-aggregates decreases the rate constant of the decay of dye positive holes,[27] which can also decrease the desensitization attributed to recombination of dye positive holes and image centers.

In the present study, the growth of dye J-aggregates aroused by fog-inhibitors, to some extent, leads to desensitization. We propose that this is the main cause for the sensitivity loss.

It has been found that TAI could bring about a decrease in internal sensitivity and increase in surface sensitivity.[9,12] Thereby, desensitization by recombination of dye positive holes and image centers also increases. It has been demonstrated[28] that internal sensitivity is not affected by dye positive holes. The extent of desensitization depends on the proximity of the dye hole to the latent-image sites, or the ability of the hole to move to the sites and bleach the latent image, and the dye positive hole must stay on the surface of grain. Silver halide emulsions containing internal chemical sensitization are observed to be much less subject to dye-induced desensitization by spectral sensitizing dyes that are comparable surface-sensitized emulsions.[29]

Two different kinds of adsorption interactions exist on the grain surface between dye and TAI. Photoelectron transfer from dye to silver halide grain might be retarded to some extent when TAI is first adsorbed on the surface of grain and then dye adsorbed on the layer of TAI.[10] But photoelectron transfer should not be affected when dye is first adsorbed and TAI subsequently adsorbed on the layer of dye. Thereby, the efficiency of sensitization by dye in the latter case must be higher than that in the former consistent with the results shown in Table I. In the latter case, TAI also can prevent electron-hole recombination in the J-aggregate of dye through dye positive hole trapping. Moreover, compared with Shapiro's "Isolation Theory,"[10] this kind of adsorption interaction between dye and TAI depresses desensitization more by inhibiting recombination of dye positive holes with free electrons because of higher efficiency of photoelectron transfer.

According to the above discussion, we consider that both recombination pathways can be deactivated by the decrease in the concentration of dye positive holes in the presence of fog-inhibitors as shown in Table IV and Figs. 12 and 13. However, it seems this is not the key reason for sensitization, in light of the results that sensitivity was decreased when TAI was added before dye, and that the ESR intensity was decreased much more under these conditions than when TAI was added after dye.[30] Furthermore, with the addition of TAI the conductivity of spectral-sensitized emulsions decreases and the lifetime of photoelectrons increases, both of which are beneficial to the growth of latent image centers and the concentration process of latent centers, leading to the increase of sensitivity.[15]

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