Hole Removal in High-pH-Induced Reduction-Sensitized Silver Bromide Grains

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High-pH-induced reduction sensitization was used to form silver clusters on the surfaces of octahedral silver bromide grains. This method had the advantage of not leaving unreacted reducing agent in the emulsion, which could cause further silver cluster formation over time. Diffuse reflection spectroscopy measurements showed these silver clusters to be similar to those formed by dimethylamine borane and $SnCl_2$, except that the absorption peaks were noticeably less intense. Large emulsion grains sensitized in this manner benefited most from the hole-removal ability of the silver clusters. The result was a linear relationship between speed and grain volume for edge lengths 0.28 to 1.22 µm, with a slope of 0.93 +/– 0.08, which is close to the theoretical slope of 1.0. Core–shell emulsions in which the cores were oversensitized with sulfur also benefited from the high-pH-induced reduction sensitization on the surface. Instead of desensitization of the core when oversensitized, these emulsions showed dramatically increased internal sensitivity, consistent with the proposed hole-removal property of the surface silver clusters. No evidence of electron trapping by these chemically produced silver clusters could be found.

Journal of Imaging Science and Technology 40: 576–581 (1996)

Introduction

Reduction sensitization is a process by which silver clusters are formed on silver halide grains. A reducing agent donates electrons to silver ions in an emulsion to form the silver clusters. Normally, reducing agents such as dimethylamine borane (DMAB) or $SnCl_2$ are used to form the silver clusters. However, all of the reducing agent may not be consumed when forming the silver clusters, leaving residual unreacted reducing agent in the emulsion. Furthermore, reduction sensitization can occur at low temperatures, although at a slower rate. These factors lead to the possibility for continued reduction sensitization while the emulsion is in liquid form and possibly after coating.

An alternative approach is to place the emulsion in a reducing environment for a period of time, followed by inactivation of the reducing species.[1] A very convenient method of accomplishing this is to raise the pH of the emulsion and then to heat the emulsion. After the high pH treatment, the emulsion pH and temperature are lowered to normal levels for subsequent treatments and coating. Assuming that the reducing species formed is reactive only at high pH levels, no residual unreacted reducing agent will remain to cause further reduction.

The mechanism for high-pH-induced reduction sensitization is only speculative at this time. The OH^- species may react with the Ag^+ ions to form the silver clusters.[2] The high-pH treatment may also activate reducing impurities in the gelatin that may contribute to reduction sensitization.[3] Fully understanding the chemistry of high-pH-induced reduction sensitization was not within the main scope of these experiments and is not addressed in this report.

The properties of these silver clusters have been a controversial subject for some time. If the silver clusters are thought of as sublatent images, the silver clusters would have electron-trapping properties. However, experiments by Spencer and coworkers have shown that these silver clusters are bleachable upon exposure,[4] whereas latent image silver clusters grow with exposure. These data strongly indicate that the silver clusters are not sublatent images, but are instead hole traps.

Experiments by Palm,[5] Tani,[6] Babcock[7] and their respective coworkers have suggested that silver clusters formed at low levels of reduction sensitization behave as hole traps, whereas those formed at higher levels have electron-trapping properties. Tani and Babcock have both proposed that this change in behavior is due to location dependence of the silver clusters. These experiments, although valuable in understanding the behavior of reduction sensitization, may not have considered all the possible interpretations. Clearly, the experiments of Spencer and coworkers show that silver clusters formed by reduction sensitization behave differently from photolytic silver. The bleachability of the silver clusters strongly suggests that the silver clusters are acting as hole traps. Proposals that suggest that higher levels of reduction sensitization form silver clusters with electron-trapping properties may be misleading.

Recombination mechanisms within the nucleation-and-growth model[8] of latent image formation provide explanations for all the above observations. Recombination can occur between free electrons and trapped holes, or, conversely, between free holes and trapped electrons. The indirect bandgap in silver halides prevents recombination between free electrons and free holes.[9] Electrons are more mobile than holes and will be more free to move through the grain than are holes. Holes, being less mobile, will spend more time in the trapped state. Therefore the primary inefficiency pathway for primitive emulsions will be free electron/trapped hole recombination.[8]

Sulfur and sulfur + gold sensitization increase the efficiency of latent image formation by two interrelated mechanisms. First, deeper electron traps form, which will encourage electrons to spend more time in the trapped

Original manuscript received February 26, 1996. Revised August 6, 1996.

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state,[8] causing nucleation to be more efficient. The second mechanism is a reduction in recombination. Improved electron trapping will reduce the population of free electrons available to participate in the free electron/trapped hole recombination pathway. Note that sulfur and sulfur + gold sensitization centers directly affect only electrons. The only influence that these sensitization centers have on holes is to alter the number of free electrons available to recombine with trapped holes.

Speed versus sensitization level plots typically show a maximum speed, beyond which increasing sensitization will result in lower sensitivity. At the sensitization level corresponding to the maximum speed, the sensitivity of the emulsion is near optimum, because the free electron/trapped hole recombination pathway has been minimized. As sensitization is further increased, an oversensitization condition is reached, in which the number of free holes relative to trapped electrons becomes significant. Now the free hole/trapped electron recombination pathway becomes important, and further sensitization results in ever-decreasing efficiency and sensitivity.[8]

Common to both recombination pathways are holes in either free or trapped states. With holes always present to cause inefficiency, it is a challenge for the emulsion scientist to reach the best compromise between increased electron trapping and the minimization of the two recombination pathways to achieve the maximum sensitivity. Whereas the sensitivity gain with sulfur and gold sensitizers is significant, holes are always present to limit the speed potential of the emulsion.

Silver clusters formed by reduction sensitization will remove holes by the mechanism illustrated in Eqs. 1 and 2. As these equations show, the holes are not merely trapped where they can potentially detrap, but are removed from the latent image process. With fewer holes available for recombination, the electrons are more likely to form latent images. Effective hole-removal processes will allow for more efficient latent image formation. Therefore, it is possible that high levels of reduction sensitization may be misinterpreted as silver clusters behaving as electron traps.

$$Ag_n^0 + h^+ \rightarrow Ag_n^+ \tag{1}$$

$$Ag_n^+ \rightarrow Ag_{(n-1)_0} + Ag_i^+ \tag{2}$$

One of the primary speed control tools available to the emulsion scientist is grain size. If the inefficiencies of latent image formation are independent of grain size, the primitive speed of the emulsion would be expected to be proportional to grain size. However, investigations by Farnell and others[10a–d] have shown that the relationship between speed and grain size is linear only up to a point, beyond which the relationship becomes sublinear. As a result, the emulsion scientist must use ever larger grains and tolerate lower image quality to achieve high speed.

The source of the increased inefficiency in large grains has been of interest for many years. Some investigators have suggested limitations in the electron range as the source of inefficiency.[10b,10d] In this proposal, it is assumed that there is a limit to the electron lifetime, which will limit the diffusion distance. Large grains are then thought to behave in a segmented fashion, as opposed to a single unit. The expected result is dispersity of the latent image, which will lower the efficiency. However, limited electron lifetime implies mechanisms that irreversibly remove the electrons from the latent image formation process. Depending on the characteristics of the grain, the removal reaction may occur in a very short time period and hence a short distance. Some candidates for electron-removal mechanisms include internal latent image formation, irreversible trapping sites such as impurities, and recombination with holes.

It is well known that large grains are more susceptible to internal latent image formation.[11] A likely cause for this behavior is a higher occurrence of electron-trapping lattice defects in larger grain volumes. Unlike surface latent images, internal latent images are not developable with conventional processing procedures. The presence of internal latent images will cause competition with surface latent image sites, resulting in desensitization of the surface sensitivity. The use of sulfur and sulfur + gold sensitization is very effective in directing latent image formation toward the surface when the internal competition is relatively weak, thereby at least reducing the effect of internal latent image formation.[12]

Impurities within the grain structure have the potential to attract and irreversibly trap electrons. Once irreversibly trapped, the electron is no longer available for latent image formation. Using high-purity materials and clean precipitation practices, it is possible to minimize this source of inefficiency.

A recombination mechanism may well be responsible for the decreased efficiency of large grains. As the grains become larger, the increased volume will result in more freedom for holes to move within the grain, but also more potential hole-trap sites. These internal hole traps might arise from lattice defects or hole-trapping impurities such as iodide. Recombination between free electrons and trapped holes will become more problematic with increasing grain size, resulting in grain-size-dependent efficiencies.

In this report we do the following:

- Demonstrate the high-pH-induced reduction sensitization process.
- Show how high-pH-induced reduction sensitization can improve the speed/grain volume relationship.
- Show how improved hole trapping may be used to improve the performance of a heavily sulfur-sensitized emulsion.

Experimental

If recombination is responsible for lower efficiency of larger grains, then improved hole removal would be expected to increase the efficiency of large grains and linearize the speed/grain size relationship. To this end, a series of silver bromide octahedral emulsions was produced with an edge length ranging from 0.28 to 1.22 μm. These emulsions were produced by a double-jet precipitation system with the following general parameters:

Batch size	1.5 mol $AgNO_3$
Initial kettle solution volume	750 mL
Initial kettle solution	2% deionized gelatin
Emulsion temperature	75°C
Run time	1 h
Nucleation	0.002 to 0.008 mol/min, pAg = 7.8 to 8.5
Growth flow rate	linear ramp to 0.050 mol/min.
Growth pAg	8.5
Growth pH	3.0
Washing	Deionized phthalated gelatin coagulated at pH = 3.25

The nucleation conditions were adjusted to allow for controlled grain number, resulting in predictable grain sizes.[13]

For the very large grains (1.00 and 1.22 μm), a seed/shell approach was used to maintain accurate flow-rate control and avoid the use of a ripener. Internal development experiments indicated that enhanced internal sensitivity at the seed/shell interface was minimal.

The grain edge lengths were determined by scanning electron microscopy (SEM) and electrolytic reduction grain size analysis.[14] The electrolytic reduction grain size analysis determined the grain volume of the emulsion by reducing the silver halide grains to silver metal. The charge required to reduce the individual grains was measured and correlated to grain volume. The edge lengths were calculated geometrically from the grain volume, assuming ideal octahedral structures. The SEM pictures showed that the grains generally had good to excellent edge quality, and measured edge lengths agreed with those calculated from the electrolytic measurements.

High-pH-induced reduction sensitization was carried out with the emulsion adjusted to pAg 8.0 at 40°C. The pH of the emulsion was adjusted with 1.0 N sodium hydroxide to the desired level. The sensitization conditions were 70°C for 40 min, with linear temperature ramps of 1.5°C per minute during the heating and cooling phases.

Emulsions sensitized at high pH levels may suffer from poor coatability as a result of a substantial portion of the gelatin being hydrolyzed during the sensitization. To improve coatability, all the emulsions were sensitized without make-up gelatin. After sensitization, the emulsions were diluted with make-up gelatin and water to achieve the final silver and gelatin concentrations.

The emulsions were coated at pH 5.6 and pAg 8.0, as measured at 40°C. The silver coating weights were adjusted to give a maximum density of approximately 1.00. Sensitometric exposure with a xenon flash sensitometer (0.01 s) and a step tablet was followed by processing in an E-AA-1 developer[15] for 40 min at 20°C with nitrogen burst agitation. The speed determinations were made at the mean density $[(D_{min} + D_{max})/2]$ on the D–log E curves. This measurement method minimized the influence of coating weight variations.

The silver clusters formed in the emulsions were examined with diffuse reflectance spectroscopy in a manner similar to that reported by Tani and Murofushi[16] and by Guo and Hailstone.[17] This procedure measured the diffuse reflectance spectrum of the emulsion samples relative to that of a barium sulfate reference between 300 and 800 nm. In all cases, the spectrum of the unsensitized emulsion was subtracted from the spectrum of the sensitized emulsion. The resultant difference spectrum contains information that is pertinent to the reduction sensitization reaction. These resultant spectra were analyzed with the Kubelka–Munk transform to yield spectra that are related to absorption.[18]

To observe the effect of hole removal, it is helpful to separate physically the locations of the hole traps from those of the electron traps, thus allowing analysis of these two kinds of sensitizer centers separately. This separation was accomplished through the use of core–shell emulsions in which the core was sulfur sensitized and the shell surface was reduction sensitized with high-pH treatment.

The cores of these core–shell emulsions consisted of 0.47 μm edge length octahedral AgBr grains identical to the 0.47 μm grains produced above. These cores were sulfur sensitized to the optimum level based upon maximum speed and minimal fog. The shells were grown over these cores, using the same growth pAg and temperature conditions as was used with the cores. The growth pH was higher (pH = 4.25), so that the phthalated gelatin remaining in the core emulsion (left over from washing) would not coagulate during shell growth. The shell growth continued until the edge length was 0.74 μm. Two other core–shell emulsions were similarly produced with internal sulfur sensitization at 1/4 and 4 times the optimum level.

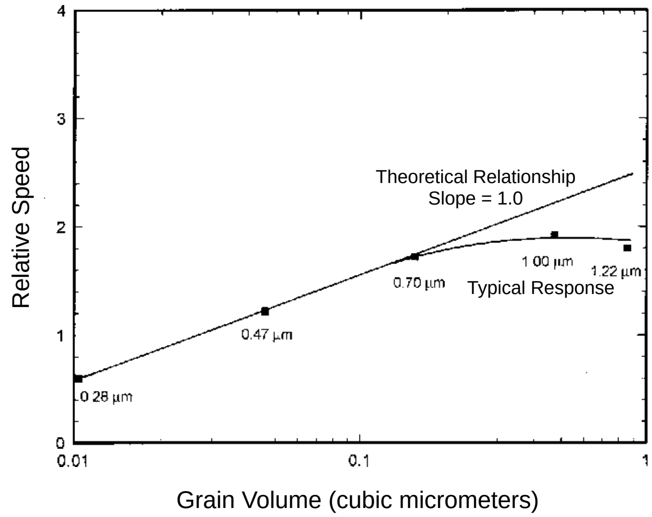

Figure 1. Comparison between the ideal and typical speed/grain volume relationships for primitive emulsions. Data points are edge lengths for AgBr octahedral grains. Development in E-AA-1, 40 min, 20°C.

The surfaces of the core–shell emulsion grains were reduction sensitized with the high-pH treatment in an identical manner to that used for the previous emulsions. The emulsions were internally developed to measure the effect of the surface silver clusters on the internal image formation. The emulsions were treated with a weak dichromate bleach at 20°C for 18 min to remove the surface latent image. This treatment was followed by internal development for 24 min at 20°C with Kodak D-l9 developer to which 0.25 g/L KI had been added.[19]

Results and Discussion

Reduction Sensitization of Primitive Emulsions. Figure 1 illustrates the relationship between speed and grain volume for unsensitized octahedral silver bromide grains with edge lengths from 0.28 to 1.22 μm. The relationship becomes sublinear with edge lengths above about 0.70 μm. Below 0.70 μm, the relationship follows approximately the theoretical 1:1 linear relationship between speed and grain volume and is consistent with the work of Farnell and others.[10a–d] As shown in Fig. 2, increasing electron trapping through the use of sulfur and sulfur + gold sensitization did not change the sublinear relationship between speed and grain volume at large sizes, although speed did increase significantly.[20] Such a response is consistent with large grains having increased recombination due to their larger volume, making them more difficult to sensitize optimally with sulfur and sulfur + gold.

The silver clusters formed by high-pH-induced reduction sensitization had absorption characteristics similar to those obtained with DMAB and $SnCl_2$.[17] The absorption maximum is at about 476 nm, as shown in Fig. 3. Even though the sensitivity gain of the high-pH-induced reduction sensitization is similar to that obtained with DMAB, the magnitude of the absorption peaks is greatly different. Guo and Hailstone[17] used 0.47 μm grains exclusively and produced very strong absorption peaks when sensitized with DMAB. The same emulsion, when reduction sensitized with high-pH treatment, produced barely detectable absorption peaks.

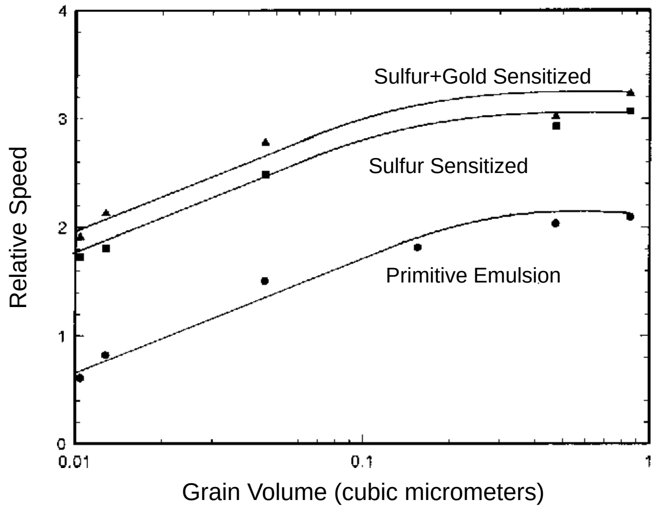

Figure 2. Speed/grain volume relationships for primitive, sulfur-sensitized, and sulfur + gold-sensitized AgBr emulsions. Development in Kodak D-l9, 12 min, 20°C.

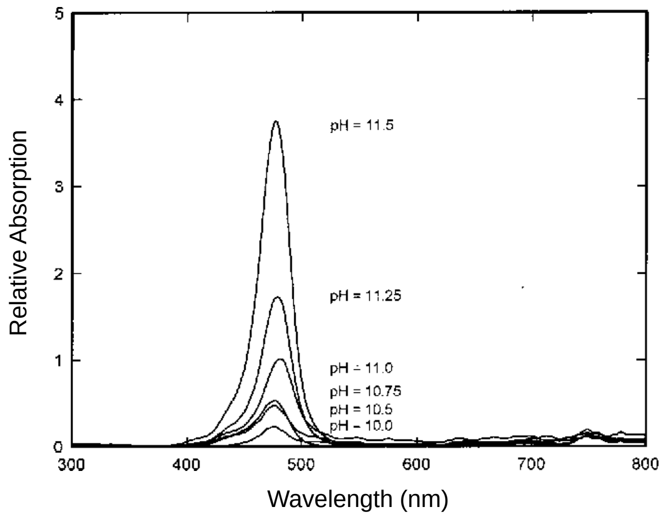

Figure 3. Diffuse reflection spectroscopic analysis of 1.22-μm AgBr emulsions with high-pH treatment. The reflection spectra have been converted to relative absorption through the Kubelka–Munk transform.

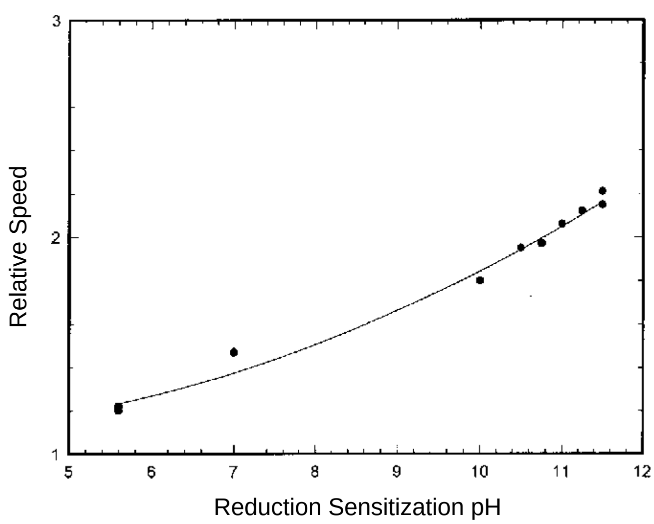

Figure 4. Speed change as a function of reduction sensitization pH level: 0.47-μm grains developed in E-AA-1, 40 min, 20°C.

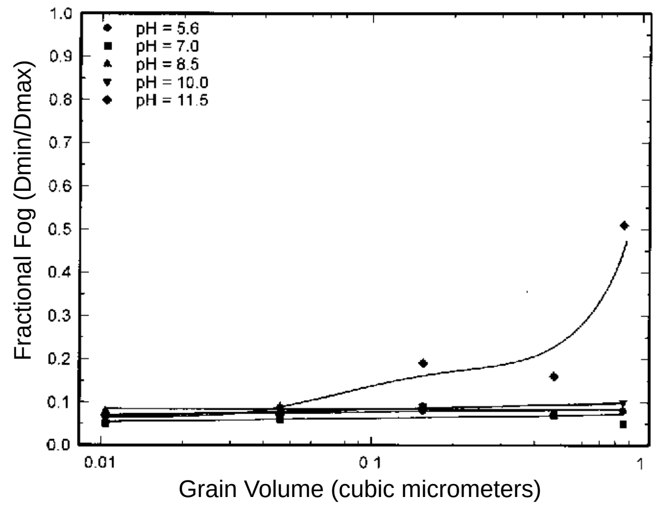

Figure 5. Fractional fog as a function of reduction sensitization pH level for various grain sizes. Each curve represents a different reduction-sensitization pH level. Development in E-AA-1, 40 min, 20°C.

Only larger grain sizes produced absorption peaks of appreciable magnitude. This observed difference between DMAB and high-pH-treatment spectra indicates a lower concentration of silver clusters formed with high-pH reduction sensitization. The similar sensitivity gains from the two sensitization methods further suggest that the silver clusters formed by high-pH treatment may be more efficient hole traps than those formed by DMAB.

Figure 4 shows the speed increase resulting from increasing pH during high-pH-induced reduction sensitization. Unlike sulfur sensitization, which gives a maximum speed, after which further sensitization results in lower speed, there is no obvious maximum speed position. However, fog density is significant at high-pH levels for larger grains, as shown in Fig. 5. Development in a nonsolvent-type developer is necessary to avoid excessive fog.[21] Therefore, all the data were obtained using E-AA-1 development for 40 min at 20°C. This development condition results in essentially the same detectivity or speed as that with Kodak D-19 developer for 12 min at the same temperature.

The effect of high-pH sensitization on the relationship between speed and grain volume is shown in Fig. 6 for emulsions that were sensitized at pH 11.5, 10.0, and 5.6, with the latter condition being the control. The sensitivity of the grains of all sizes showed significant increase with the higher pH treatments, but the larger grains showed larger sensitivity gains. The latter result leads to a linear relationship between speed and grain volume for all the emulsions studied. The slope for the pH 11.5 treated emulsions was 0.93 with an experimental error of ±0.08 (95% confidence limits), which is statistically equivalent to the theoretical slope of 1.0.

Reduction Sensitization of Internally Sulfur- Sensitized Emulsions. It is sometimes thought that at high levels of reduction sensitization some silver clusters act as electron traps.[16,22] The observed speed increase shown in Fig. 6 could be due to hole removal, electron trapping, or a combination of the two. Unfortunately, photographically measuring the relationship between hole removal and electron trapping by silver clusters is hampered by the strong response that electron trapping and latent image formation produce. Distinguishing between these two effects is quite difficult when they both occur at the grain surface. However, when they occur at different locations

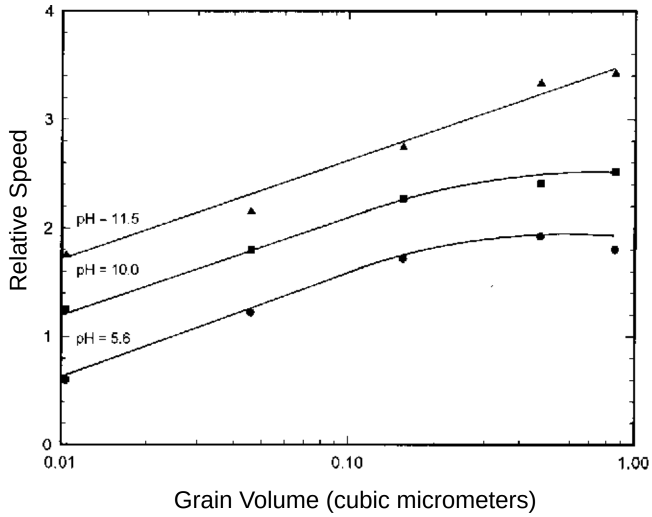

Figure 6. Speed/grain size relationship for emulsions sensitized at various pH levels. Development in E-AA-1, 40 min, 20°C.

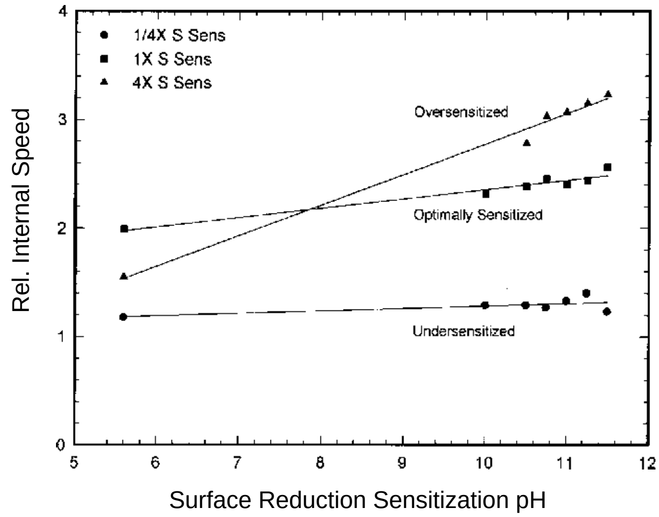

Figure 7. Internal sensitivity of internally sulfur-sensitized/surface high-pH reduction-sensitized core–shell emulsions.

in the grain, such as with internally and surface-sensitized core–shell grains, mechanistic insight can be obtained.

Figure 7 displays the internal speed of the internally sulfur-sensitized/surface high-pH reduction-sensitized core–shell emulsions. For the core–shell emulsion that was internally sulfur sensitized at 1/4 optimum level, the internal sensitivity did not change appreciably with increased pH of the surface reduction sensitization. This is to be expected, because such a low sulfur sensitization level will not form enough internal electron traps to compete effectively with the surface electron traps.

The emulsions with optimum internal sulfur sensitization showed a noticeable increase in internal sensitivity with increased pH of surface reduction sensitization (Fig. 7). The internal speed for the emulsion in which no high-pH treatment was used (pH 5.6) was about 0.8 log E higher than that of the 1/4× sulfur level core–shell emulsion. This result is consistent with the sensitivity increases found when the cores alone were studied. At higher pH levels, the sensitivity increased about 0.55 log E over that of the pH 5.6 emulsion.

In the case of the 4× internally sulfur-sensitized core–shell emulsion, the pH 5.6 emulsion was about 0.5 log E slower than the 1× internally sulfur-sensitized emulsion, which is consistent behavior for an oversensitization condition. Yet, when this oversensitized emulsion was surface-treated at pH 11.5, the internal sensitivity increased to about 1.65 log E over that of the pH 5.6 emulsion. The maximum sensitivity of this emulsion was about 0.70 log E above that for the 1× internally sulfur-sensitized emulsion.

These observations are consistent with increased hole trapping on the grain surface induced by the high-pH treatment. Surface silver clusters formed by high levels of reduction sensitization behaving as electron traps cannot explain the internal sensitivity increase. Increased surface electron trapping with high-pH treatment would be expected to **decrease** internal sensitivity through surface trapping by the silver clusters. If such clusters form, they are expected to be irreversible electron traps, which can dominate the response of an emulsion.[23] These data strongly suggest that high levels of reduction sensitization promote increased hole-trapping ability. Hole removal by the surface silver clusters minimizes free hole/trapped electron recombination characteristic of the oversensitization condition. Thus, the 4× sulfur level now displays the highest internal sensitivity.

Collier's experiments examined primitive grains with high-pH-induced reduction sensitization. In her experiments, the intrinsic surface speed was about 0.60 log E lower than the internal speed.[22a] Our control (pH 5.6) core–shell emulsions had greater than 2.0 log E decrease in surface sensitivity between the 1/4× and the 4× internal sulfur levels. This speed decrease supports the assumption that intrinsic electron traps are shallow and result in inefficient nucleation. Effective hole removal would be expected to allow latent images to form more effectively at intrinsic electron-trap sites in the case of grains without sulfur or sulfur + gold sensitization. Therefore, what appears as electron trapping from high levels of reduction sensitization in Collier's experimental results could be merely shallow intrinsic surface electron traps becoming effective as latent image sites.

Other studies have interpreted a decrease in 77 K microwave photoconductivity as evidence of increased electron trapping at high reduction sensitization levels.[7] However, at this temperature, the interstitial release process in Eq. 2 may be greatly slowed down. With the extended Ag_n^+ lifetime, these sites could act as electron traps that would be detected as a decrease in photoconductivity.

Conclusions

Reduction sensitization induced by high-pH treatment was shown to be an effective means of increasing the sensitivity of an emulsion. Spectroscopic data indicate that the silver clusters formed are similar to those formed by DMAB and $SnCl_2$. The absorption peaks are significantly smaller than those formed by DMAB and $SnCl_2$; yet the sensitivity gains were similar. This result suggests that the silver clusters responsible for the 476-nm absorption peak form at different concentrations for the two sensitization methods. Furthermore, the hole-trapping efficiency of the silver clusters formed by the two sensitization methods may also be different.

The hole removal brought about by these silver clusters reduces recombination much more in larger grains than in smaller grains. The result is a linear speed/grain volume relationship for silver bromide octahedral grains in the size range 0.28 to 1.22 μm. The slope of this relationship was 0.93 ± 0.08, which is statistically equivalent to the theoretical slope of 1.0.

High-pH-induced reduction sensitization applied to the surface of an internally sulfur-sensitized core–shell emulsion has shown that hole-removal ability continues to increase with increased surface reduction sensitization. This effect allowed for significantly improved internal speed in an emulsion that was oversensitized.

The marked surface desensitization with increased internal sulfur sensitization indicates that surface electron trapping is occurring only at shallow electron traps that cannot effectively compete with deep internal traps. This observation suggests that what appears as increased electron trapping at high levels of reduction sensitization in other investigations, using emulsions with much less internal competition than ours, could be merely the intrinsic surface electron traps being made more effective as latent image sites as a result of efficient hole removal.

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