Supersensitization Aroused by Capture of Dye Positive Hole

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Introduction

A lot of photographic fog inhibitors, such as hydroxy-tetraazaindene (hereafter named TAI) and some thiolic compounds, show sensitizing effect when they were introduced into silver halide emulsion and processed digestions[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 aggregate of dye at the silver halide grains,[8] and c) depression of desensitization of dye.[9,10]

It was considered that sensitizing dyes could bring about desensitization because of the recombinations of dye positive holes with photoelectrons and/or with image centers.[11] Tani[9] concluded that the interactions of TAI with emulsion grains increase the fraction of the photoelectrons captured by the sensitivity centers of sulfur sensitization and decrease the mobility of dye positive holes in dye aggregates, accordingly, depress the dye desensitization, and the sensitization was attributed not to the desorption of dyes caused by TAI, but to the changes in the states of the dye aggregate and /or of the emulsion grains. However, Shapiro et all[10] explained the depression of dye desensitization by TAI with an "isolated theory" It was 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 isolated layer formed between the dye and the grain surface, leading to the decrease of the recombination of positive hole with electron.

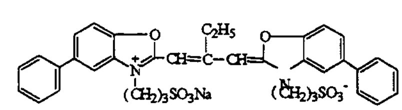
We recently observed the sensitization in unsensitized and sulphur-sensitized silver chloride emulsion by TAI and some thiolic antifoggants[5,6]. In this report, the photographic properties and the formation of dye positive holes at the presence of TAI is studied by ESR measurement. On these bases, the mechanism of sensitization by inhibitor in spectralsensitized emulsion is discussed.

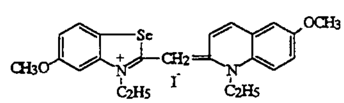
Experimental

The molecular structures of the sensitizing dyes and the fog-inhibitors used in this paper are as follows:

The photoemulsion was cubic silver chloride grains which is similar to that previously used[12]. After sulfur-sensitized, the emulsion was digested at 45 °C with the addition of sensitizing dye and inhibitor which were designed as: a) dye before inhibitor; b) in the meantime and c) dye after inhibitor.

ESR signals of dye adsorbed on silver chloride grains were obtained by use of a Uarian E-109ESR spectrometer with X-band and magnetic field modulation of 100KHz. Silver chloride grains, which were prepared as described in a former paper, 12 dye solution and TAI were put into an air-tight vessel with agitation for 2.5 hours at 25°C. Then the grains were separated by centrifuging and dried by means of vacuum freezed-drying. The obtained grains were put into a quartz tube and exposed to a Xenon lamp for 5 sec.

Dye 1


Dye 3


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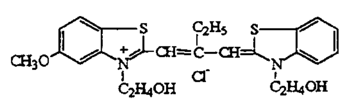
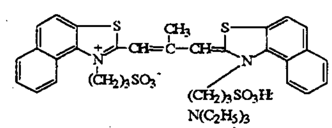
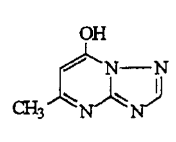
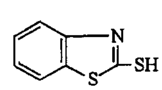
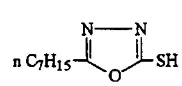
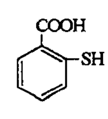


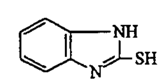
Dye 4


TAI


MBT


MHO


MB


MBM


Results and Discussion

Photographic properties

Table 1 shows sensitivity of emulsions with different adding orders of dye and fog inhibitor. It could be found that different adding orders of fog-inhibitor and dye resulted in different sensitizing effect. Only when TAI was added after these dye, could sensitization be brought about. Similar effects for other inhibitors also took place. Specially to MB, when it was added into emulsion before dye or at the same time with dye, desensitization is serious and a definite value of sensitivity can not be obtained.

When digestions were performed in the case TAI was added after dyed the obtained results are shown in Figure 1, which is the sensitivity of emulsion with the digestion of various amount of dye at the absence and presence of TAI. Within the conditions of the present experiments, the sensitivity was increased with increasing amount of dye added, and also, sensitizing effect existed at the presence of TAI. Experiments indicated that the sensitizing effect was determined by several factors, such as dye, inhibitor and the amount of addition of them.

Effect of inhibitors on the dye positive holes and its' decay speed

Measurement of ESR spectra in this paper was made at room temperature. Experiments indicated that only dyed AgCl power underwent exposure to light can give ESR signal and neither AgCl power without dye adsorption or dye underwent exposure to light nor AgCl power with dye adsorption in the dark could. All of the light-induced ESR signals of dyes adsorbed on silver chloride grains are structureless at g = 2.004. And the intensity of ESR signal increases with the increasing of exposure time till it is over 3 minutes. Moreover, intensities of ESR signal increase with increasing amount of dye, which indicates that more dye positive holes formed with increasing amount of dye. The ESR signals were obviously observed for dye1 and dye4 but not for dye2 and dye3. It is possible that the highest occupied levels of dye2 and dye3 were not high enough.

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 signal. However, our experiments indicated that intensity of ESR signal obviously decrease at the present of inhibitors, as results shown in Table 2.

Table I . Relative sensitivity of emulsion affected by the adding order of dyes and fog inhibitors

Inhibitor	Amounts of inhibitors (mmol/molAgCl)	Dye	Relative Sensitivity		
			A*	B*	M*
TAI	3	dye1	1.82	0.69	0.59
TAI	3	dye2	1.66	1.05	0.98
TAI	3	dye3	1.04	0.97	0.91
TAI	3	dye4	1.06	0.82	0.76
MHO	0.45	dye1	1.19	0.68	0.57
MB	2.76	dye1	1.22	-	-
MBT	0.54	dye1	1.12	0.95	0.93
MBM	3	dye1	1.10	0.44	0.32

* A, B and M, respectively represent inhibitors were added after, before and at the meantime with dye.

Table 2 Intensity of ESR signal affect by inhibitors

Inhibitor	Amount of inhibitor mol/mol AGCl	Intensity of ESR Signal	
		dye1	dye4
-	-	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

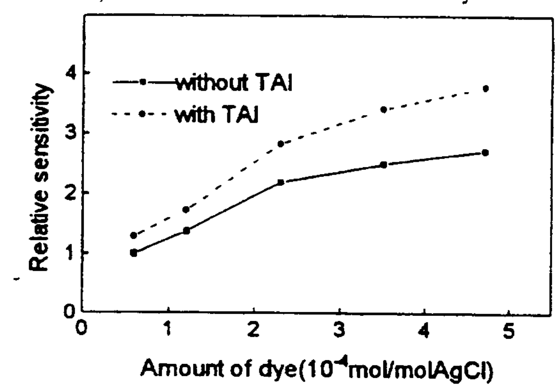


Figure 1. Effect of TAI on sensitivity of spectral- sensitized emulsion in which various amounts of dye1 were added.

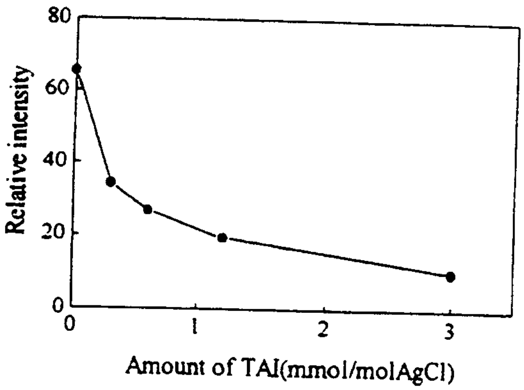


Figure 2. Intensity of ESR signal of dyel absorbed on AgCl grains with various amounts of TAI.

Intensities of ESR signal of dye adsorbed grains with various amounts of TAI are shown in Figure 2. As shown in the figure, intensity of ESR signal decrease with increasing of amounts of TAI adsorbed. Namely, desensitization by dye can be reduced with increasing amount of TAI.

Decay of ESR signal at the present of TAI is shown in Figure 3. As seen in this figure, the decay of ESR signal of emulsion at the presence of TAI are faster than that at the absence of TAI.

It was demonstrated[13] that dye positive holes were trapped by supersensitizers to form another kind of stabler positive holes which could decrease the possibility of recombinations between positive hole and photoelectron. On the contrary, above results suggest that TAI decreased the number of dye positive holes and made the dye positive holes even more unstable. It is known that most of the adsorption of TAI on silver halide grain is chemisorption,[5] that is to say, TAI exists as TAI-. And it is possible that there exists interaction between TAI and dye. Therefore, it could be reasonably proposed that dye positive holes are trapped by TAI anions, $Dye^{+} + TAI^{-} \rightarrow Dye \bullet TAI$, leading to the above results.

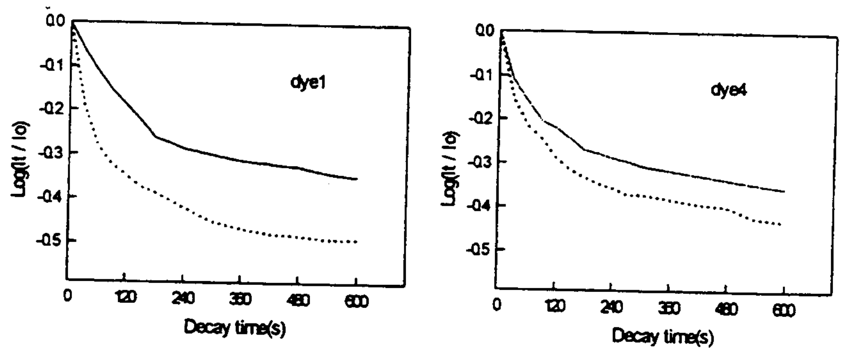


Figure 3. Decay of ESR signal affected by TAI.

On the condition there exists adsorption between dye and TAI,[10] it could be considered that, if TAI firstly adsorbed on the surface of grains and then dye adsorbed on the layer of TAI, transfer of photoelectrons from dye to silver halide grains should be retarded to some extent; on the contrary, if dye firstly adsorbed and TAI adsorbed on dye layer, photoelectron transfer will not be affected. This is also coincide with the sensitizing results shown in Table 1.

Thereby, trapping of dye positive hole by TAI' could also be easy understood. Then the concentration of dye positive hole is decreased and desensitization caused by dye positive holes arises from recombinations of dye positive holes with photoelectrons and/or image centers can be reduced.

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