JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 46, Number 2, March/April 2002

Silver Halide Recrystalization: I. Qualitative Kinetics for the Conversion of AgCl to AgClBr

Joaquin Calcines,▲ Heather M. Dolan,▲ Kristyn R. Falkenstern,▲ Conor D. Kelly,▲ Erin P. Murphy,▲ Rosalyn L. Klinger, Bruce E. Kahn▲*

Imaging and Photographic Technology, Rochester Institute of Technology, Rochester, New York

A. Gary DiFrancesco▲ and Richard K. Hailstone✦

Center for Imaging Science, Rochester Institute of Technology, Rochester, New York

The reaction rates for the conversion of AgCl to AgClBr were studied qualitatively using a reflection spectrophotometric technique. The conversion rate was found to be dependent upon many factors, including the source of bromide and the presence and concentration of ripeners and restrainers. Soluble bromide (KBr) reacts faster with AgCl than does AgBr. Ripeners (1,1,3,3-tetramethyl-2-thiourea, 3,6-dithia-1,8-octanediol) greatly increase the rate of halide conversion. 4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene greatly reduces the rate of halide conversion or can completely eliminate it using either soluble bromide or AgBr as the bromide source.

Journal of Imaging Science and Technology 46: 101–111 (2002)

Introduction

Most photographic emulsions consist of mixed silver halide grains such as AgClBr, AgBrI, AgClI, or AgClBrI. These mixed halide grains can be obtained by a variety of methods. Often, mixed halides are obtained by introducing a less soluble halide into an emulsion containing a more soluble silver halide.[1] This process is known as halide conversion.[2] Halide conversion is one of the most fundamental processes in the precipitation of silver halide emulsions. It is particularly useful in forming heterojunctions of different silver halide compositions on silver halide grains.[3] These heterojunctions are thought to have beneficial electronic properties.

Halide conversion has been studied by many techniques, including electron microscopy,[4–11] X-ray powder diffraction,[7–9,12] Coulter particle counting[7] and electron beam diffraction.[8–9] Klein, and co-workers found that the conversion of AgCl to AgBrCl was one of nucleation and growth of new grains.[4] This however does not adequately explain the findings of Eggert and Fischer[13–14] and subsequent studies by Berg and Keller[15] who found that silver chloride emulsions maintain a latent image throughout a conversion process. This indicates that the conversion process is one of partial halide replacement within the existing grains. Studies by Zuckerman,[7] Sugimoto and Miyake[8–10] and Mydlarz[11] found that the conversion process of AgCl to AgClBr occurs by a multi-step process with an initial epitaxial growth of a $AgCl_{1-x}Br_x$ phase on the host AgCl grain followed by a slower process of diffusion of a bromide rich phase to the faces and interior of the substrate. This secondary process has been found to be temperature, time and concentration dependent.

The above-mentioned studies involve *ex-situ* sample analyses from which kinetic rates can only be inferred. Kumai, and co-workers conducted a dynamic, *in-situ* potentiometric study of the conversion of AgBr sols to AgBrI, and also investigated the presence of a number of polymers such as gelatin, polyvinyl alcohol, polyethylene oxide, and polyvinyl pyrrolidone.[16] Using similar techniques, Leyshon and Hillson studied the conversion of AgCl sols into AgClBr, and AgBr sols into AgBrI,[17] and Sugimoto and Miyake studied the conversion of AgCl emulsions into AgClBr.[8–10] Turbidimetric techniques[18–20] are well established for determining silver halide particle size,[21–29] and this technique has also been used to study the conversion of AgBr sols to AgBrI.[25]

This study uses an *in-situ* spectrophotometric technique to follow the dynamic conversion of AgCl to AgClBr. This technique gives qualitative information about the reaction rates of the conversion and demonstrates the influence of physical and chemical factors, such as halide source, temperature, and the presence of ripening and restraining agents on the halide conversion reaction.

Experimental

Monodisperse cubic AgCl and AgBr emulsions used in this study were prepared without organic ripeners using computer-controlled double-jet precipitation methods. The average grain size of the emulsions used was 1.0 µm cubic edge length for AgCl, and 0.1 or 0.35 µm cubic edge lengths for AgBr. Grain size distributions were deter-

---

Original manuscript received June 5, 2000

▲ IS&T Member

✦ IS&T Fellow

* Corresponding Author; e-mail: bkahn@mail.rit.edu

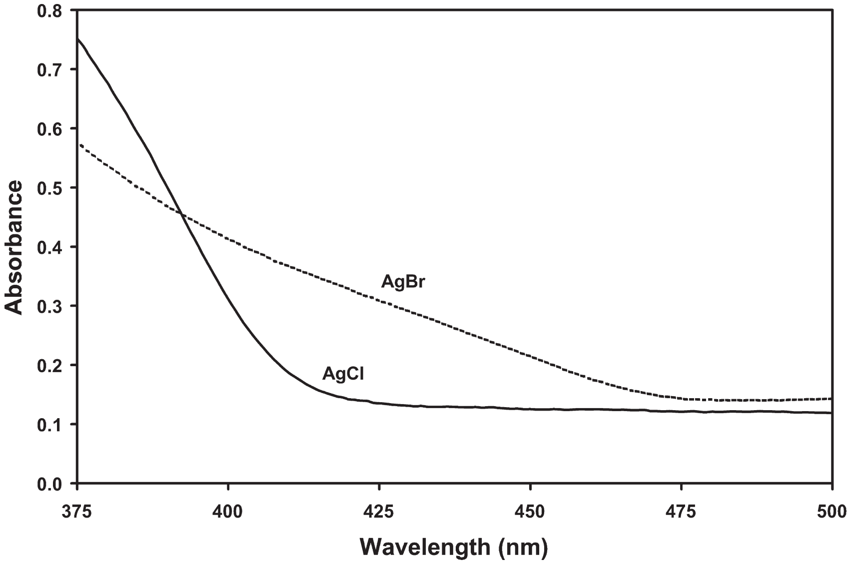

Figure 1. Absorption spectra of (——) AgCl (1.0 μm) and (- - - -) AgBr (0.1 μm) emulsions.

mined by electrolytic grain size analysis.[30] The AgCl concentration was 0.77–1.0 mole AgCl per kg emulsion. The AgBr concentration was 0.76 mole/kg for the 0.1 μm emulsion and 1.04 mole/kg for the 0.35 μm AgBr. Experiments were conducted at pH = 5.8, pCl = 1.25, pAg = 8.55.

Spectral absorbances log(1/R) were determined using a Cary 100 UV/Vis spectrophotometer, equipped with a LabSphere DRA-300 diffuse reflectance integrating sphere in a diffuse reflectance configuration excluding the specular beam (SPEX). Transmission through the cell was negligible. There was virtually no change in absorption between a 1mm or 2 mm path length cell. A Spectralon disk was used for a 100% Reflectance standard. Spectra were typically obtained from 370–500 nm (scanned from 500 nm to 370 nm). A complete scan was taken every 11–17 sec.

Reactions were conducted in a jacketed glass vessel, equipped with magnetic stirring. The reactor temperature was controlled to within ± 0.2°C using a Haake d8 heating circulator. The emulsions were pumped through a glass flow cell (1 mm path length) at approximately 60 ml/min using a Masterflex 7014 peristaltic pump and Tygon tubing.

1,1,3,3-Tetramethyl-2-thiourea (Acros Organic Chemicals, Fisher Scientific), 3,6-dithia-1,8-octanediol (Acros Organic Chemicals, Fisher Scientific), and 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (5-methyl-s-triazolo-(1,5-a)-pyrimidin-7-ol) (Aldrich Chemical Company) were used as received.

Solution concentrations were 1 M KBr, 0.055 M 3,6-Dithia-1,8-octanediol (DTOD), 0.076 M 1,1,3,3-tetramethyl-2-thiourea (TMTU), and 0.033 M 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI).

Results

Halide Source

The optical absorption characteristics of mixed crystals of AgCl and AgBr have been studied in detail by Meinig, Metz, and Teltow at high temperatures,[31] and by Joesten and Brown at low temperatures.[32] In general, the absorption edge of AgBr occurs at longer wavelength than that of AgCl with the absorption edge for mixed chlorobromides occurring between those of AgCl and AgBr. The absorption spectra of a monodisperse cubic 1 μm AgCl emulsion and a monodisperse cubic 0.1 μm AgBr emulsion are shown in Fig. 1. The concentration of AgBr used in this comparison was 5 mole % of the AgCl concentration. As expected, there is very little absorption of AgCl at wavelengths > 425 nm.

A variety of halide sources are commonly employed for halide conversion. Two different types were investigated in this study—soluble bromide and AgBr emulsions. When soluble bromide (1 M KBr) is added to an AgCl emulsion, the bromide reacts very rapidly with the AgCl. Figure 2 shows the change in absorption behavior at 400 nm. Initially, a rapid increase in absorption at 400 nm is seen, followed by a much slower increase, consistent with a multi-step conversion process.

Figure 3 shows a series of consecutive scans from 375–500 nm. The above behavior observed at 400 nm seems to be observed at all wavelengths in this region. There is an initial rapid rise in absorbance upon addition of KBr, followed by a slower absorption increase. Because KBr does not absorb in this region, this absorption increase is due to the rapid formation of AgClBr phases on the AgCl substrate. This absorption behavior is consistent with an initial rapid reaction of the KBr with AgCl, followed by a slower redistribution of the bromide rich phases over the surface of the grain, or a fast reaction at the most reactive sites (corners, edges) followed by a slow reaction at less reactive sites.

As expected, the reaction of AgCl with AgBr occurs much more slowly. This can be seen in Fig. 4, where a series of scans are plotted, and more clearly in Fig. 5 where the absorption at 400 nm is plotted as a function of time for KBr and AgBr. There is an initial increase in absorption upon the addition of AgBr (Fig. 7a), due to the absorption and scattering of AgBr. This absorption increase does not indicate that any conversion between AgCl and AgBr has occurred (see **Restrainer** section). After this initial absorption, a very slow absorption increase can be seen, due to the (partial) conversion of AgCl to AgClBr.

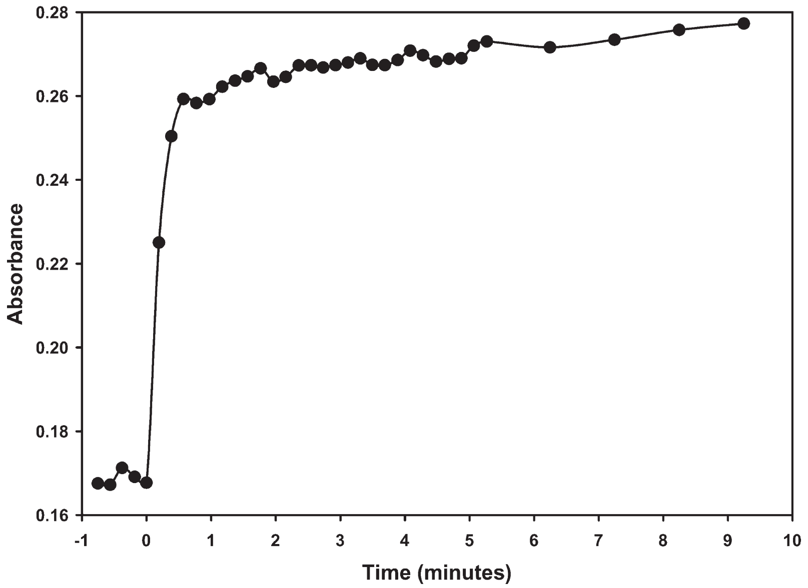

Figure 2. Absorbance (400 nm) versus time, AgCl + 5 mole % KBr, 40°C.

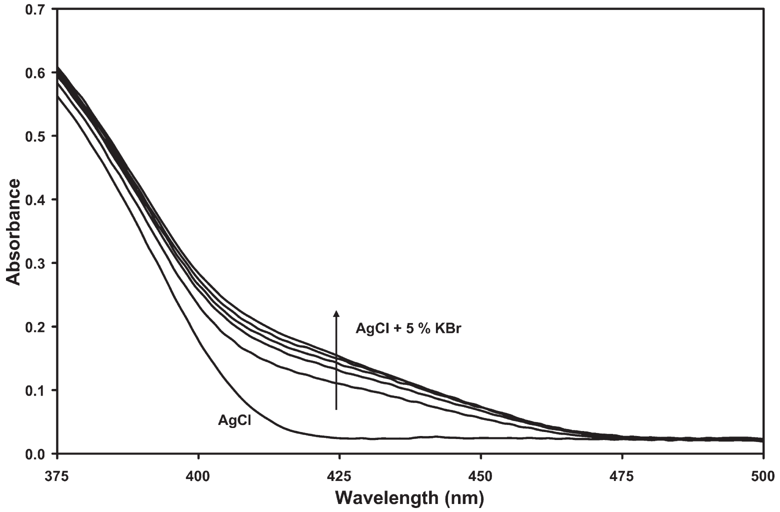

Figure 3. Absorbance versus wavelength, AgCl + 5 mole % KBr, 40°C.

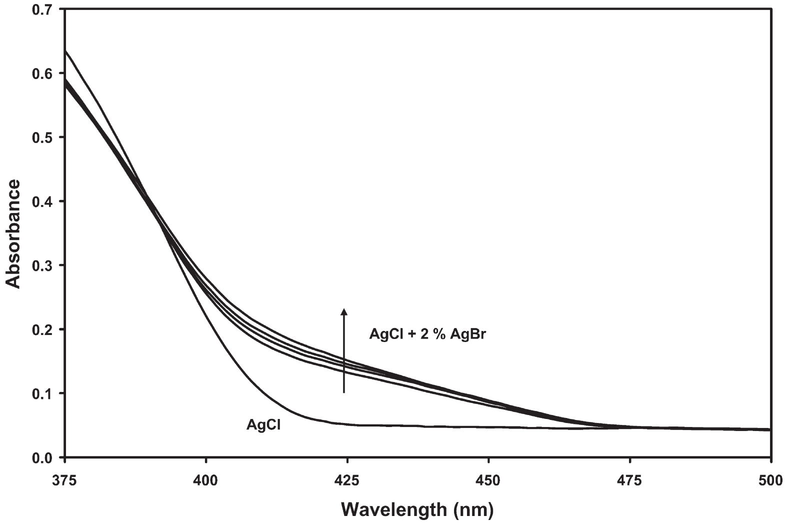

Figure 4. Absorbance versus wavelength, AgCl + 2 mole % AgBr, 40°C.

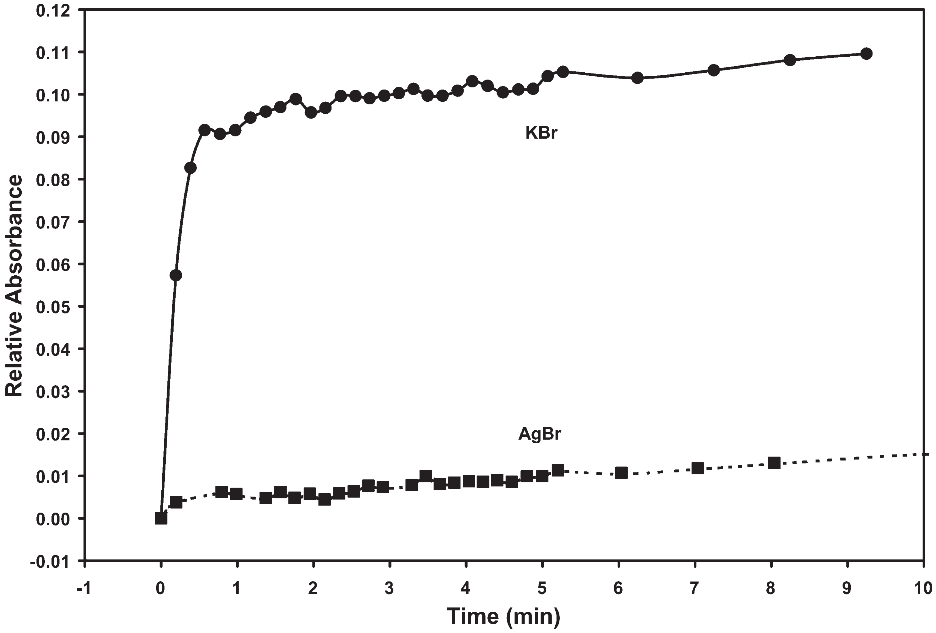

Figure 5. Absorbance (400 nm) versus time 40°C, (——) AgCl + 5 mole % KBr, (- - - -) AgCl + 2 mole % AgBr, 40°C.

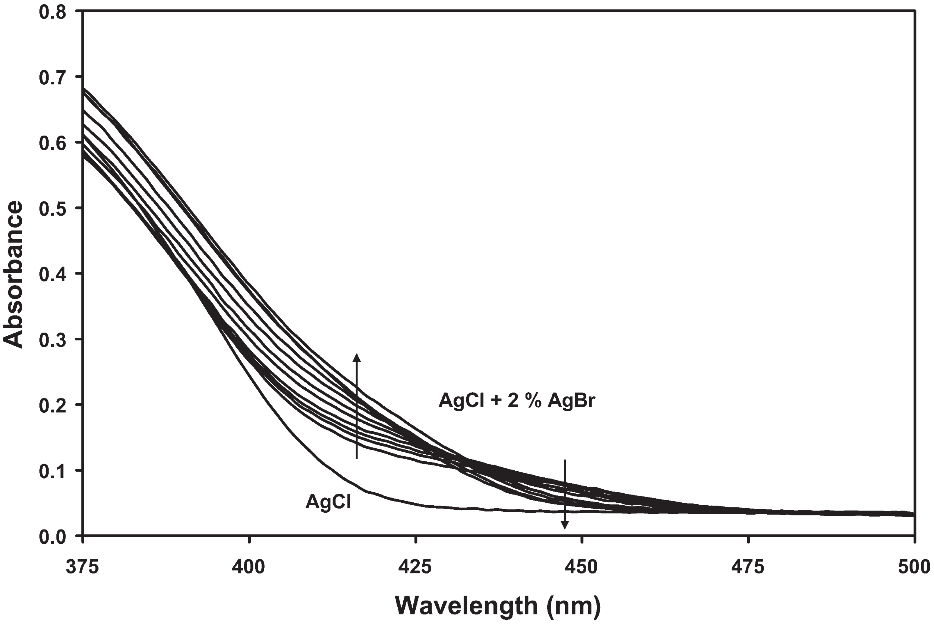

Figure 6. Absorbance versus wavelength, AgCl + 2 mole % AgBr, 70°C.

Temperature

By increasing the temperature to 70°C, the reaction rate of AgCl with AgBr can be significantly increased, as shown in Figs. 6 and 7. At 40°C, there is little additional 400 nm absorption change due to halide conversion. At 70°C however, there is a steady absorption increase at 400 nm, indicating reaction of the AgBr with AgCl. As seen in most other examples, the initial rapid reaction is followed by a slower reaction.

Figure 6 (70°C) shows an interesting feature not seen in Fig. 4 (40°C). At wavelengths less than about 430 nm, the absorbances increase with time. At wavelengths greater than about 430 nm, the absorbances decrease with time. This family of spectra appears as if there is an isosbestic "range" at approximately 430 nm.

Figure 7b shows that the absorption behavior at 450 nm is essentially complimentary to that observed at 400 nm (Fig. 7a). At 450 nm, there is almost no absorption by AgCl. This suggests that the absorption at 450 is predominantly caused by AgBr. Apparently, the absorption profile at 400 nm qualitatively shows the formation of AgClBr, whereas the absorption profile at 450 nm shows the disappearance of AgBr. In this way, absorption profiles at two different wavelengths can be used qualita-

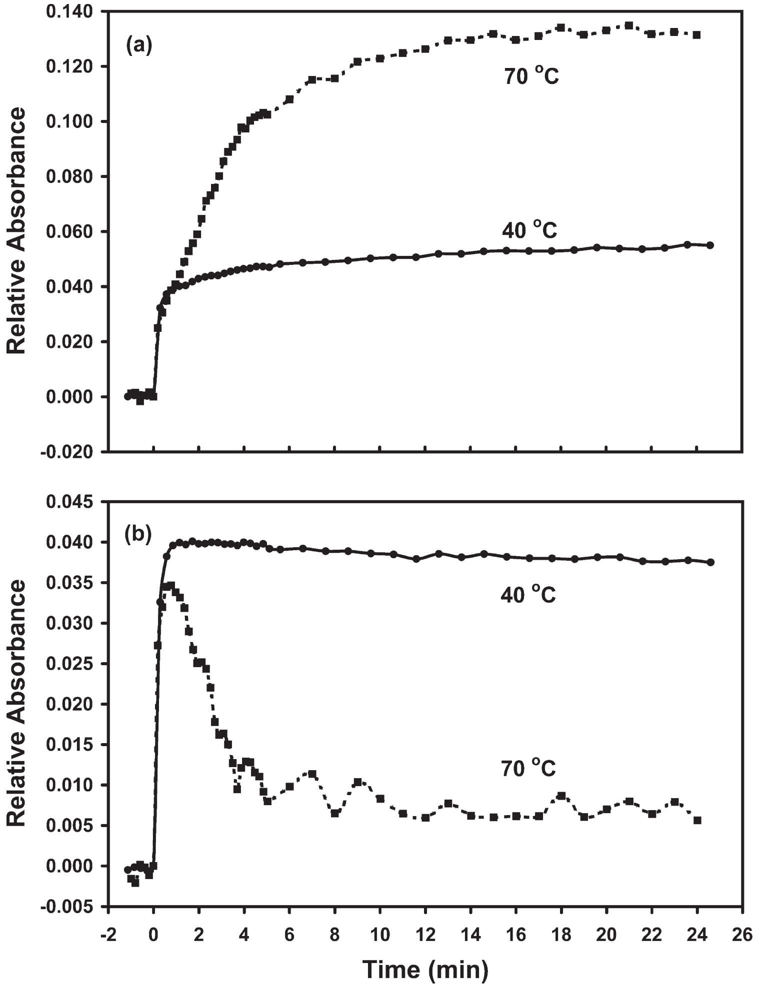

Figure 7. Absorbance versus time, AgCl + 2 mole % AgBr; (a) 400 nm and (b) 450 nm.

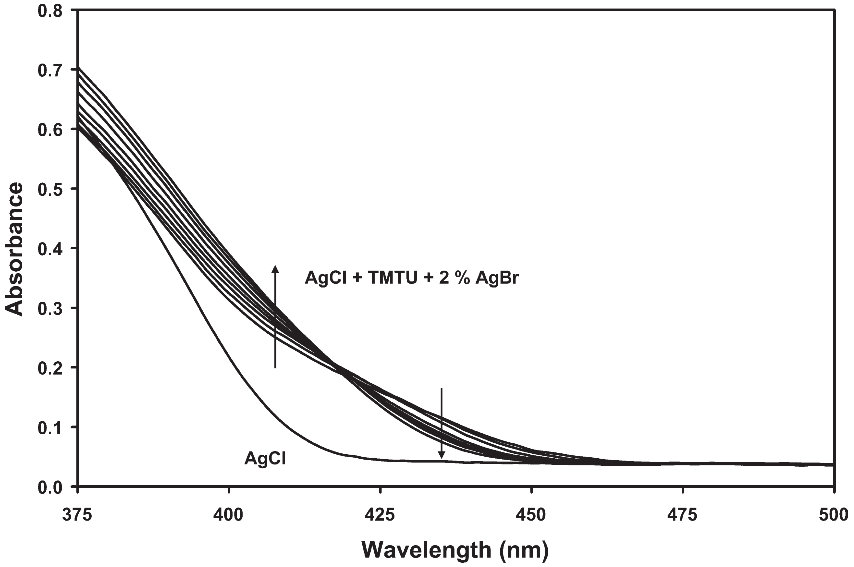

Figure 8. Absorbance versus wavelength, AgCl + 2 mole % AgBr, 1.379 mM TMTU, 40°C.

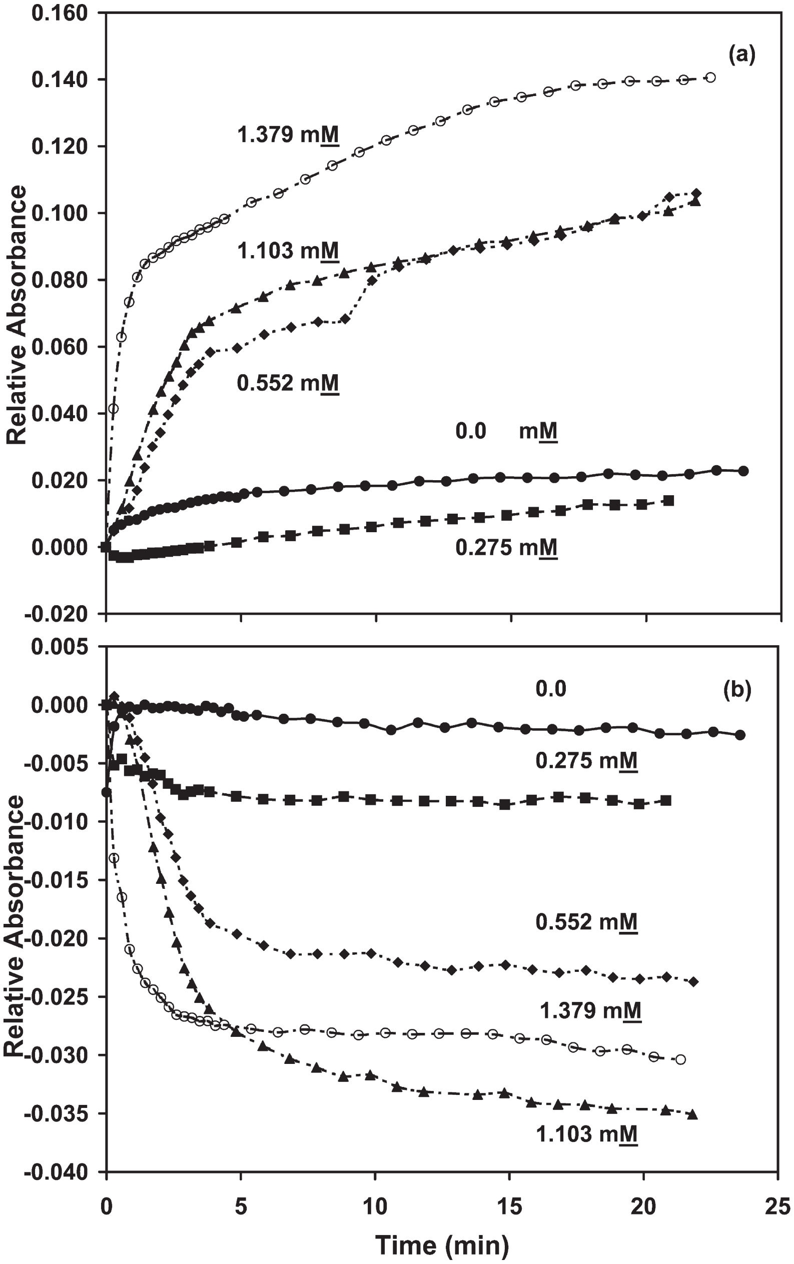

Figure 9. 1,1,3,3-Tetramethyl-2-thiourea (TMTU) level series, AgCl + TMTU + 2 mole % AgBr, 40°C; (a) 400 nm and (b) 450 nm.

tively to monitor the rates of different processes. In this case, both the disappearance of reactants and the formation of products can be observed.

Ripeners

The presence of chemical ripeners has a dramatic effect on the rate of halide conversion. This is clearly shown in Figs. 8 through 10. Figure 8 shows the change in absorbance as a function of wavelength for the reaction of AgCl + 2% AgBr in the presence of 1,1,3,3-tetramethyl-2-thiourea (TMTU). There is a very distinct isosbestic point at 417.5 nm. As seen before (Fig. 6), the absorbance increases with time at wavelengths less than the isosbestic point, and decreases with time at wavelengths greater than that of the isosbestic point.

As shown before, there is little reaction of AgBr with AgCl at 40°C. In the presence of ripener, however, the rate of this reaction can be greatly increased. Both the rate of halide conversion (Fig. 9a) and the rate of AgBr loss (Fig. 9b) increase with TMTU concentration. Similar behavior was observed with 3,6 dithia-1,8-octanediol, as shown in Fig. 10. The exact cause of this rate increase is not known, but could be due to the increased halide solubility, morphological changes, or both.

Restrainers

Compounds that strongly adsorb to silver halide surfaces can also greatly influence the rate of halide conversion. 4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) is commonly used as an antifoggant and crystal

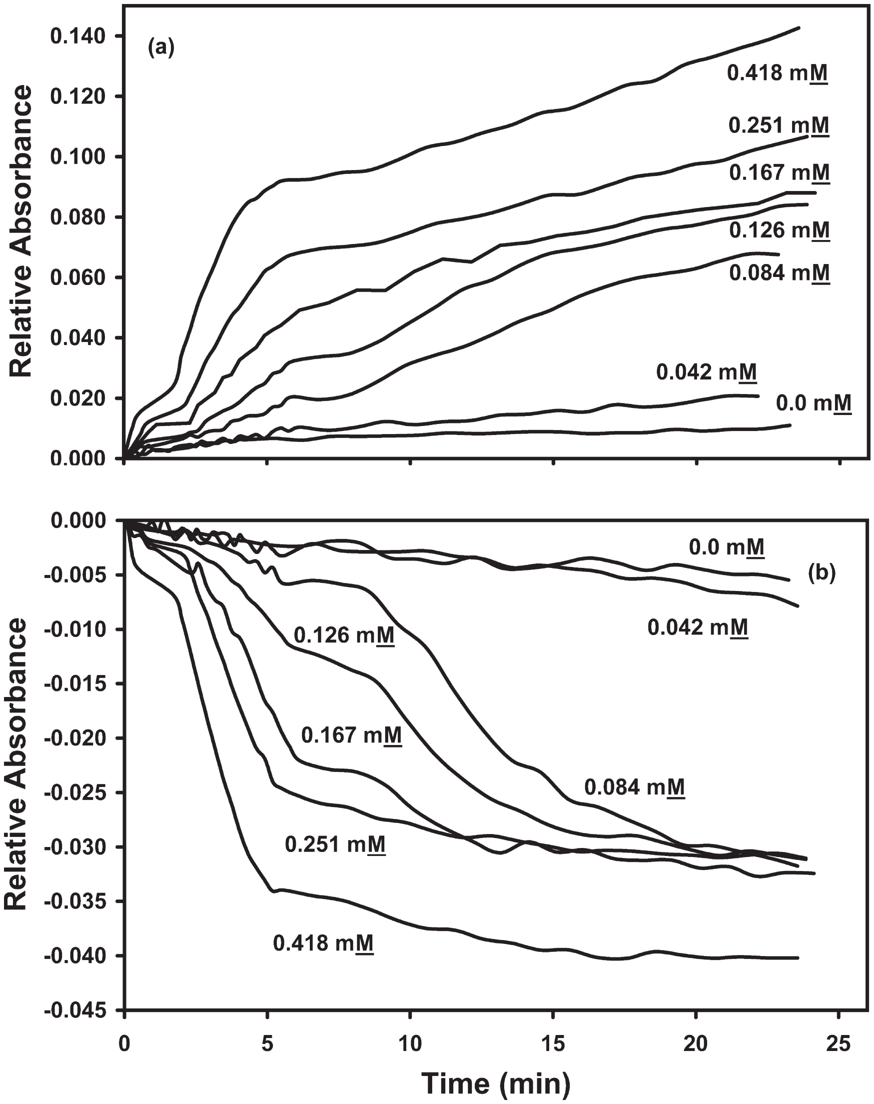

Figure 10. 3,6-Dithia-1,8-octanediol (DTOD) level series, AgCl + DTOD + 2 mole % AgBr, 40°C; (a) 400 nm and (b) 450 nm.

growth restrainer.[33–34] TAI is known to stabilize emulsions and affect the sensitivity of silver halides.[3]

When TAI is added to AgCl prior to the addition of AgBr, the reaction of AgBr with AgCl can be greatly reduced or even completely suppressed. This can be seen in the TAI level series shown in Fig. 11. Percent coverages are based upon the maximum coverage of 6.6×10^{-3} mmol/m^2 at pH = 5.8.[33] SEM images of this emulsion mixture clearly shows the presence of both AgCl and AgBr crystals, confirming that the TAI has suppressed the halide conversion reaction.

Furthermore, if a monolayer of TAI is added to the AgBr prior to the addition of AgBr to AgCl, the reaction can also be completely suppressed. In this latter instance, much less TAI is required, because the molar amounts of AgBr are only a few percent of the amount of AgCl. Figure 12 compares the absorption profiles at 400 and 450 nm, with TAI added to the AgCl or to the AgBr.

Given the sluggishness of the reaction of AgBr with AgCl, it was expected that TAI could suppress this process. Surprisingly, even though the reaction of KBr with AgCl was rapid, addition of TAI to the AgCl was able to completely suppress this reaction as well (Fig. 13).

Discussion

Optical techniques have proven to be very useful for the study of silver halides. Most commonly, tubidimetric techniques are used to analyze particle size and or distribution.[18–20] These techniques focus on the scattering of light by particulate suspensions, and minimize or neglect aborption of the particles. In order to minimize the effects of absorption, turbidimetric techniques tend to use relatively long wavelengths where the silver halide particles do not absorb. These techniques also generally employ very dilute silver halide suspensions (~10^{-4} $\underline{M}$), and have been widely used for the analysis of dilute silver halide sols where no gelatin is present.[21–29]

In most of the previous studies on the silver halide conversion process, a relatively large ratio of less soluble halide to more soluble halide was used. This is probably due to the detection limits of the techniques used

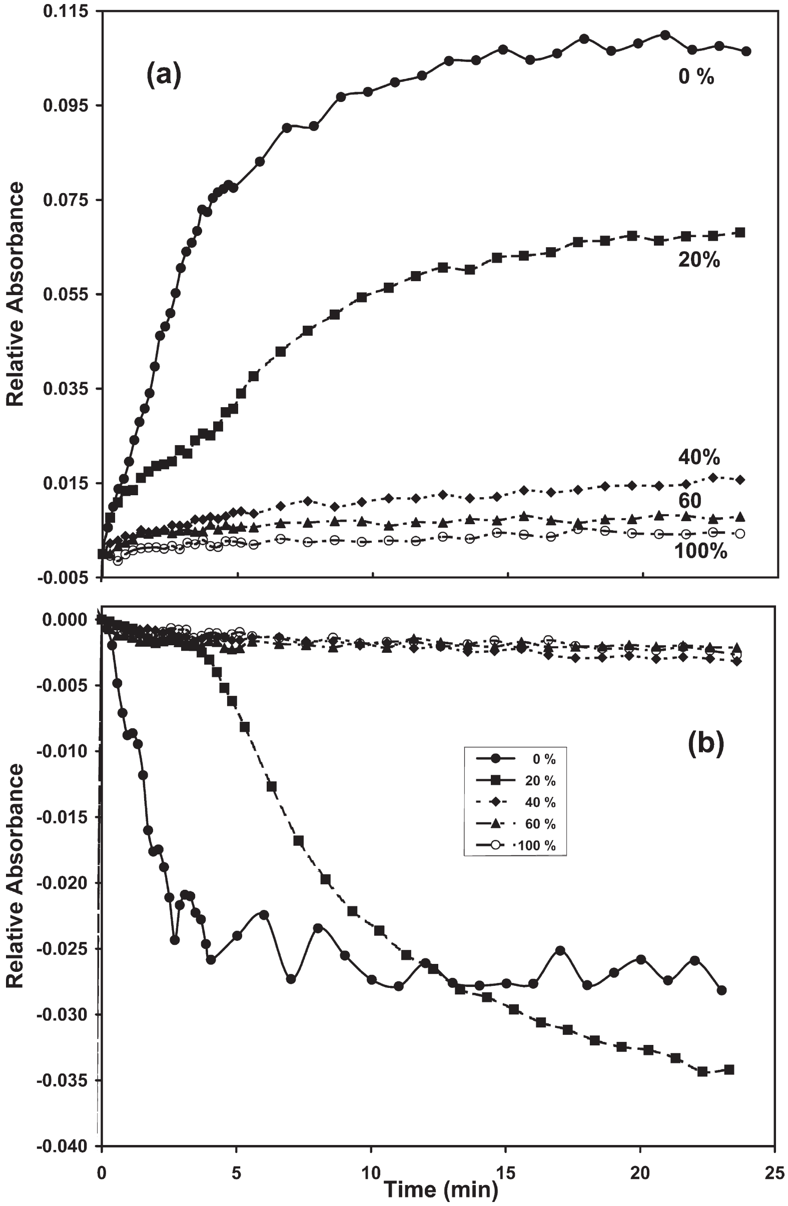

Figure 11. 4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) level series, (AgCl + TAI) + 2 mole % AgBr, 70°C; (a) 400 nm and (b) 450 nm.

for studying these systems. On the other hand, many commercial AgClBr emulsions use relatively small amounts (< 5%) of the less soluble halide.[35–39]

For these reasons, we wanted to study the halide conversion process under conditions that more closely resemble those actually used in practice. We chose diffuse reflection spectrophotometry in order to meet these requirements. In this optical configuration, essentially all of the light reflected from the emulsion is collected, except for that which is absorbed by the sample. The concentrated, highly scattering sample causes multiple reflections, which increases the effective path length of the cell, and the sensitivity of the system. Furthermore, the optical absorption of AgCl has been shown to be very sensitive to small amounts of AgBr.[32] Using our optical configuration, we have sufficient sensitivity to follow reactions with amounts of the less soluble halide that are only a few percent of the amount of the more soluble halide.

The conversion of AgCl to AgClBr by soluble bromide ions has been studied in detail by Sugimoto and Miyake.[8–10] In their work, a multistep mechanism for the conversion process was found. The first step of the mechanism is an almost instantaneous conversion of the surface of AgCl to AgClBr. This surface layer was shown to be less than 1.0 atomic layer thick.[10] The second step of their mechanism was the rapid epitaxial growth of AgBr crystals primarily at the corners, and somewhat on the edges (depending on conditions) of the cubic AgCl crystals. The AgBr deposits on the corners of the AgCl crystals slowly diffuse over the surface and into the bulk of the AgCl substrate. According to Sugimoto and

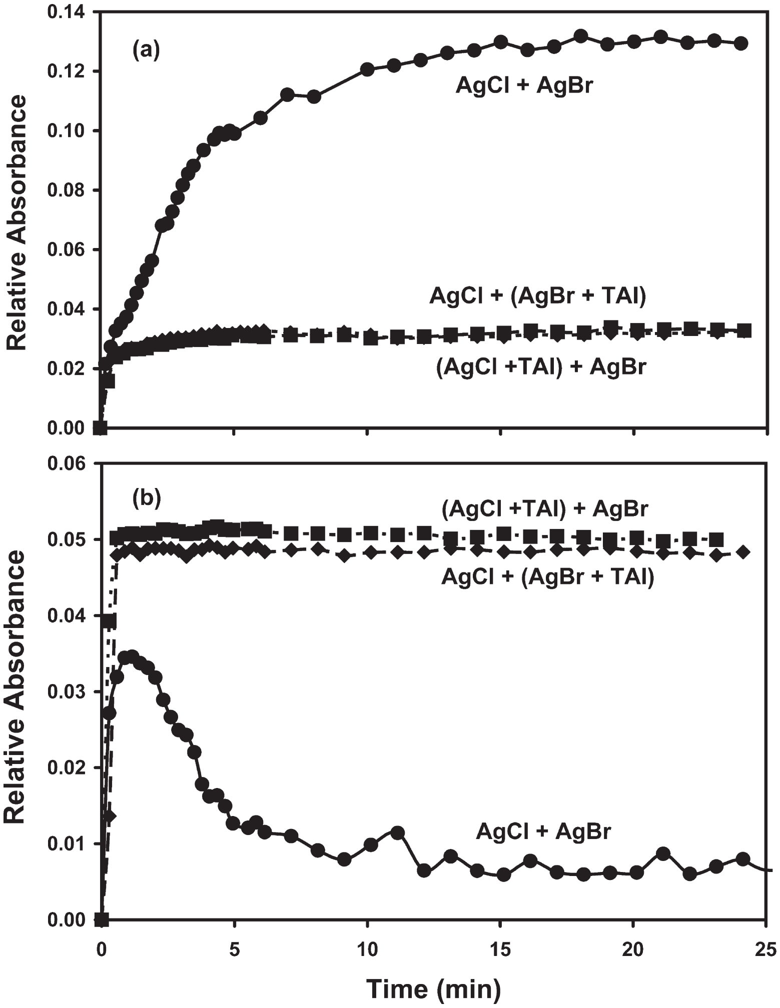

Figure 12. AgCl + 2 % AgBr, 70°C; (a) 400 nm and (b) 450 nm.

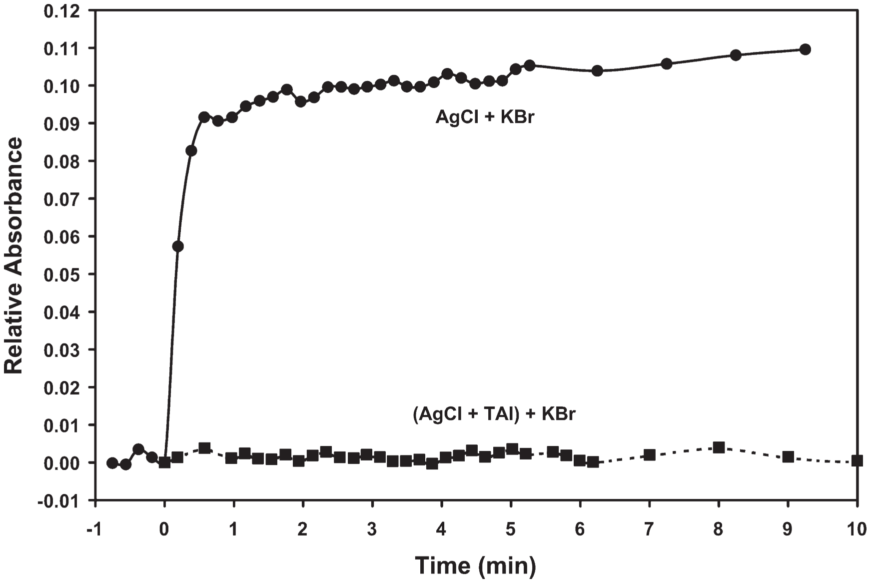

Figure 13. Absorbance (400 nm) versus time, (AgCl + TAI) + KBr, 40°C.

Miyake, an $AgCl_{0.5}Br_{0.5}$ phase is formed first, followed by further recrystallization of the bromide ions into the rest of the AgCl host until the bromide distribution is completely uniform. The distinction between the last two steps (formation of $AgCl_{0.5}Br_{0.5}$, followed by recrystallization) of the mechanism depends upon the ratio of bromide to chloride, and is not very distinct. We believe that these two steps are more likely really part of the same slow recrystallization process.

Zuckerman suggested that the latter stages of the halide conversion process (Sugimoto and Miyake steps three and four) occur by a direct diffusion of bromide ions from the epitaxy into the chloride substrate.[7] Based upon measurements of the chloride exchange rate,[40] and the low mobility of halide ions in silver halide crystals,[41] this appears not to be the case.[9] The measurements of the chloride exchange rate, however, were performed on polydisperse (single-jet precipitation) colloidal suspensions of AgCl, prepared in the absence of gelatin.[40] Gelatin has been shown to inhibit or restrain conversion reactions by several researchers.[16,17,25,42]

Our results for the conversion of AgCl to AgClBr by soluble bromide ions (Fig. 2) supports the mechanism given by Sugimoto and Miyake. The initial instantaneous conversion of the AgCl surface reported by Sugimoto and Miyake occurs too rapidly to be observed by our technique. We observe a fast initial reaction followed by a slower one. The initial rapid reaction that we observe is probably the second step reported by Sugimoto and Miyake (growth of AgBr deposits at the corners of the AgCl). The slow step that we observe equates to the third and fourth step of Sugimoto and Miyake (diffusion of AgBr from the corners of the AgCl into the remainder of the crystal). We are currently investigating the relationship between the absorption behavior and the physical properties of the mixed crystals, in order to understand this process better.

The extremely rapid reaction of soluble bromide ions with AgCl makes it very difficult to employ this reaction commercially. It is difficult, if not impossible, to disperse the bromide ions controllably and effectively in the emulsion before they have a chance to react with the AgCl substrate. The soluble bromide added reacts immediately upon contact with the AgCl crystals, and leads to polydispersity of bromide content among the AgCl crystals.

For this reason, many manufacturers use other sources of bromide for which the conversion reaction can be more effectively controlled. One such “slow release” source of bromide is small (Lippmann) silver bromide emulsions.[35–39] In spite of common industrial usage, we only know of one mention of this process outside of the patent literature.[11]

As expected, our experimental data (Fig. 5) shows that the reaction of AgCl with AgBr is indeed much slower than the reaction of AgCl with soluble bromide. The most likely mechanistic effect of using AgBr as a bromide source instead of soluble bromide ion is to reduce the epitaxial growth rate of AgBr on the corners of the AgCl cubes. The amount of free bromide ion in solution during what Sugimoto and Miyake described as stage two should be substantially less when AgBr is used as a bromide source than when soluble bromide is used. This gives rise to slower, more well defined epitaxial growths,[35–37] and possibly more selectivity for corners over edges of the AgCl substrate. Further investigations of these aspects of the crystal growth are currently being conducted. Following dissolution of the Lippmann AgBr grains, and growth of the initial epitaxial deposits, the remainder of the growth mechanism should be just like that described by Sugimoto and Miyake in stages three and four.

It is well known that many compounds can influence the growth and recrystallization of silver halides.[43] We were interested in investigating the influence of compounds which increase (ripeners) and those which decrease (restrainers) the rate of grain growth on the silver halide conversion process. As expected, ripeners increase the rate of halide conversion, whereas restrainers can reduce or eliminate it (Figs. 8 through 13). This is also consistent with the suggested role that Ostwald ripening plays in the halide conversion process.[9]

It is important to be aware of the effect that these (and other) compounds can have on the halide conversion process, because many of these types of compounds are present during chemical sensitization procedures. The interaction of the presence and level of these (and other) compounds, with halide conversion processes would be expected to influence the ultimate sensitometric performance of the emulsions.

Summary

The halide conversion process was followed spectrophotometrically for a number of halide sources and addenda. This technique allowed the conversion process to be studied *in-situ*, and was sensitive to small ($< 5\%$) amounts of bromide. Observation of the conversion process at 400 nm allowed the study of species that were primarily AgCl, whereas observation at 450 nm showed species that were primarily AgBr. This technique is very useful for following conversion processes, as it allows both the reactants and products to be observed. For most conversion reactions, two processes were seen—a fast initial reaction followed by a slower reaction. Soluble halides like KBr react extremely quickly with AgCl, whereas the relatively insoluble AgBr reacted much more slowly. Ripeners increased the reaction rate, whereas restrainers were able to completely suppress it.

Acknowledgment. The authors would like to thank Dr. Bruce Resnick for the generous donation of some of the equipment used in this work. We would also like to thank Mr. Aaron Vanglish for fabrication of the cell holder, and Mr. Glenn Robinson for his assistance in obtaining some of the materials.

References

1. E. P. Davey, E. B. Knott, U. S. Patent 2,592,250.
2. T. H. James, The Theory of the Photographic Process, 4th ed., Eastman Kodak Company, Rochester, NY, 1977, 98.
3. T. Tani, Photographic Sensitivity, Oxford University Press, Oxford, 1995, p. 27.
4. E. Klein, E. Moisar and G. Münch, *Photogr. Korr.* **102,** 59 (1966).
5. T. Shiozowa, *Bull. Soc. Photo. Sci Tech. Japan* **22,** 7 (1972).
6. T. Shiozowa, *Bull. Soc. Photo. Sci Tech. Japan* **22,** 14 (1972).
7. B. Zuckerman, *Photo. Sci. Eng.* **20**(3), 111 (1976).
8. T. Sugimoto and K. Miyake, *Process Technol. Proc. 6 Ind. Cryst.* **87,** 1989, p. 487.
9. T. Sugimoto and K. Miyake, *J. Coll. Interface Sci.* **140**(2), 335 (1990).
10. T. Sugimoto and K. Miyake, *J. Coll. Interface Sci.* **140**(2), 348 (1990).
11. J. Mydlarz, International Symposium on Silver Halide Technology, IS&T, Springfield, VA, 1997, p. 178.
12. H. Ullmann, H. Besserdich, J. Siegel, and M. Sydow, *J. Inf. Rec. Mats.* **20,** 401 (1993).
13. J. Eggert and H. Fischer, *Z. Elektochem.* **62,** 230 (1958).
14. J. Eggert and H. Fischer, *Z. Elektochem.* **62,** 393 (1958).
15. W. F. Berg and H. E. Keller, *Congress Int. Sci. Photogr.,* Paris, 1965, p. 436.
16. A. Kumai, Y. Inaba and T. Ueda, *J. Photogr. Sci.* **18,** 220 (1970).
17. L. J. Leyshon and P. J. Hillson, *J. Photo. Sci.* **24**(4), 142 (1976).

18. E. J. Meehan and W. H. Beattie, *J. Phys. Chem.* **64,** 1006 (1960).
19. C. R. Berry, *J. Opt. Soc. Amer.* **52**(8), 888 (1962).
20. E. J. Meehan, *J. Coll. Interface Sci.* **27**(3), 388 (1968).
21. E. J. Meehan and W. H. Beattie, *J. Phys. Chem.* **65,** 1522 (1961).
22. C. R. Berry and D. C. Skillman, *J. Phys. Chem.* **68**(5), 1138 (1964).
23. E. J. Meehan and G. Chiu, *J. Phys. Chem.* **70,** 1384 (1966).
24. E. J. Meehan and J. K. Miller, *J. Phys. Chem.* **72**(6), 2168 (1968).
25. S. Nishiyama and W. F. Berg, *Photogr. Sci. Eng.* **17**(3), 299 (1973).
26. T. Tanaka, T. Matsubara, N. Saeki, and H. Hada, *Photogr. Sci. Eng.* **20**(5), 213 (1976).
27. T. Tanaka, T. Matsubara, H. Hada, *Photogr. Sci. Eng.* **23**(2), 118 (1979).
28. T. Tanaka, H. Saijo and T. Matsubara, *J. Photogr. Sci.* **27,** 60 (1979).
29. T. Tanaka and T. Matsubara, *Photogr. Sci. Eng.* **21**(1), 1 (1981).
30. A. B. Holland and A. D. Feinerman, *J. Applied Photgr. Eng.* **8,** 165 (1982).
31. K. Meinig, J. Metz and J. Teltow, *Phys. Stat. Sol.* **2,** 1556 (1962).
32. B. L. Joesten and F. C. Brown, *Phys. Rev.* **148**(2), 919 (1966).
33. D. D. F. Shiao, M. T. Nieh and A. H. Herz, *J. Photogr. Sci.* **30,** 208 (1982).
34. E. J. Birr, *Stabilization of Photographic Silver Halide Emulsions*, Focal Press, New York, 1974.
35. K. Hasebe, M. Asami, N. Ohshima, K. Shiba, T. Nishikawa, K. Sakanoue, and A. Abe, U.S. Patent 4,865,962 (1989).
36. A. Kase and T. Kojima, U.S. Patent 5,061,615 (1991).
37. H. Kawai, U.S. Patent 5.393,653 (1995).
38. M. T. Olm, W. G. McDugle, S. A. Puckett, T. Y. Kuromoto, R. S. Eachus, E. L. Bell, and R. D. Wilson, U.S. Patent 5,360,712 (1994).
39. T. Y. Kuromoto, E. L. Bell, W. G. McDugle, R. S. Eachus, S. A. Puckett, M. T. Olm, and R. D. Wilson, U.S. Patent 5,462, 849 (1995).
40. T. Sugimoto and G. Yamaguchi, *J. Phys. Chem.* **80**(14), 1579 (1976).
41. A. P. Batra and L. M. Slifkin, *J. Phys.* C. **9,** 947 (1976).
42. W. Romer and A. Sidorowicz, *J. Photogr. Sci.* **15,** 115 (1967).
43. A. H. Herz, *J. Imaging Sci. Tech.* **39**(1), 40 (1995).