# Quantitative Study of Photohole-Induced Bleaching of Latent Image Centers in AgBr Emulsions

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The photohole-induced bleaching of latent image and subimage centers in AgBr emulsions in the intrinsic absorption region has been studied quantitatively by using phenosafranine dye as an effective photoelectron scavenger. The quantum bleaching efficiencies of the minimum latent image centers in our standard development condition were thus estimated to be typically ~$0.8 \times 10^{-3}$ ($1 \times 10^{-3}$), ~$3 \times 10^{-3}$ ($3 \times 10^{-3}$), and ~$5 \times 10^{-3}$ ($4 \times 10^{-3}$), respectively, for primitive, S-sensitized, and S + Au-sensitized emulsions consisting of 0.4 – 0.53-$\mu$m cubic (0.55-$\mu$m octahedral) grains. A much higher quantum bleaching efficiency of ~$1 \times 10^{-2}$ was measured for what we identified with a two-atom subimage center. The hole-induced bleaching efficiency measured in this way correlates well but inversely with the energy gap between the highest occupied level of the center to be bleached and the valence band edge that can be derived from the corresponding photoionization threshold independently measured elsewhere. The observed energy-gap dependence suggests that the quantum bleaching efficiency is controlled kinetically by hole capture cross section that increases with decreasing hole-trapping depth, as expected for nonradiative, multiphonon processes. The present study also provides additional evidence to support that S + Au-sensitized grains allow latent image centers both with and without built-in gold atoms to form under high-intensity exposure.

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## Introduction

The photographic sensitivities of silver halide emulsions depend critically on how efficiently photoelectrons are separated from positive holes to help as large a fraction of the photoelectrons as possible to participate in the formation of a developable latent image center. The system must be optimized also with respect to undesirable secondary reactions between latent image centers and positive holes, which cause additional loss in the photographic sensitivity. Nevertheless, our knowledge of the exact photohole behavior, particularly in emulsion grains, is still limited, although much effort has been made to gain relevant information by using a variety of experimental approaches, such as delayed development study,[1,2] Dember photovoltage measurement,[3,4] radiowave photoconductivity measurement,[5] the multiflash exposure method,[6] and a photostimulated desorption study.[7] Furthermore, based on a computer simulation of microwave photoconductivity decay signals for AgBr emulsion grains, Hailstone and Erdtmann[8] have recently proposed that the electron–hole recombination can play a significant role in controlling the photoelectron decay kinetics, and they questioned the preclusion of an electron–hole recombination that simply relies on the lack of excitation-intensity dependence in the decay time. Thus, even such dynamic behavior of photoelectrons in emulsion grains may not necessarily be understood properly without reliable, complementary knowledge about positive holes.

In the present study, our focus is on the photohole-induced bleaching of latent image and subimage centers in AgBr emulsions. A similar process in a bulk AgBr crystal was utilized by Malinowski[9] for the measurement of the corresponding photohole drift mobility, which in prefogged emulsion grains is known as the basis of direct positive films.[10] Our purpose is to measure the quantum efficiency for this hole-induced process, thereby elucidating the essential physics involved. This also helps us to infer to what extent the process of latent image formation can be influenced by such secondary reactions between positive holes and latent image centers under growth, and to gain information on how other hole processes compete with the bleaching event.

In more specific terms, the hole-induced bleaching of latent image centers may be regarded as a special case of hole-trapping events involving photolytically produced silver clusters on the grain surface. Then what immediately comes up is their electronic energy levels, or more specifically the position of the highest occupied level relative to the valence band edge. In this respect, we expect that the hole-induced bleaching should be intimately correlated with the photoionization-induced bleaching,[11,12] wherein the same energy level relative to the bottom of the conduction band plays the critical role. The present study offers a good opportunity to examine whether or not such a correlation can really be established. Our present results also illuminate some essential differences from the "chemical" bleaching of latent image centers in, e.g., redox buffer solutions, which has been used extensively to study the redox properties of latent image and subimage centers.[13–15] In general, when one deals with such chemical bleaching processes, strict discrimination is necessary between the thermodynamic driving force and the kinetic one and, more importantly, between the *microelectrode potential*[16] and the *ionization redox potential*[16] for silver clusters. It is the latter quantity that directly correlates with the electronic energy levels of such metal clusters, but cannot easily be assessed without careful kinetic analysis[14] of the corresponding bleaching data. The hole-induced bleaching experiment introduced in this study, in which the quantum efficiency measurements are a major concern, is also kinetic in nature, but it helps us to gain more quantitative information relevant to the electronic properties of latent image centers.

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## Experimental

The AgBr emulsions used in this work consist of monodisperse cubic grains with mean edge lengths ranging from 0.40 to 0.53 $\mu$m, or of monodisperse octahedral grains 0.55 $\mu$m in equivalent edge length. Along with primitive emulsions given no deliberate chemical sensitization, S-sensitized and S + Au sensitized samples were also prepared. The corresponding chemical ripening took place for 40 min at 70°C, at the added sensitizer level for the S-sensitization 5.0 mg/mol Ag (cubic grains) or 2.0 mg/mol Ag (octahedral grains) $Na_2S_2O_3{\cdot}5H_2O$, and that for the S + Au sensitization 4.8/5.0 mg/mol Ag (cubic grains) or 2.0/3.0 mg/mol Ag (octahedral grains) $Na_2S_2O_3{\cdot}5H_2O/KAuCl_4$. The emulsions were coated on a clear support at silver and gelatin coverages of 1.10 and 2.2 g/m$^2$, respectively.

Latent image or subimage centers to be subjected to the hole-induced bleaching were produced by uniformly preexposing each sample film (approximately 3 × 3 cm$^2$) to band-pass-filtered blue light for ~$10^{-6}$ s (high-intensity exposure) or 1 to 100 s (moderate- to low-intensity exposure) at room temperature (~25°C) in the ambient air.

The thus preexposed sample films were treated by a solution of phenosafranine (PS), which is known as a strong desensitizing dye that can remove photoelectrons from the conduction band of AgBr. This treatment must meet some critical requirements to serve the purpose of this study. Among others, the coverage of PS molecules on the grain surface, or the corresponding electron-trapping efficiency, needs to be so high that neither formation of additional silver centers nor growth of the preformed ones occurs during the bleaching exposure. It is also desirable to make certain that the PS treatment does not cause any negative effects on development (such as development-retarding effect) and, more importantly, to prevent the preformed silver centers from being chemically bleached when the preexposed sample film is placed in the PS solution, which may potentially provide an oxidative environment. The optimum conditions for the PS treatment that best satisfy these requirements have been determined on a trial-and-error basis. The preferred solution is water/ethanol 1:1 by volume containing PS and KBr at $2.5 \times 10^{-4}$ M and $10^{-2}$ M, respectively. The sample films were immersed therein for 2 min at a relatively low temperature of 8°C and quickly air-dried thereafter. Once treated in this way, previously unexposed films exhibited virtually no photographic sensitivity in the exposure condition (see below) employed for the hole-induced bleaching, and even for films that had been rather heavily preexposed to a level beyond the shoulder region of the corresponding $D$–log $E$ curve, complete bleaching of latent image centers could be effected. It was also confirmed that the above conditions of PS treatment allow the maximum bleaching efficiency to be reached, in the sense that no further efficiency could be gained by increasing the PS concentration or the immersion time.

The hole-induced bleaching of latent image centers was caused by interference-filtered blue exposure at 440 nm (10 nm FWHM) at room temperature (~25°C) in ambient air. The exposure was given through an optical step tablet to obtain a series of intensity-scale bleaching data on a single piece of sample film, which had been uniformly preexposed and PS-treated as mentioned above. The total exposure time was typically 1000 s, but otherwise ranged from 10 to 30,000 s. The choice of an adequately low intensity condition for the bleaching exposure is another requirement for preventing the formation of additional silver centers and the growth of preformed silver centers.

The average total number of absorbed photons per grain (hereafter denoted by $Q$) was calculated by using the absorptance of the sample film, grain volume, coating weight, incident photon flux, and bleaching time. The absorptance of the sample film was measured as a function of wavelength by using an end-on photomultiplier that could satisfactorily collect the transmitted and forward-scattered light. Correction for the reflected and backward-scattered light was made by subtracting the linear background that was extrapolated from the long-wavelength data outside the intrinsic absorption. The corresponding absorption spectrum agreed well with that known for bulk AgBr, and we estimate the overall uncertainty in this measurement to be within ±20%. At the wavelength of 440 nm chosen for the bleaching exposure, the measured absorptance of the sample film is only 9.8%. This ensures that every AgBr grain in the emulsion layer absorbs an approximately equal number of incident photons to generate positive holes.

Processing of the exposed films was done in our standard development condition by using a metol–ascorbic acid surface developer (M-AA-1)[17] at 20°C for 5 min. Detection of subimage centers that are hard to develop in this standard processing condition was achieved through 10 min of gold latensification followed by 10 min of development in the same developer. The gold bath used for this post-exposure latensification was prepared according to the method described by James and colleagues.[18]

The fraction of bleached grains ($\Delta F$) was defined by the following formula, in which $D_0$ and $D$ stand for the normalized densities, i.e., the fog-corrected fractions of grains that are initially made developable by the preexposure and remain developable after the bleaching exposure, respectively.

$$\Delta F = (D_0 - D)/D_0 \tag{1}$$

The bleaching data were collected for various levels of $D_0$ controlled by preexposure adjustment.

## Results and Discussion

Figure 1(a) shows a $D_0$ versus log $E$ (log relative preexposure) curve measured for a primitive cubic emulsion (0.46 $\mu$m in edge length) in a relatively low-intensity exposure condition, 100 s in exposure time. Inclusion of the PS treatment before development did not influence the $D_0$–log $E$ curve in this case, suggesting that the PS treatment neither disturbed the development nor caused chemical bleaching, as mentioned before. However, in particular for the S-sensitized samples exposed at relatively high intensities, a noticeable speed loss, as much as 0.1 to 0.2 log $E$, was caused by subjecting the preexposed films even to the optimized PS treatment, indicating that the subsidiary effects of this treatment could not necessarily be removed completely. The cause of this speed loss, which was not overcome by prolonged development, seemed to be more like a residual chemical bleaching effect.

A collection of hole-induced bleaching curves, which were obtained at the discrete levels of $D_0$ as identified by number in Fig. 1(a), is shown in Fig. 1(b). Regardless of $D_0$, $\Delta F$ increases monotonically with log $Q$ to the limiting value of unity, at which all the preformed latent image centers lose their developability. As $D_0$ increases, however, the bleaching curve significantly shifts toward the higher exposure region, thereby gradually increasing its slope. These systematic changes of the bleaching curve can be understood easily, because the average size of latent image centers (as well as their average number/grain, depending on the preexposure intensity) is expected to increase with $D_0$, and bleaching of larger and/or more latent image centers to subdevelopable ones requires multistep bleaching events that take up more positive holes. In addition, just as the slope of the $D$–log $E$ curve increases

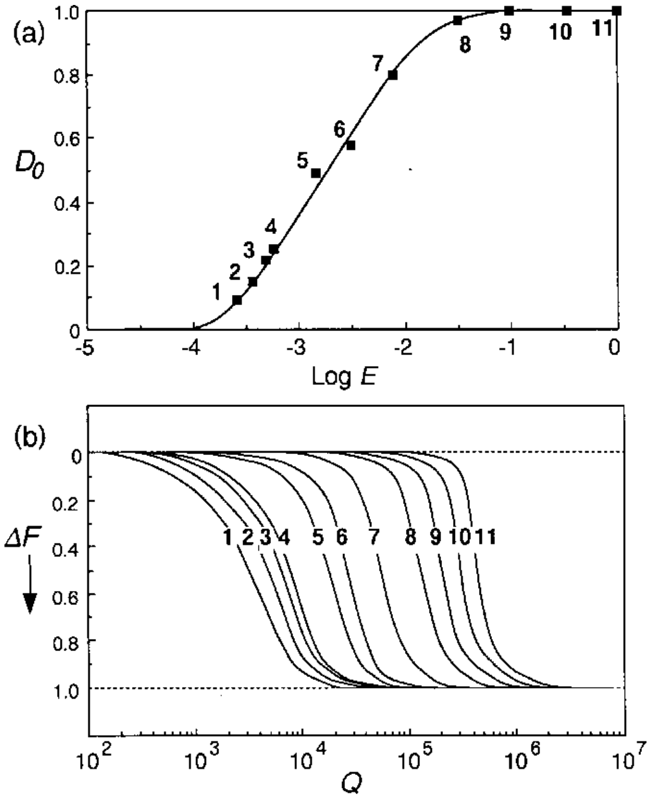


**Figure 1.** (a) Relationship between the normalized density ($D_0$) and log relative exposure (intensity-scale exposure 100 s in exposure time) to preform latent image centers for a primitive cubic emulsion (0.46 $\mu$m in edge length). The preexposed sample was treated by the PS solution in the standard manner before development to obtain the control density data without bleaching exposure. (b) A series of bleaching curves obtained for the primitive cubic emulsion at the discrete levels of $D_0$, as numbered on the $D_0$–log $E$ curve shown in part (a). The fraction of bleached grains ($\Delta F$), defined by Eq. 1 in the text, is plotted downward as a function of log average number of absorbed photons/grain ($Q$) during the bleaching exposure. Each curve was drawn through ~30 data points covering the corresponding $Q$ range.

with the increasing minimum size of developable latent image, owing to the increase in the number of growth events to make a grain developable,[19] the greater the number of hole events required to bleach a developable grain, the steeper the bleaching curve looks when drawn in the semilogarithmic $\Delta F$ versus log $Q$ format.

The quantitative information we would like to extract from the present bleaching experiment is more concerned, however, with the average number of positive holes that are required to induce a single-step bleaching of the minimum latent image center in the given development condition. The reciprocal of this quantity then represents the corresponding quantum efficiency. We have used a relatively simple extrapolation method to determine this quantum efficiency from the series of bleaching curves measured at various levels of $D_0$. For this purpose we first define the apparent quantum bleaching efficiency $\Phi_{bl}$ as a function of $D_0$ by the reciprocal of $Q$ that corresponds to $\Delta F = 0.5$, the point at which half of the initially developable grains are bleached. Efficiency $\Phi_{bl}$ defined in this way represents an average bleaching efficiency (not necessarily for single-step bleaching) for the latent image centers formed at each level of $D_0$. Of course, for the definition of $\Phi_{bl}$, $\Delta F = 0.5$ is not necessarily the only possible choice. Nevertheless, if the statistical nature of the hole-induced bleaching process, as well as that of the light absorption by individual grains, is taken into account, it is clear that a $\Delta F$ that is too small or too large cannot be used to define such a statistical average. For example, Curve 1 in Fig. 1(b), obtained at $D_0 \sim 0.1$, indicates that a minor but noticeable fraction of developable grains already begins to be bleached at $Q \ll 10^{-3}$ ($\Delta F \sim 0.1$ or less). However, these grains apparently correspond to those that absorbed more photons than the average and in which the hole-induced bleaching occurred with the highest possible efficiency, far above the average. At present it is difficult to know exactly how each bleaching curve reflects the changes in the average number and the average size of developable latent image centers as a function of $Q$. If so, the inverse average number of positive holes ($=1/Q$) required to bleach half of the initially developable grains would be the most reasonable quantity to be chosen as the $D_0$-dependent "average quantum efficiency" $\Phi_{bl}$.

The relationship between $\Phi_{bl}$ and $D_0$ can then be used for extrapolating to the limiting value of $\Phi_{bl}$ (denoted by $\Phi_{bl}^0$) at $D_0 = 0$. The average size and the average number of latent image centers formed in developable grains should be minimized to the limit at this zero optical density, so that the corresponding quantum efficiency $\Phi_{bl}^0$ is thought to be a good representative of (though could still be the upper limit of) the quantum bleaching efficiency for the minimum latent image center. Besides, except for the region of $D_0$ greater than ~0.8, log $\Phi_{bl}$ proved in many cases to be an approximately linear function of $D_0$, thus allowing a simple linear extrapolation to infer the limiting value. (Note that the normalized density $D_0$ never exceeds unity, but the latent image size continues to increase by increasing the preexposure level. As a result, log $\Phi_{bl}$ changes quite steeply with $D_0$ as $D_0$ approaches unity.) Moreover, the validity of this approach can be strengthened by comparing one limiting value with another extrapolated from a set of log $\Phi_{bl}$-versus-$D_0$ relationships, which can be obtained for varied preexposure conditions that alter the way $\Phi_{bl}$ depends on $D_0$. This can be done most easily by changing the preexposure condition.

Figure 2 shows typical relationships between log $\Phi_{bl}$ and $D_0$ measured for the primitive emulsions consisting of cubic and octahedral grains. The preexposure here was given at three different intensities: 100, 1, and ~$10^{-6}$ s in exposure time. Note that the $D_0$ dependence of log $\Phi_{bl}$ becomes steeper as the preexposure intensity is decreased. This trend is not particularly surprising, considering that the nucleation efficiency in the process of latent image formation can be considerably reduced with decreasing exposure intensity while the growth efficiency may be almost unaffected. Thus, to make the same fraction of grains developable (to gain the same level of $D_0$), heavier exposure is needed at lower intensity. Once nucleated, however, each silver center may grow even more efficiently than at higher intensity. The corresponding grains with such growing silver centers thus tend to be overexposed. As a result, when averaged among the grains that have been made developable at each level of $D_0$, the latent image size may increase more rapidly with $D_0$ at lower exposure intensity, which in turn increases the slope with which log $\Phi_{bl}$ changes with $D_0$.

In Fig. 2 we can see that simple linear extrapolations work considerably well and, except for the cubic emulsion preexposed at the lowest intensity, the linearly extrapolated $\Phi_{bl}^0$ values for the varied preexposure conditions coincide reasonably with each other, particularly well in the case of the octahedral emulsion. The exceptional behavior of the 100-s data of the cubic emulsion may be interpreted as suggesting that the initial slope in this case could be significantly higher than that of the approximate, single

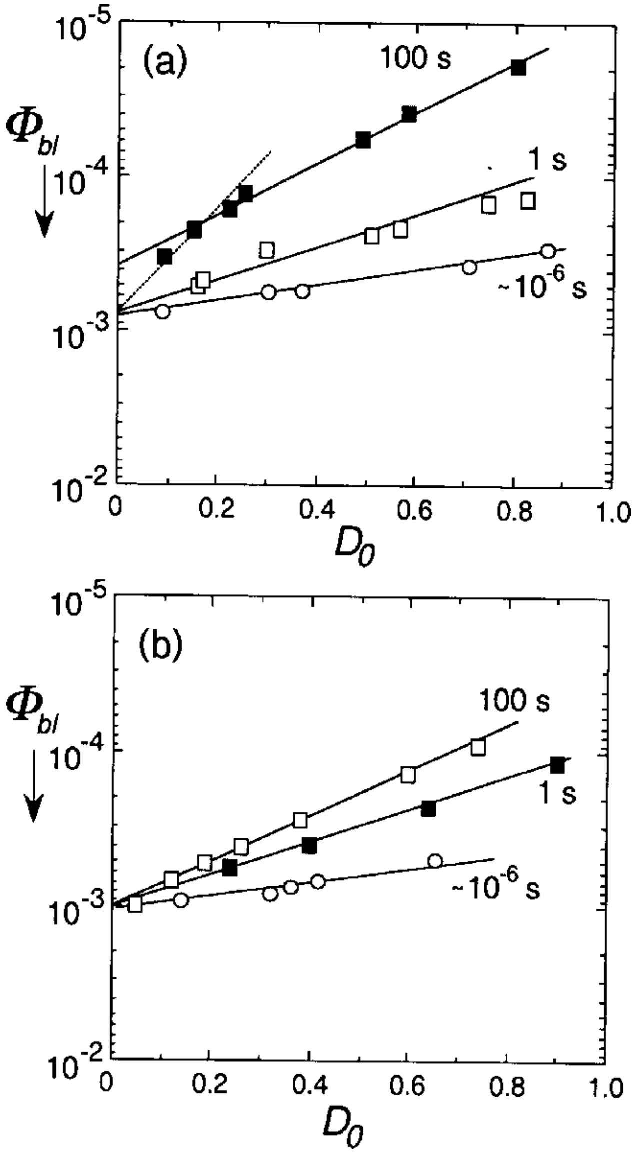


**Figure 2.** Log apparent bleaching efficiency ($\Phi_{bl}$) versus $D_0$ relationships measured for primitive emulsions consisting of (a) cubic (0.46-$\mu$m) and (b) octahedral (0.55-$\mu$m) grains. Efficiency $\Phi_{bl}$ is defined by the reciprocal of $Q$ that corresponds to the point on the bleaching curve at which half of the initially developable grains are bleached (i.e., $\Delta F = 0.5$). The preexposure was given at varied intensities (100-, 1-, and ~$10^{-6}$-s exposure times), thereby the $D_0$ dependence is altered significantly. Simple linear extrapolations (solid lines), however, give approximately the same limiting value of $\Phi_{bl}$ at $D_0 = 0$, except for the 100-s data of cubic emulsion. An alternative way of extrapolation (dotted line) assumes a relatively large initial slope for this exceptional case, leading to almost the same limiting value as that extrapolated from the 1-s and ~$10^{-6}$-s data.

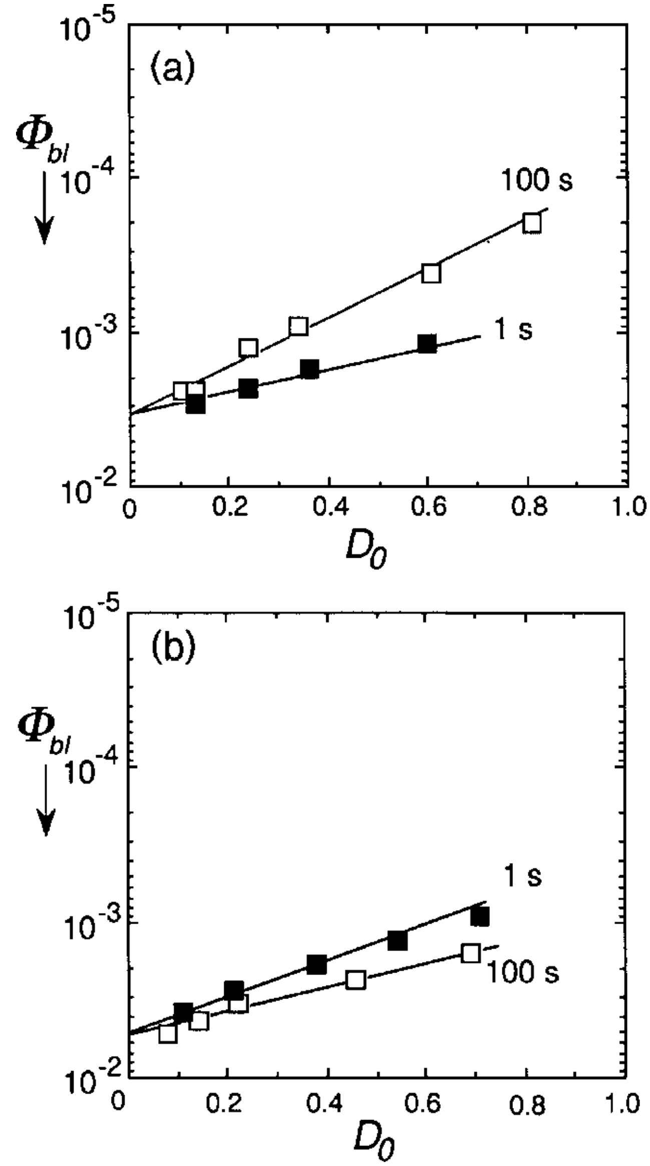


**Figure 3.** As in Fig. 2 but for (a) S-sensitized and (b) S + Au-sensitized cubic (0.46-$\mu$m) emulsions.

linear function [solid line in Fig. 2(a)]. When the slope (particularly the initial slope) in the log $\Phi_{bl}$-versus-$D_0$ relationship becomes too large, it is not particularly surprising that a single linear function fails to approximate the whole relationship. An alternative way of extrapolation [see the dotted line in Fig. 2(a)], which is still linear but applied to the data in the small $D_0$ region less than 0.2, may indeed lead to almost the same limiting value as derived from the 1- and $10^{-6}$-s data. At any rate, $\Phi_{bl}^0$ determined by the above method seems to be a good representative, with minor exceptions, of the quantum efficiency with which the minimum latent image center undergoes hole-induced bleaching. From Fig. 2 the specific values of $\Phi_{bl}^0$ for the cubic and octahedral emulsions are estimated to be ~$0.8 \times 10^{-3}$ and ~$1.0 \times 10^{-3}$, respectively, and not much different from each other. In addition, no significant grain-size dependence of $\Phi_{bl}^0$ could be observed for the cubic emulsions, though in the restricted size range, 0.4 to 0.53 $\mu$m in edge length. We may thus associate the quantum bleaching efficiency of around $10^{-3}$ fairly uniquely with the minimum latent image center formed on the primitive AgBr grain surface.

Figure 3 shows how S- and S + Au-sensitizations affect the photohole-induced bleaching of latent image centers. Here again, the log $\Phi_{bl}$-versus-$D_0$ relationships (measured in two different preexposure conditions) exhibit sufficient linearity to allow simple linear extrapolation for determining the limiting quantum efficiency. It is worth mentioning, however, that for the S + Au-sensitized emulsion the corresponding slope appears to become greater at higher preexposure intensity, contrary to the general trend discussed already. This exceptional behavior of the S + Au-sensitized emulsion is discussed later in connection

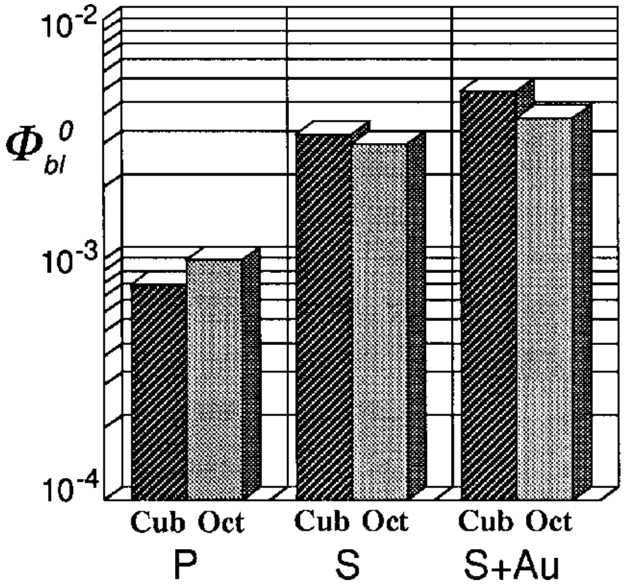


**Figure 4.** Histogram to summarize and compare the limiting quantum bleaching efficiencies determined for the minimum latent image centers formed in various kinds of sample emulsions.

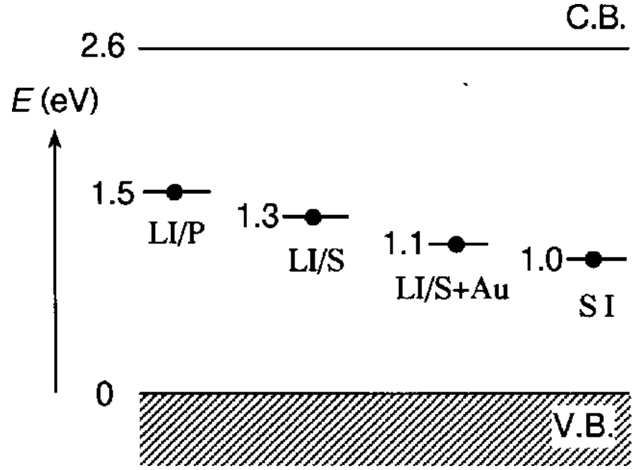


**Figure 5.** Simple energy-level diagram showing the positions of the highest occupied levels of the minimum latent image centers in primitive (LI/P), S-sensitized (LI/S), and S + Au-sensitized (LI/S+Au) emulsions, along with that associated with a two-atom subimage center (SI), as estimated from the corresponding photoionization thresholds measured elsewhere.[11,12]

with another set of useful bleaching data obtained for this type of emulsion.

By comparing Fig. 3 with Fig. 2 one can readily see that the bleaching efficiency $\Phi_{bl}$ given as a function of $D_0$ is increased significantly as a whole by the S and S + Au sensitizations, as is the limiting quantum efficiency, $\Phi_{bl}^0$, which is estimated to be ~3 × $10^{-3}$ and ~5 × $10^{-3}$ for the S and S + Au-sensitized emulsions, respectively. The results indicate that the minimum latent image center formed on the S + Au-sensitized grain is easiest to bleach of all the latent image centers we have investigated. This strongly contrasts with the fact that latent image centers formed on the S + Au-sensitized grains, being generally composed partly of gold atoms, are hardest to bleach chemically in redox solutions.[12] Here we should stress again that $\Phi_{bl}^0$ is concerned with the single-step bleaching of the minimum developable center for each emulsion type and development condition. Thus the mere size effect that larger centers have to experience multistep bleaching events before they lose developability has little or no relevance to the observed trend of the limiting bleaching efficiency. It should also be noted that positive holes, located at the top of the valence band in energy, can be credited with an effective redox potential much more positive than those of conventional redox solutions used for chemical bleaching, so as to be capable of bleaching any kinds of photolytic centers in a thermodynamic sense. In other words, the hole-induced bleaching efficiencies being studied here must be controlled by kinetic factors. On the other hand thermodynamic considerations become much more important for chemical bleaching processes, particularly when the redox stabilities of latent image centers are of major concern.[14] Note in addition that the term "quantum efficiency" is itself a strongly kinetic concept.

In the histogram shown in Fig. 4, the limiting quantum bleaching efficiencies, $\Phi_{bl}^0$, measured for various types of emulsions are summarized and compared with each other. Irrespective of the kinds of chemical sensitizations, the difference between cubic and octahedral emulsions is not very significant, and the increasing trend of quantum efficiency in the order of P (primitive) < S < S + Au can be readily confirmed. If the hole-induced bleaching occurs through direct interaction between latent image centers and positive holes, the most important kinetic factor associated with latent image centers is probably their hole-capture cross section. There are two primary parameters underlying this quantity: the effective charge and the hole-trapping depth of the center to be bleached. It is quite probable that latent image centers carry some partial positive charge. The comparatively small quantum efficiencies, as a whole, of the order of $10^{-3}$ could possibly be due to this repulsive positive charge. However, there is no ground on which we can associate the least net positive charge with latent image centers formed on the S + Au-sensitized grains to account for the observed largest quantum efficiency. We are thus left with the hole-trapping depth, of which the variation, as described below, indeed correlates reasonably with the variation in the quantum bleaching efficiency.

To first approximation, the hole-trapping depth of an arbitrary latent image center may be equated with the energy gap between its highest occupied electronic energy level and the top of the valence band. This is complementary to the energy level relative to the bottom of the conduction band, which we previously studied through a series of photoionization-induced bleaching experiments.[11,12] Note that in these experiments what was measured was the photoionization threshold, i.e., the minimum photon energy required to induce the photobleaching, which is never the energy at which the photoionization cross section is maximized. Thus this energy, though measured by an optical method, does not really give the optical depth or the vertical ionization energy, but should rather be identified, within the experimental uncertainty (less than ±0.1 eV) associated with the threshold determination, with the adiabatic ionization energy or the thermal depth of the highest electron occupied by the latent image center. The corresponding photoionization thresholds determined in our standard development condition can therefore be directly transformed to the above-noted energy gaps with respect to the valence band edge. By using 2.6 eV for the band gap of AgBr it follows that the minimum latent image centers in primitive, S-sensitized, and S + Au-sensitized AgBr emulsions have the highest occupied levels (~1.5, ~1.3, and ~1.1eV, respectively), above the valence band edge.

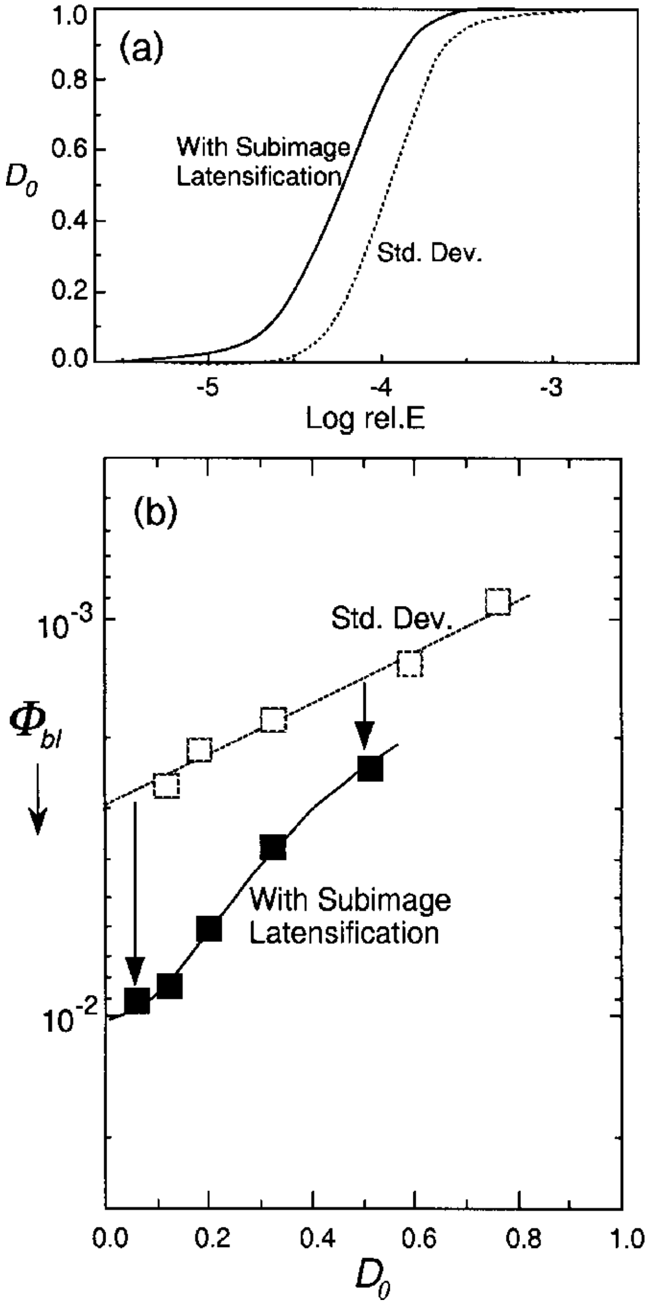


**Figure 6.** Effect of subimage latensification (gold latensification) on log $\Phi_{bl}$-versus-$D_0$ relationship for the S-sensitized octahedral emulsion. The latent image and subimage centers were produced by relatively low-intensity preexposure, 100 s in exposure time. Effective subimage detection is illustrated by the upper set of $D_0$–log $E$ curves measured with and without subimage latensification.

For reference, the locations of these levels are illustrated in a simple energy-level diagram (Fig. 5), which also includes the level associated with the two-atom subimage center discussed later. Thus the hole-trapping depth decreases in the order P > S > S + Au, which inversely correlates with the order of hole-induced bleaching efficiency, P < S < S + Au. One may interpret this correlation as reproducing the known trend in photocarrier dynamics that deeper carrier traps tend to have smaller capture cross sections.[20] Note also that, for such hole traps, which are deeper than 1 eV, the corresponding hole-trapping process should be essentially irreversible in nature. In this situation the hole-capture cross section becomes an even more important and decisive factor in controlling the reactivity of positive holes with latent image centers.

The qualitative correlation between the hole-trapping depth and the hole-induced bleaching efficiency may still be weak at this stage, in the sense that latent image centers formed in primitive or S-sensitized emulsion and those in S + Au-sensitized emulsion differ in chemical composition if the latter contain built-in gold atoms. We therefore extended our experiment to examine also the bleaching characteristics of subimage centers. The S-sensitized emulsions best serve this purpose, because stable two-atom silver centers formed therein can be detected relatively easily by using a gold latensification.[21] The highest occupied level of this center relative to the valence band edge, estimated again from the corresponding photoionization threshold, is ~1.0 eV,[12] thus being nearest to the valence band edge of all the photolytic centers discussed in this article (see Fig. 5). If the proposed correlation between the hole-trapping depth and the hole-induced bleaching efficiency is valid, these subimage centers must be bleached with the highest quantum efficiency.

In Fig. 6(a) we show that when applied to S-sensitized emulsions the gold latensification indeed produces a considerably large (~0.3 log $E$) speed increase, even in such a low-intensity exposure condition as a 100-s exposure time.[22] Obviously some significant fraction of otherwise undevelopable grains has been made developable after the gold bath treatment, which we attribute specifically to the detection of two-atom subimage centers. Then, the question is, what would happen to three-atom silver centers that must be also integral parts of subimage centers if the minimum latent image centers consist of at least four silver atoms. In our opinion, based on the relevant redox-stability study by Hada and colleagues,[23] three-atom silver centers are chemically so unstable that even in a weakly oxidative environment they are subjected to partial oxidation to the more stable two-atom state. As mentioned before, a residual chemical bleaching effect of the PS treatment could not completely be removed in some cases. If so, it would be hard for three-atom centers to survive through this pretreatment before the bleaching exposure. We therefore suggest that the hole-induced bleaching characteristics associated with three-atom centers do not show in the present experimental results. It has been shown that the highest occupied level of three-atom centers goes to the opposite extreme from that of two-atom centers.[11,12] In this respect their behaviors including the redox stability continue to be an important issue requiring further pursuit.

Under the above assumption concerning three-atom centers, the relationship between log $\Phi_{bl}$ and $D_0$ measured in this subimage-detecting development condition [Fig. 6(b)], exhibits features fully consistent with the proposed correlation between hole-trapping depth and hole-induced bleaching efficiency. In Fig. 6(b), a curved line connecting through the data points (closed squares) is just for emphasizing these features. Also included in Fig. 6(b) for comparison are the reference data (open squares) taken in the standard development condition. It can be seen that in the region of $D_0$ less than ~0.2, $\Phi_{bl}$ deviates farthest from the reference data and takes values close to $1 \times 10^{-2}$. Note that according to Fig. 6(a) the majority of grains contributing to $D_0$ in this region are those which contain only subimage centers that are made developable by gold latensification. It thus follows that these subimage centers, which we specifically identified with two-atom silver centers, are bleached certainly with much higher quantum efficiency than that associated with the minimum latent image center developable in the standard development

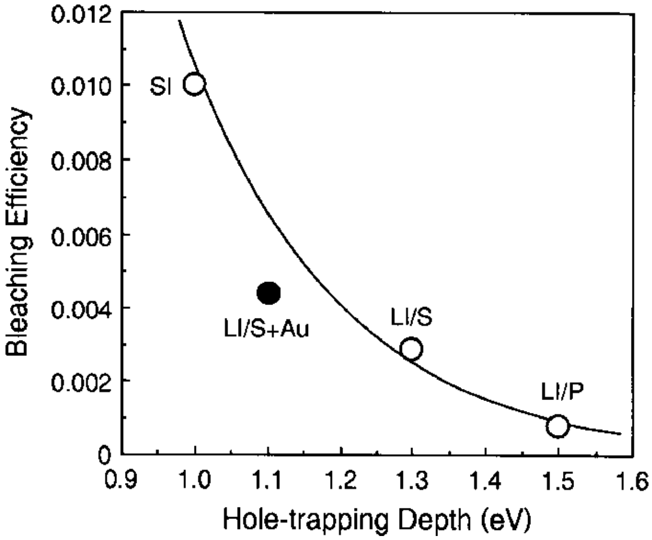


**Figure 7.** Correlation between the quantum bleaching efficiencies (averaged for cubic and octahedral grains) evaluated in this study and the hole-trapping depths from Fig. 5. The specific identity of each data point is shown by the same notation as used in Fig. 5. The curve represents the least squares exponential fitting to the three data points (open circles) for silver centers.

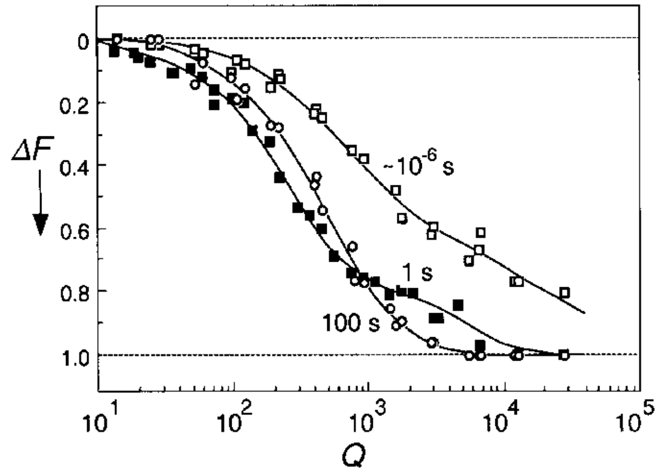


**Figure 8.** A set of bleaching curves measured for S + Au-sensitized cubic (0.4-$\mu$m) emulsion in three different preexposure conditions (100-, 1-, and ~$10^{-6}$-s exposure times) used to preform latent image centers. The fraction of developable grains before bleaching, $D_0$, was adjusted to ~0.5. Contribution of latent image centers much harder to bleach becomes noticeable and larger as the preexposure intensity is increased.

condition. This is another indication of qualitative difference between the hole-induced bleaching and the chemical bleaching, as the subimage centers made developable by gold latensification have been shown to be more difficult than the latent image centers to oxidize in redox buffer solutions.[13,15] In the subsequent stage, where $D_0$ increases to the level allowing a meaningful fraction of grains to form latent image centers, the apparent bleaching efficiency, $\Phi_{bl}$, should be determined by a mixed contribution of subimage and latent image centers characterized by the markedly different bleaching efficiencies. Thus a gradual transition occurs from the subimage-controlled to latent-image-controlled bleaching, thereby $\Phi_{bl}$ gradually approaches the reference data. This trend can also be confirmed in Fig. 6(b). Note also that there is no particular need for making extrapolation to the limiting quantum efficiency in the case of two-atom subimage centers, because they are the smallest photolytic center. Thus the $\Phi_{bl}$ value of $\sim 1 \times 10^{-2}$ suggested by the data in the smallest $D_0$ region already represents well the corresponding quantum efficiency. (Even if the linear extrapolation is applied to these data, the limiting value will be only slightly greater than $1 \times 10^{-2}$.) In addition to the octahedral emulsion used to obtain the data shown in Fig. 6, a similar experiment was also carried out with an S-sensitized cubic emulsion. Because the gold latensification caused noticeably higher development fog in this case, reliable bleaching data for the smallest $D_0$ region below 0.1 could not be obtained. Even so, the results were qualitatively similar to that shown in Fig. 6, and a quantum bleaching efficiency around $1 \times 10^{-2}$ could also be assigned to the corresponding subimage centers.

Even though the cluster sizes and environments (with or without chemical sensitization) are different, we now have three sets of data for silver centers to examine a little more quantitatively the correlation between the hole-trapping depth and the hole-induced bleaching efficiency. Figure 7 shows how these quantities correlate with each other. For reference we have also included in this plot a data point for the S + Au-sensitized samples. The smooth curve drawn in Fig. 7 represents the least squares exponential fit to the three data points for the silver centers. It may merely be fortuitous, but interestingly the corresponding fitting parameters predict a quantum efficiency of the order of unity at the zero energy gap. In any case the number of data available at present is too limited to allow us to make any conclusive remark on the quantitative energy-gap dependence of the hole-induced bleaching efficiency. We note, however, that this efficiency is most likely controlled by the hole-capture cross section of the respective silver center, and the hint of an exponential energy-gap dependence is not necessarily difficult to rationalize if positive holes are captured by the silver centers through a nonradiative, multiphonon process.[24]

In Fig. 7 the data point for the S + Au-sensitized samples comes to a position a little too far from the exponential fitting curve, perhaps because the latent image centers formed on the S + Au-sensitized grains generally consist partly of gold atoms. Yet, as emphasized already, the corresponding bleaching efficiency is the largest among those for various latent image centers detected in the standard development condition. It is of considerable interest to know what then would happen to photolytic centers that are formed on the same S + Au-sensitized grains but do not contain gold atoms. In a previous article concerning the photoionization-induced bleaching,[12] we have proposed that when produced by high-intensity exposure some fraction of the latent image centers consists of only silver atoms. If so, this must be somehow reflected in the hole-induced bleaching characteristics as well.

A series of bleaching curves shown in Fig. 8, measured at varied preexposure intensities (100-, 1-, and ~$10^{-6}$-s in exposure time) but at approximately the same level of $D_0$ around 0.5, indeed exhibit unusual features that are closely associated with such an intensity-dependent variation in the latent image composition, characteristic of S + Au-sensitized grains. We can see that the curve measured in the pulsed preexposure condition with the highest intensity apparently comprises two components, with which markedly different bleaching efficiencies can be associated. The component with the smaller bleaching efficiency is still visible in the curve derived by using the 1-s preexposure with a moderate intensity, but disappears in the condition of the lowest preexposure intensity, 100 s in exposure time. This systematic change in the bleaching curve is fully consistent with an above-

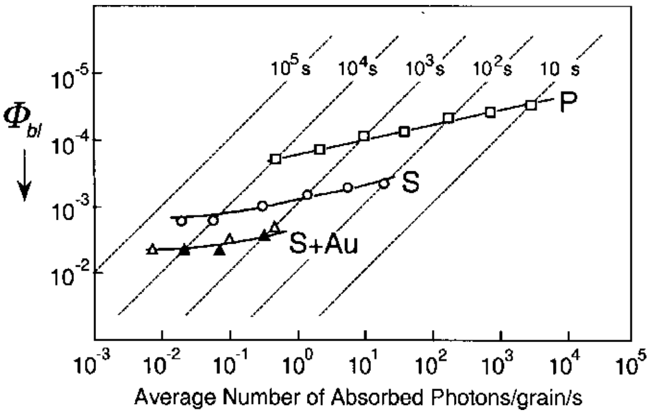


**Figure 9.** Relationships between the apparent bleaching efficiency and the intensity of bleaching exposure at a constant level of $D_0$ adjusted to ~0.3. The data were obtained with cubic (0.53-μm) emulsions, except for the S + Au-sensitized samples, for which both cubic and octahedral (0.55-μm) data (open and closed triangles, respectively) are included.

noted feature of latent image formation in S + Au-sensitized emulsions, i.e., that centers with no built-in gold atoms can be produced concurrently under high-intensity exposures, provided that these centers are bleached with considerably low quantum efficiencies comparable with those in the primitive emulsions. It was mentioned before that, contrary to the general trend, the log $\Phi_{bl}$-versus-$D_0$ profile becomes steeper at higher intensity in the case of the S + Au-sensitized emulsion [see Fig. 3(b)]. This exceptional behavior also can be understood on the same basis. It is quite significant that, even if they are formed on the same S + Au-sensitized grains and subjected to the attack of identical positive holes, the corresponding bleaching efficiencies of latent image centers with and without built-in gold atoms are markedly different. This result strengthens the conclusion that the hole-induced bleaching efficiency depends critically on the properties of latent image centers.

Note that all of the bleaching data presented above were obtained by using intensity-scale bleaching exposure with the exposure time fixed at 1000 s. To complement these data, therefore, it would be helpful to give some additional information about how the intensity of bleaching exposure affects the experimental result. First, it would be obvious that if the intensity is too high not all of the photoelectrons are removed by the PS molecules, and some fraction thereof will be taken up by the preformed latent image centers. It is meaningless to refer to the quantum bleaching efficiency in such circumstances. Taking this fact into account, we show in Fig. 9 reciprocity-failure type curves for the hole-induced bleaching over the range of light intensity (expressed by the average number of absorbed photons/grain/s) in which we can trust that the majority of photoelectrons are successfully removed by PS. In this region, the apparent bleaching efficiency, $\Phi_{bl}$, still exhibits a tendency to increase with decreasing intensity of bleaching exposure. However, this residual intensity dependence is not so strong and seems to fade away in the low-intensity limit. It appears that the intensities corresponding to 1000 s in exposure time are still not low enough to reach this intensity-independent region. However, using longer exposure times is too time-consuming to acquire the necessary number of bleaching data, without producing any useful additional information. We believe that the series of bleaching data obtained by the fixed 1000-s bleaching exposure represents approximately intensity-independent hole-induced bleaching characteristics in our sample emulsions.

It would still be useful to discuss further the cause of the residual intensity dependence shown in Fig. 9. This also relates to the important question that, if the hole-induced bleaching efficiency is of the order of $10^{-2}$ at best, where do the majority of positive holes go that failed to induce bleaching of the preformed photolytic centers. It is particularly important here to realize the self-evident fact that, without such competitive hole processes, the concept of *quantum bleaching efficiency* becomes meaningless. One possible candidate for such competitive hole processes is the coupling of positive holes on the grain surface whereby they can be released as bromine gas molecules.[7] This process, which is apparently second order in nature, will become more effective at higher intensity. Although this trend is qualitatively in agreement with the observed intensity dependence, we doubt if this surface hole-coupling process plays the dominant role in competing with the hole-induced bleaching. The reason is that the measured bleaching efficiencies are not significantly different between cubic and octahedral grains, whereas these two kinds of grains must be considerably different in terms of the surface structure and property that will probably have some significant influence on the coupling reaction. In our experimental condition, the recombination of positive holes with the electrons trapped by the PS molecules is thus thought to be a more likely competitive process, which also becomes more effective at higher intensity. Note, however, that in the lowest intensity region of Fig. 9 one positive hole is generated after another in each grain at an average time interval far greater than 1 s. In this extreme situation, one cannot expect to observe any significant intensity dependence, even for the second-order recombination process.

The extremely small hole generation rate just mentioned has yet another significance. In this condition, unless a significant number of positive holes (and hence electrons generated together and then trapped by PS molecules) are accumulated with bleaching time, it is only a minor fraction of the large number of adsorbed PS molecules that, by trapping electrons, can effectively compete with the photolytic center for positive holes. In other words, the competition in question can be virtually between one photolytic center and an electron trapped by one of the PS molecules. Then the fact that even the maximum quantum bleaching efficiency, which was measured for the two-atom subimage centers in the S-sensitized emulsions, still remains as small as ~$1 \times 10^{-2}$ suggests that direct attacks of positive holes on subimage and latent image centers are far less efficient processes than recombination with the electron trapped by the PS molecule. Thus, unless the electron trapped at the PS molecule has an unusually large capture cross section for a positive hole, the hole-induced bleaching event should be regarded as an essentially inefficient process. As mentioned earlier, the small probability of this direct hole attack on latent image centers could be due partly to some partial positive charge potentially carried by the photolytic centers. According to Fig. 7, the significantly large hole-trapping depths greater than ~1 eV may also be the likely cause to suppress the hole-induced bleaching efficiency to that extent.

Of course, the quantitative information about the hole-induced bleaching efficiency in the PS-treated samples is not directly applicable to practical emulsions with no PS. There, however, photoelectrons obviously assume much higher freedom, so that another, generally more efficient, type of recombination involving trapped holes and free electrons comes to play an important role in controlling the efficiency of latent image formation. It is questionable that the hole-induced bleaching event, being a much less efficient process relative to the PS-mediated recombination as discussed above, becomes as efficient as that type of recombination between trapped holes and free electrons. Thus, though the present study concerns the hole processes in the PS-treated samples, the results additionally give us a hint that the direct interaction between latent image centers and positive holes could be of rather minor importance in practical emulsions in determining the photographic sensitivity.

Finally, there are some related issues that remain to be investigated further. Among them, we are strongly concerned with the bleaching behavior of reduction sensitization centers and how it compares with that of subimage centers. We have already confirmed on a preliminary basis that for reduction-sensitized emulsions the efficiency of hole-induced bleaching efficiency was drastically decreased by roughly an order of magnitude, as compared with the nonreduction-sensitized counterparts. This certainly lends strong support for the participation of positive holes in the bleaching processes studied in this work. It should be also noted that for this large effect of reduction sensitization on the bleaching efficiency, the speed increase gained by the same, relatively low level of reduction sensitization was only about 0.3 log $E$ at most. This fact may provide further indirect support for the proposed minor importance of the hole-induced bleaching event in determining the photographic sensitivity. The remaining problem is that we have not yet succeeded in extracting reliable information about how efficiently each of some large number of reduction sensitization centers on the single grain surface reacts with positive holes. Further study is thus necessary to gain this kind of information, prerequisite for making careful comparison between reduction sensitization centers and subimage centers in terms of the reactivity with positive holes.

## Summary and Conclusions

The photohole-induced bleaching of latent image and subimage centers in AgBr emulsions has been studied quantitatively by using phenosafranine (PS) dye as an effective electron acceptor to prevent formation of additional centers and growth of preformed latent image centers. By optimizing the PS treatment and choosing the bleaching exposure of comparatively low intensity, the number of positive holes required for the hole-induced bleaching, or equivalently the quantum bleaching efficiency, has been determined for various photolytic centers. The main conclusions are:

1. The quantum bleaching efficiencies of the minimum latent image centers in our standard development condition, as determined by using a simple linear extrapolation method, are typically ~$0.8 \times 10^{-3} (1 \times 10^{-3})$, ~$3 \times 10^{-3} (1 \times 10^{-3})$, and ~$5 \times 10^{-3} (4 \times 10^{-3})$, respectively, for primitive, S-sensitized, and S + Au-sensitized AgBr emulsions consisting of 0.4 to 0.53-$\mu$m cubic (0.55-$\mu$m octahedral) grains.
2. The largest quantum bleaching efficiency observed for the S + Au-sensitized emulsions strongly contrasts with the highest chemical stability generally associated with the corresponding latent image centers. Thus the kinetic hole-induced bleaching efficiency does not necessarily reflect the thermodynamic redox stability.
3. The quantum bleaching efficiency measured for what we identify with a two-atom subimage center in the S-sensitized emulsions is ~$1 \times 10^{-2}$, the highest of all the values determined in this study. This result also contrasts with the relatively large thermodynamic redox stability that can be associated with these subimage centers.
4. The series of quantum bleaching efficiencies measured in this study correlates inversely with the hole-trapping depth, i.e., the energy gap between the highest occupied level of each respective center to be bleached and the top of the valence band, as evaluated from the corresponding photoionization threshold previously determined relative to the bottom of the conduction band.
5. This energy-gap dependence of the quantum bleaching efficiency, tentatively fitted by an exponential function, is most probably controlled by the hole capture cross section, which becomes greater with decreasing hole-trapping depth.
6. It has been reconfirmed that two types of latent image centers with different chemical compositions can be produced on S + Au-sensitized grains, depending on the exposure intensity—one with built-in gold atoms bleachable with higher quantum efficiency and the other consisting of only silver atoms characterized by much lower quantum efficiency, comparable to those for primitive emulsions.

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## References

1. T. Tani, *J. Soc. Photogr. Sci. Technol. Japan* **43**: 27 (1980).
2. T. Tani, *Photogr. Sci. Eng.* **26**: 213 (1980).
3. M. Kawasaki, *J. Soc. Photogr. Sci. Technol. Japan* **49**: 421 (1986).
4. T. Kaneda, N. Ohshima, and T. Tani, *J. Imaging Sci.* **31**: 50 (1987).
5. L. Kellogg, J. Hodes, and J. Muenter, *SPSE/ SPSTJ International East-West Symposium II,* 1988, p. C-11.
6. M. Kawasaki, S. Hiraoka, and H. Hada, *J. Imaging Sci. Technol.* **36**: 525 (1992).
7. T. Kaneda, *J. Imaging Sci. Technol.* **38**: 135 (1994).
8. R. K. Hailstone and D. E. Erdtmann, *J. Appl. Phys.* **76**: 4184 (1994).
9. J. Malinowski, *Photogr. Sci. Eng.* **14**: 112 (1970).
10. W. Vanasshe, H. Borginon, H. Pattyn, W. Peelaers, and E. Moisar, *J. Photogr. Sci.* **22**: 121 (1974).
11. M. Kawasaki, Y. Tsujimura, and H. Hada, *Phys. Rev. Lett.* **57**: 2796 (1986).
12. M. Kawasaki, T. Yoshiki, and Y. Oku, *J. Imaging Sci. Technol.* **37**: 568 (1993).
13. T. Tani, *Photogr. Sci. Eng.* **27**: 75 (1983).
14. M. Kawasaki, H. Hada, and S. Ohtani, *J. Photogr. Sci.* **33**: 29 (1985).
15. T. Matsubara and M. Levy, *J. Imaging Sci.* **32**: 178 (1988).
16. A. Henglein, *Ber. Bunsenges. Phys. Chem.* **94**: 600 (1990).
17. T. H. James, W. Vanselow, and R. F. Quirk, *PSA J.* **19B**:170 (1953).
18. T. H. James, W. Vanselow, and R. F. Quirk, *PSA J.* **14**: 349 (1948).
19. See, e.g, J. F. Hamilton, in *The Theory of the Photographic Process*, 4th ed., (T. H. James, Ed.), Macmillan, New York, 1977, Chap. 4.
20. J. F. Hamilton, *Photogr. Sci. Eng.* **27**: 225 (1983).
21. M. Kawasaki and H. Hada, *J. Imaging Sci.* **35**: 129 (1991).
22. According to the earlier work reported by Harbison and Hamilton [*Photogr. Sci. Eng.*, **19**: 322 (1975)], the speed increase gained by gold latensification for their S-sensitized emulsion decreased at lower exposure intensity to less than 0.1 log $E$ on the average for a 5-s exposure. We note, however, that a larger speed increase comparable to that (~0.3 log $E$) found in this study can be seen in the toe region of the corresponding $D$–log $E$ curves. In general, the effect of subimage latensification is highly sensitive to development conditions, but if the latent image centers developable in the standard processing condition contain at least four silver atoms while two-atom subimage centers can be detected by gold latensification, ~0.3 log $E$ speed increase does not seem to be too large to be gained by gold latensification.
23. H. Hada, M. Kawasaki, and H. Fujimoto, *Photogr. Sci. Eng.* **24**: 232 (1980).
24. R. Englman and J. Jortner, *Molecular Phys.* **18**: 145 (1970).