

# Observations of the Effects of Temperature and the Addition of Bromide on AgCl Cubic Emulsions

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## Abstract

The fundamental theory and mechanism of the halide conversion process, in a suspension of AgCl microcrystals by bromide ions, is well documented in the literature (for example: Sugimoto and Miyake in *Journal of Colloid and Interface Science*, Vol. 140, No. 2, December 1990).

We have shown that the bromide distribution on the AgCl cubic host emulsion is strongly related to the position of bromide addition in the finish. With addition at low temperatures, a high silver bromide phase localized on the corners and edges of the cubic grain is created; however, highly localized distribution of AgBr occurs in the center portion of each surface of the cubic AgCl grains when bromide is added at higher temperature. The high silver bromide phase localized on the corners and edges of the cubic grain is not stable; it will spread away from the corners and edges of the host grain if the silver chloride host emulsion is heated to and held at the temperature employed to achieve chemical sensitization.

The link between bromide distribution and the reciprocity characteristic of AgCl cubic emulsion is discussed in this paper.

## Introduction

Photographic emulsions normally consist of mixed silver halide grains such as  $\text{AgCl}_{1-x}\text{Br}_x$ ,  $\text{AgCl}_{1-x}\text{I}_x$  and  $\text{AgBr}_{1-x}\text{I}_x$ . Thus, the halide conversion is one of the most fundamental processes in the manufacture of photographic emulsions. The mechanism of the halide conversion process of AgCl microcrystals by bromide ions was extensively studied by Sugimoto and Miyake<sup>1, 2</sup> and consists of more than three sequential steps<sup>2</sup>: (1) surface conversion to establish the surface equilibrium with solution phase, (2) epitaxial growth of AgBr mainly on the corners of the AgCl cubes by the dissolution of their {100} faces, (3) growth of an  $\text{AgCl}_{0.5}\text{Br}_{0.5}$  solid solution from the AgBr/AgCl joints by the simultaneous dissolution of the AgBr grains and the open surface areas of the AgCl hosts, and (4) growth of a solid solution higher in chloride content by the concurrent dissolution of the foregoing solid solution and the AgCl hosts.

The fundamental theory of the halide conversion process of colloidal AgCl microcrystals by bromide ions has been developed by Sugimoto and Miyake<sup>3</sup>. They have introduced a new concept of the surface stress energy built up within a AgBr surface layer on dissolving AgCl particles, due to the lattice mismatch between the AgBr surface layer and the AgCl substrate. They have assumed that the rate-determining step is a specific surface reaction of the adsorbed complexes on growing particles.

In this paper we will show how the distribution of a bromide phase on the AgCl cubic host grains is affected by the temperature of bromide conversion. The link between bromide distribution and the reciprocity characteristic of AgCl cubic emulsion will also be discussed.

## The Cyan Finish Formats

The emulsions were each optimally sensitized to red light by the customary techniques using chemical sensitizers, soluble bromide, and antifoggants. Positions and amounts of all addenda are the same for each finished emulsion; however, finish temperature profiles varied depending on the particular emulsion being sensitized.

### Emulsion A:

A portion of the silver chloride primitive emulsion was sensitized by the addition of the optimum amount of colloidal gold sulfide, followed by a heat ramp up to 65°C for 30 minutes and subsequent addition of 1-(3-acetomidophenyl)-5-mercaptotetrazole, followed by addition of potassium bromide. Next, the emulsion was cooled to 40°C and red spectral sensitizing dye was added.

### Emulsion B:

A portion of the silver chloride emulsion was sensitized by the addition of the optimum amount of colloidal gold sulfide, followed by a heat ramp up to 65°C for 30 minutes. The emulsion was cooled to 40°C and 1-(3-acetomidophenyl)-5-mercaptotetrazole was added, followed by addition of potassium bromide and red spectral sensitizing dye.

These two emulsions were coated together with a cyan dye-forming coupler on resin coated paper support at 17 mg Ag/ft<sup>2</sup>. The coatings were given a standard white light exposure and a diode laser exposure (50 ns at 685 nm) and processed in Kodak Ektacolor RA-4 processing.

The D-log E curves for optical and laser exposures are reproduced in Figure 1. In the optical exposure, emulsion B has a similar toe (density measured at  $D_{\min} + 0.15$ ), better contrast and a significantly higher shoulder (density measured at  $D_{\min} + 1.95$ ). Figure 1 also shows D-log E curves for the laser exposure. Emulsion A shows significant losses both in the mid and upper areas of the sensitometric curve, while emulsion B shows a high upper part of the D-log E curve with sharp toe and good contrast for the entire D-log E curve.

Reciprocity comparisons (speeds taken at toe, mid part of the D-log E curve ( $D_{\min} + 1.35$ ), and shoulder) for emulsion A and emulsion B are presented in Figure 2. Both emulsions show similar and flat high intensity reciprocity (HIR) and similar low intensity reciprocity (LIR) in the toe area. In the mid part of the D-log E curve, emulsion B has similar LIR but significantly better HIR in comparison to emulsion A. Emulsion B's shoulder HIR continues to deviate from the flat shape, while emulsion A's shoulder collapses completely.

### The "Bromide Decoration" Experiment

The sensitization of AgCl emulsions can involve the epitaxial growth of small amounts of bromide onto the AgCl substrate. Depending on the type of finish, soluble bromide, or Lippmann bromide, may be used. The bromide can be added almost anywhere during the finish, but very different sensitizations can result.

The "bromide decoration" experiment was conducted in order to learn about the effect of addition temperature of bromide on bromide epitaxy. The emulsion that was studied is a very cubic, 1.0  $\mu\text{m}$  edge length precipitated without any ripener.

Electron micrographs show that highly localized distributions of AgBr occur in the center portion of each surface of the cubic AgCl grains when soluble bromide is added at 65°C (see Figure 3). Conversely, the distribution of AgBr is localized to the outer perimeter of the surfaces of cubic grains when bromide is added to the AgCl grains at 40°C (Figure 3). The bromide directing capability of temperature on this emulsion is clearly. An explanation of "bromide decoration" caused by different addition temperature of soluble bromide is as follows:

The kinetics of all reactions taking place on the sensitized crystal surface is temperature dependent. Higher temperatures usually catalyze the sensitization process. In order for grain sensitization to occur, the chemical species (doctors) must move from the bulk solution to the crystal surface, be absorbed on the crystal surface, and finally move to a "desired" place on the crystal surface<sup>4</sup>. The latter step is so-called "surface integration". In general, the nucleation work on a substrate is grain "shape dependent". For

identical wetting, the nucleation work is lower (i.e., nucleation is easier) on a "rough surface" than on a flat surface<sup>4</sup>. Therefore, we can expect that recrystallization of bromide on the silver chloride substrate will take place not on the flat surface, but rather on the corners and edges of the AgCl grains regardless of recrystallization temperature. Due to a different bromide concentration on the AgCl grains surface, the bromide species will migrate on the surface (surface diffusion). The kinetics of this process (as of any diffusion process) is temperature dependent<sup>4,5</sup>. Higher temperature significantly catalyzes this process. Therefore, the addition of bromide to the silver chloride host emulsion at high temperature results in a very similar non-localized bromide distribution over all the surfaces of the AgCl grain. For bromide addition at low temperatures, a high silver bromide phase localized on the corners and edges of the cubic grain is created.

If the silver chloride host emulsion having a high bromide localized phase is heated to and held at 65°C, the silver bromide phase spreads away from the corners and edges of the host grain, unless another compound (preferably photographically useful), which is strongly adsorbed to the silver halide grain surfaces, is added. A wide choice of photographic compounds are available from among conventional spectral sensitizing dyes, antifoggants, and stabilizers<sup>6</sup>.

While it is demonstrated in Figure 2 that the bromide rich phase located at the corners and edges dramatically improves the high intensity reciprocity failure (compared to emulsions having more uniform bromide distributions), the mechanism by which shoulder reciprocity has been improved is not known with certainty. It can be stated with some confidence that the latent image is preferably formed at the corners and edges of the cubic grains. For bromide addition at lower temperatures, a high silver bromide phase localized at the corners and edges of the host grain is created (see Figure 3), thus providing a different substrate for subsequent spectral sensitization reactions. The silver bromide phase adsorbs the red spectral sensitizing dye much better than the silver chloride phase. A bromide rich phase is preferably located at the same region where the latent image is formed. The photoefficiency is significantly improved particularly for very short exposures times (Figures 1, 2).

Figure 4 shows the soluble bromide transition during the following heat treatment:

**melt at 40 °C > KBr; hold for 20 min > heat to 65°C > hold for 30 min > cool to 40°C > hold for 20 min**

Three samples of the emulsion were removed out at the following points during the heat treatment:

- (a) before the heat ramp
- (b) 30 min after the start of the 65°C hold
- (c) after cool down, at 40°C

The SEM micrographs of the samples are shown in Figure 4. It is clear from the micrographs that the distribution of AgBr is localized to the outer perimeter of the surfaces of the cubic grains when bromide is added to the

AgCl grains at 40°C (Figure 4a). After heating that emulsion to 65°C and holding it at this temperature for 30 minutes, the localized bromide in the edges and corners of the bromide rich phase spread away from the corners and edges of the host grain (see Figure 4b), significantly changing the bromide distribution on the host, AgCl, cubic emulsion. The bromide distribution will again change if we cool down the emulsion to 40°C (Figure 4c). The bromide distribution is more localized in comparison to the sample taken out at 65°C (Figure 4b). However, the bromide rich phase is rather localized in the center of the {100} face of host grain. It is obvious that the photographic responses of all three emulsions shown in Figure 4 could be significantly different.

We repeated the "heat treatment" experiment for the same host emulsion, which the addition of Lippmann bromide instead of soluble bromide was used. Figure 5 shows the transition of Lippmann bromide during the described early heat treatment. A very different "bromide decoration" is obtained without heat treatment when Lippmann bromide is a source of bromide (compare Figure 4a and Figure 5a.). In this case, the bromide rich phase is located not only on the edges and corners of the host grain, but also in the center portion of each surface of the host grain. After the heat treatment, however, transition of bromide is very similar to the case when soluble bromide is the source of bromide (compare Figure 4b with Figure 5b and Figure 4c with Figure 5c).

### Summary

As a result of this work we conclude that emulsions with halide, antifoggants, and dye added at lower temperature, but after the chemical sensitization is completed, (emulsion B) produces better contrast, shoulder, and high intensity reciprocity (HIR) than emulsions chemically sensitized in the same way, but all the compounds added at high temperature.

The bromide distribution on the AgCl cubic host emulsion is directly related to the position of bromide in the finish. For bromide addition at low temperatures (emulsion B), a high silver bromide phase localized on the corners and edges of the cubic grain is created. However, highly localized distribution of AgBr occurs in the center portion of

each surface of the cubic AgCl grains when bromide is added at 65°C.

If the silver chloride host emulsion having a high bromide localized phase is heated to and held at 65°C, the silver bromide phase will spread away from the corners and edges of the host grain, unless another compound (preferably photographically useful) that is strongly adsorbed to the silver halide grain surfaces is added.

The contrast and shoulder HIR reciprocity changes are due to different bromide distribution on the AgCl host grain, and this different bromide distribution is caused by the different temperature addition of bromide during the finish. The highly localized distribution of AgBr occurs in the center portion of each surface of the cubic AgCl host grains when soluble bromide is added at 65°C. Conversely, the distribution of AgBr is localized to the outer perimeter of the surfaces of grains when soluble bromide is added at 40°C, thus providing a different substrate for subsequent spectral sensitization reactions. The silver bromide phase adsorbs the red spectral sensitizing dye much better than the silver chloride phase. A bromide rich phase is preferably located at the same region where the latent image is formed; the photoefficiency is significantly improved particularly for very short exposures times used in digital printers.

### References

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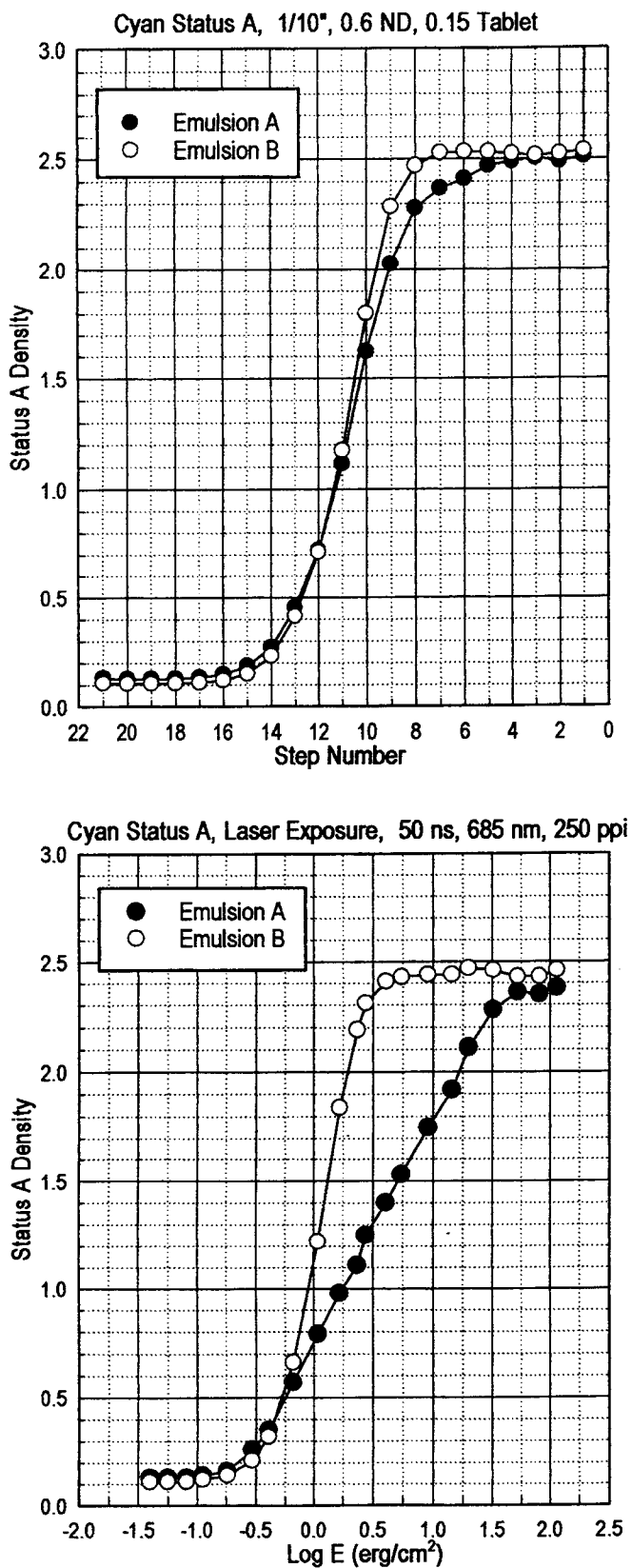


Figure 1. Effect of finish temperature profile on D-log E curve shape for optical and laser exposures.

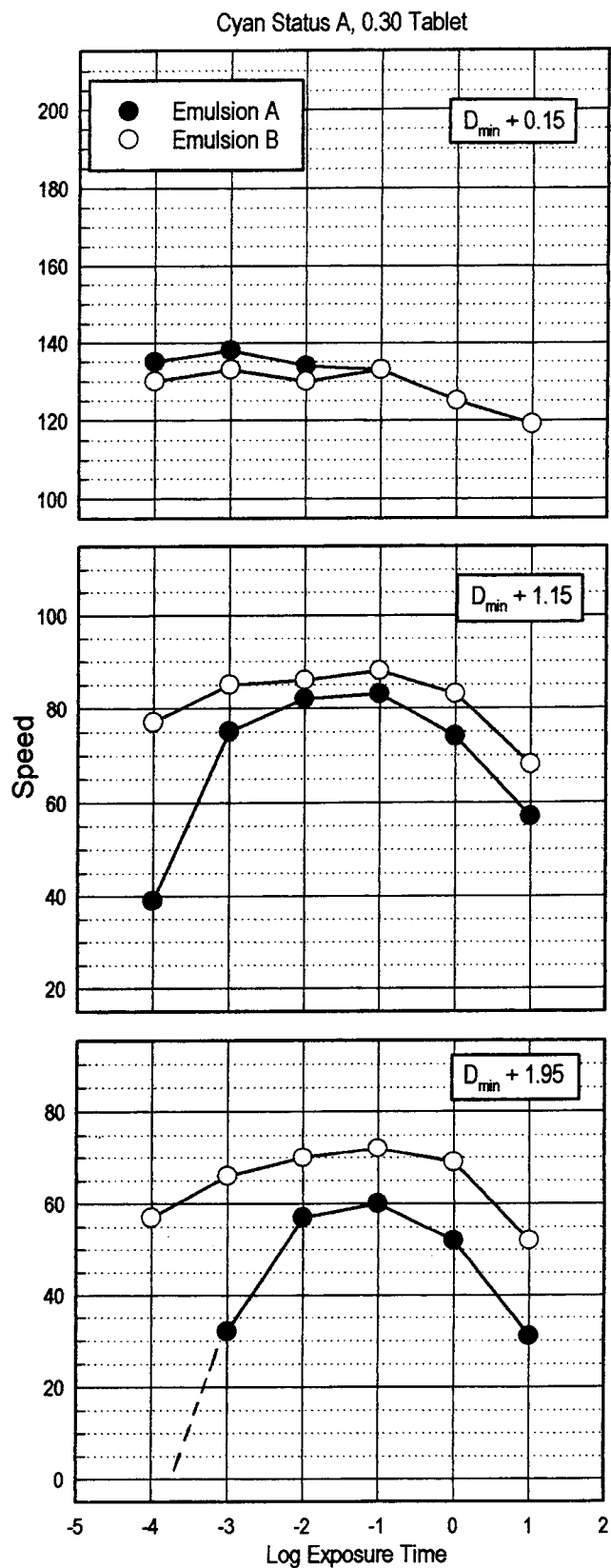


Figure 2. Effect of finish temperature profile on reciprocity.

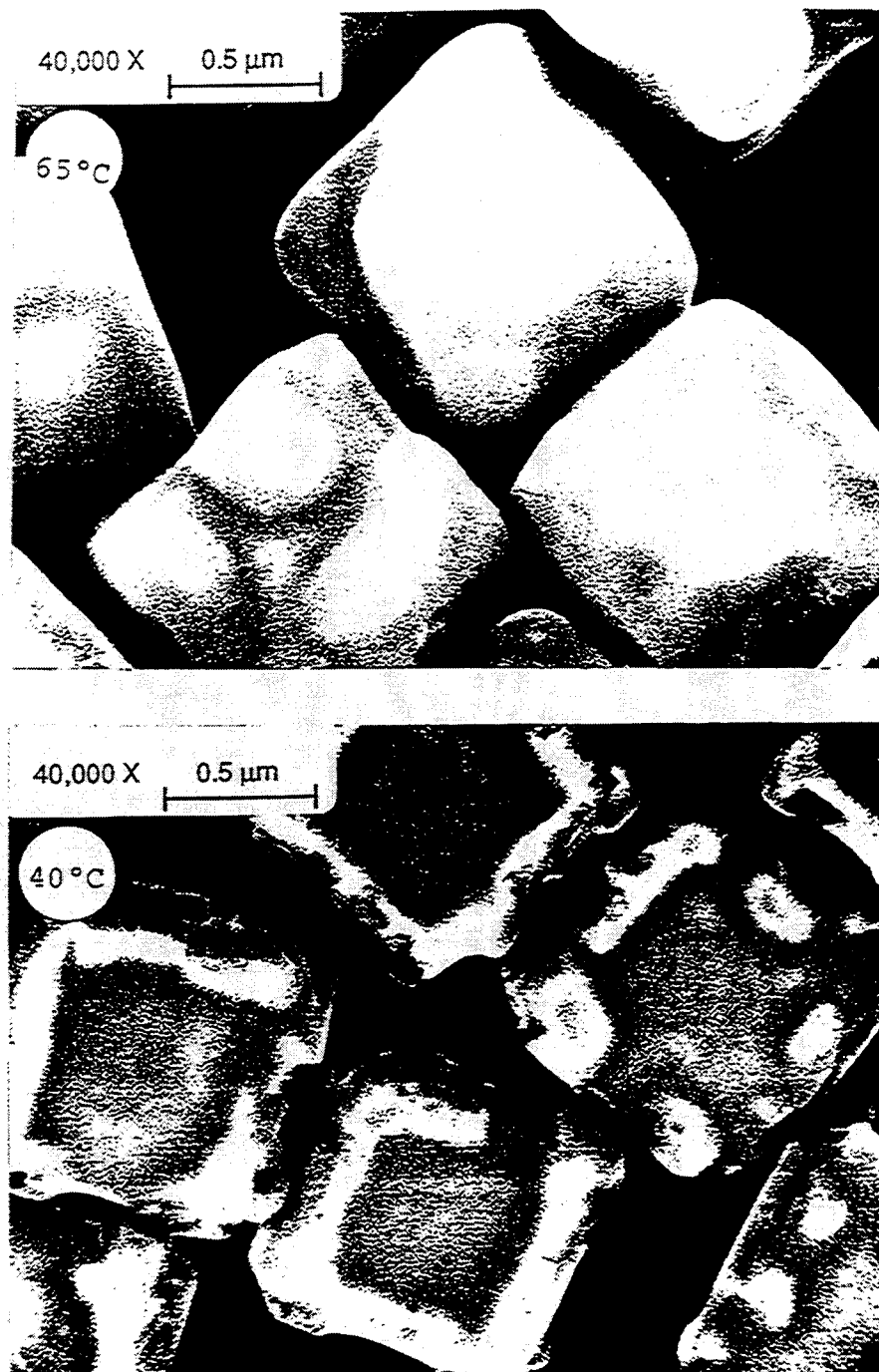


Figure 3. Bromide decoration (5 mol % bromide) of AgCl host grain at 65°C and 40°C.

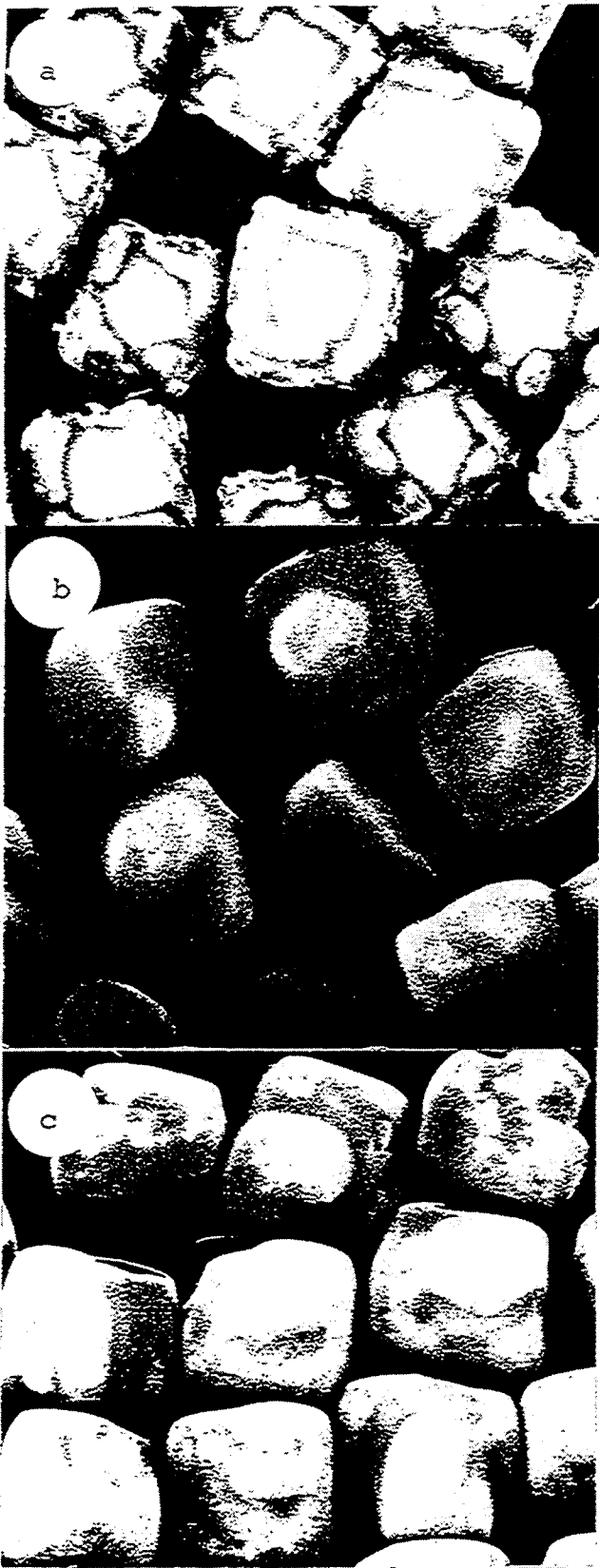


Figure 4. The soluble bromide transition during the heat treatment.

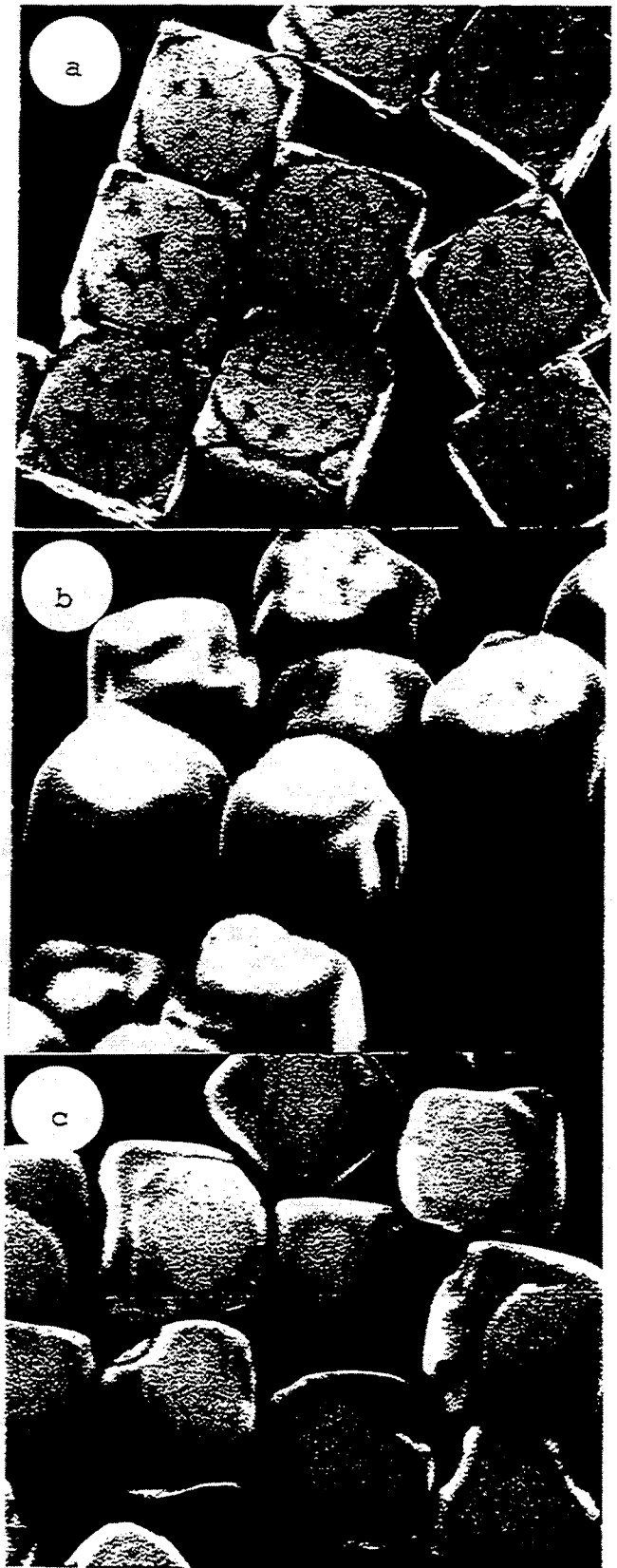


Figure 5. The Lippmann bromide transition during the heat treatment.