Reciprocity Behavior of High-Aspect Ratio Silver Chloride Tabular Grain Emulsions

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Abstract

A process for preparation of inherently stable, high-aspect ratio, silver chloride tabular emulsions has been recently developed along with the conventional methods of spectrochemical sensitization. Photographic performance consistent with the high surface-to-volume ratio has been demonstrated. An interesting aspect of the photographic performance has been reciprocity behavior of these grains. While conventional silver chloride cubic grain emulsions suffer from the reciprocity problems, especially at very high irradiance and short time exposures, these effects can be minimized using silver chloride tabular emulsions. Some potential reasons for the grain morphology-related reciprocity effects are presented in this paper.

Introduction

With the introduction of RA-4 process, silver chloride emulsions gained widespread use in color paper. One of the characteristics of silver chloride cubic emulsions is their high degree of high intensity reciprocity failure (HIRF). The effect is especially apparent in larger grains, as are commonly used in the blue-sensitive layer of color paper. With the advent of direct printing on paper using a variety of print engines (CRT, LED, laser, and others) HIRF becomes even more important property of the emulsions designed for these applications.

Stable, high-aspect ratio, silver chloride tabular emulsions has been recently developed along with the conventional methods of spectrochemical sensitization.[1,2] By adding small amounts of iodide, early in the process to induce anisotropic growth, the rectangular thin tabular grain crystals can be produced. Unlike the traditional tabular morphology with parallel twin planes, these new crystals have major faces of <100> lattice orientation, no twin planes, and do not require tightly adsorbed organic growth modifiers and stabilizers. Photographic performance consistent with the high surface-to-volume ratio has been demonstrated.[2]

This paper presents a study of the photographic performance of silver chloride tabular emulsions sensitized for optimum performance in RA-4 chemistry. Special emphasis will be placed on the reciprocity behavior of these emulsions as compared to the same-volume cubic grain silver chloride emulsions.

Precipitation and Sensitization

Silver chloride tabular grain emulsion was precipitated as described in the literature.[1,2] Briefly, a double-jet precipitation was carried out at 35 °C and at pCl of 2.0, followed by controlled addition of a dilute solution of potassium iodide to promote anisotropic growth of the forming AgCl seeds. This step was followed by a short hold

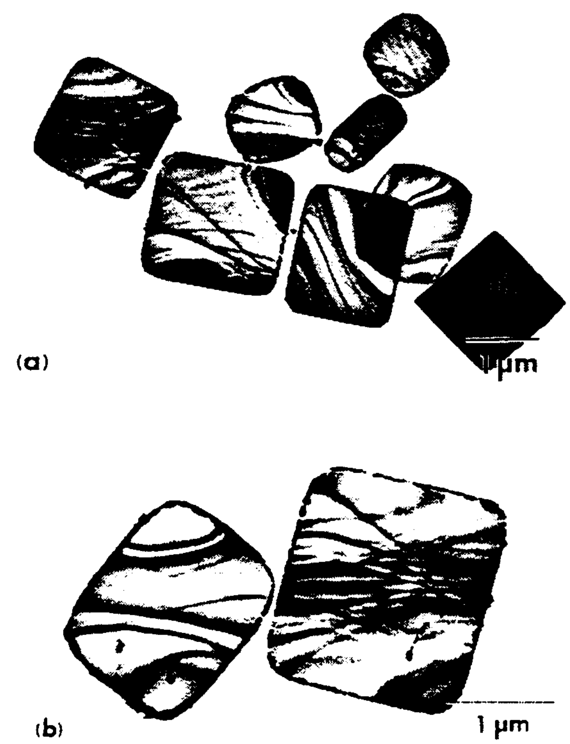

Figure 1. Low (a) and medium (b) magnification TEM images of AgCl tabular grains after sensitization including bromide.

to allow ripening, then a double-jet growth with sodium chloride and silver nitrate was employed to maintain a constant excess halide level. The final iodide content of this emulsion was less than 0.1%. Low methionine gelatin was used. The resultant emulsion grains were characterized by an average equivalent circular diameter (as measured by the image analysis of electron photomicrographs) equal to 1.6 μm and thickness of 0.11 μm. One should note, however, that there are several other methods of precipitation of high chloride tabular grains of this morphology.[3-10] At the same time, two "conventional" AgCl cubic emulsions were precipitated using double-jet precipitation: one with low methionine gelatin (designated Cube (1)) and the other in regular methionine gelatin (designated as Cube (2)). The size of both was 0.6 μm edge length, corresponding to the same grain volume as an average tabular grain.

All three emulsions were chemically and spectrally sensitized using blue sensitizing dye, bromide, colloidal gold sulfide, heat digestion and 1-(3-acetamidophenyl)-5-mercaptotetrazole. The use of bromide during spectrochemical sensitization is very important for optimizing the performance of silver chloride emulsions. It is also important to introduce bromide after the dye. Depending on potassium bromide concentration and delivery rate, a deposition of bromide-rich phase starts at corners and edges, and then spreads over the grain until a shell is created. As an example, bromide deposition at the edges and corners of tabular grains used in this work can be easily detected from the transmission electron microscope micrographs, as illustrated in Figure 1. Bromide-rich phases are clearly visible as darkened areas around tabular grains. Careful studies of bromide deposition on AgCl grain surfaces are reported in the literature.[11-13]

In order to perform photographic evaluations, all emulsions were mixed with yellow coupler dispersion, coated on paper support, exposed with Hg-line (365 nm) and white light sensitometers, and processed in RA-4 chemistry. Hg-line speed and white light exposure speed correspond to the intrinsic grain sensitivity and that enhanced by the presence of blue sensitizing dye (blue/minus blue), respectively. Speed was measured as 100 x log(H) needed to achieve an absolute density of 1.0. The effects of bromide on emulsion photographic speed is presented in Table 1. D_{min} is a measure of the fogging propensity.

Table 1. Effect of bromide on AgCl tabular grain emulsion sensitization.

KBr (%)	D_{min}	Hg line speed	White light speed
none	0.09	145	189
0.4	0.08	160	206
0.6	0.08	159	206
0.8	0.08	158	207
1.2	0.08	152	199

Large increases in tabular emulsion speed with the addition of bromide are very clear. However, at the highest level of bromide, speed is decreased, probably due to development inhibition effects. Evidence in the literature[14-18] suggests that the localized bromide deposition leads to the localized latent image formation on the AgCl grains, thus enhancing emulsion efficiency. Consequently, bromide was used in all the emulsions of this work as an essential component to achieve the optimum photographic performance.

Results and Discussion

The intrinsic speed of AgCl tabular emulsion is compared with both iso-volume cubic emulsions in Figure 2. The tabular emulsion can be sensitized to much faster speed than both cubic counterparts, suggesting better photoelectron processing within the same silver chloride grain volume. It is important to note, however, that there is significant difference between cubic emulsions prepared in regular gelatin (Cube (2)) and low methionine gelatin (Cube (1)). Since tabular grains are also made in low methionine gelatin, its morphology-related performance can be better judged against the latter (Cube (1)). Figure 3 compares white light exposure speed of the emulsions under study. Because all emulsions were blue sensitized using standard blue sensitizing dye at the levels proportional to the specific area, the relative tabular grain emulsion speed advantage over both cubic emulsions is further advanced due to the effect of its larger surface-to-volume ratio.

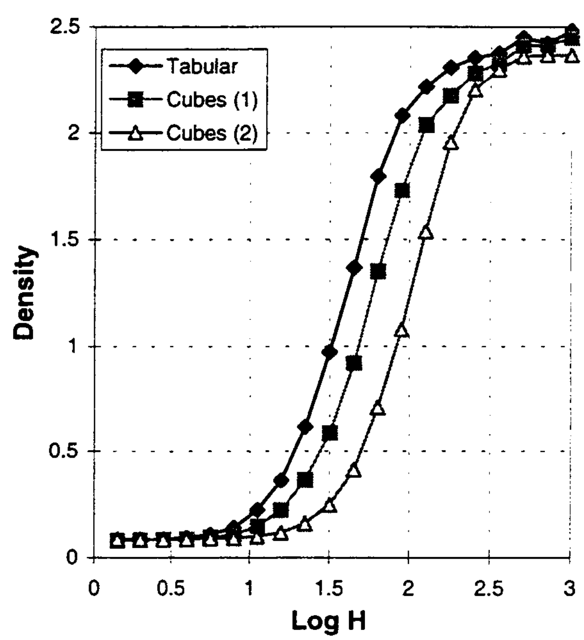

Figure 2. Sensitometric curves of tabular and cubic AgCl emulsions: 365 nm line exposure at 1/10 sec.

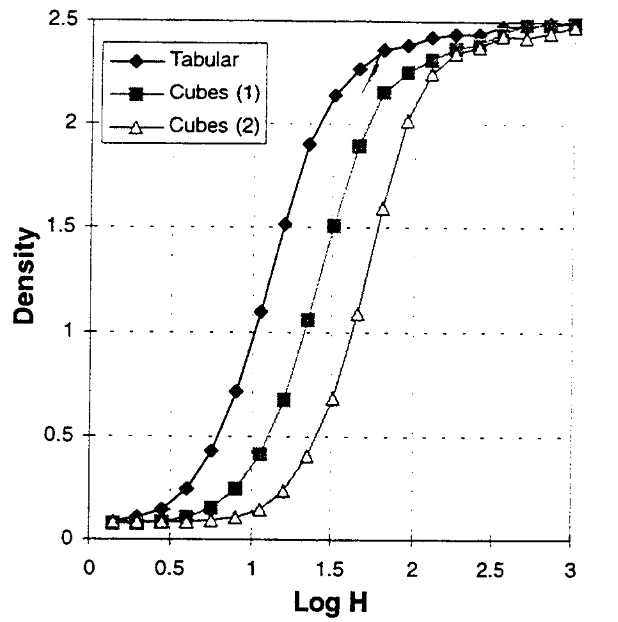

Figure 3. Sensitometric curves of tabular and cubic AgCl emulsions: white light exposure at 1/10 sec.

Reciprocity behavior of the studied emulsions was measured using white light xenon lamp at the exposure times of 1, 10^{-1}, 10^{-2},10^{-3}, 10^{-4}, and 10^{-5} seconds. At the same time, the total energy of each exposure was kept constant by adjusting its corresponding irradiance. In Figure 4 the reciprocity comparison is presented. The cubic emulsion made in regular gelatin exhibits a high degree of high intensity reciprocity failure, whereas both low-methionine-made emulsions look comparable with a hint of better tabular grains performance. At the same, time low intensity reciprocity failure is very similar in all three cases.

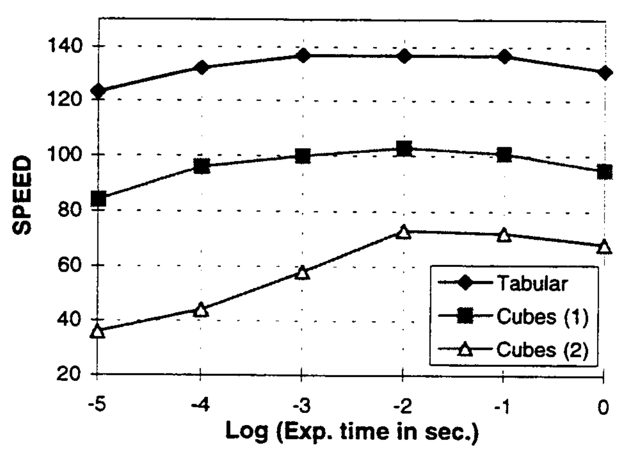

Figure 4. Speed reciprocity of tabular grain and cubic AgCl emulsions: white light exposure.

In order to better appreciate the emulsions' behavior under high irradiance exposures, the comparison was extended beyond optimum sensitization conditions. One way to achieve this is to under and over-sensitize emulsions. The "degree" of sensitization can be effected by changing the level of the chemical sensitizer. Usually, with increasing sensitization degree, the HIRF magnitude becomes more visible, as the number of potential latent image centers (and thus their subsequent dispersity) grows. To quantify the HIRF effect, the photographic speed at each exposure was measured at the absolute density of 1.15. The speed difference between the speed at 10^{-2} second and 10^{-5} second was chosen as a measure of high intensity reciprocity failure. Results are presented in Figure 5. The general trend of increased HIRF with sensitization degree is obeyed by all emulsions, but again, regular gelatin-made cubes (Cubes (2)) are much worse than both low methionine emulsions. It is significant, however, that tabular grain emulsion exhibits much less HIRF than identical (except for morphology) cubic grain counterpart (Cube (1)). Similar reciprocity behavior of silver bromide {100} tabular grains and the practical importance of good reciprocity of silver chloride tabular emulsions are reported in the literature.[19,20]

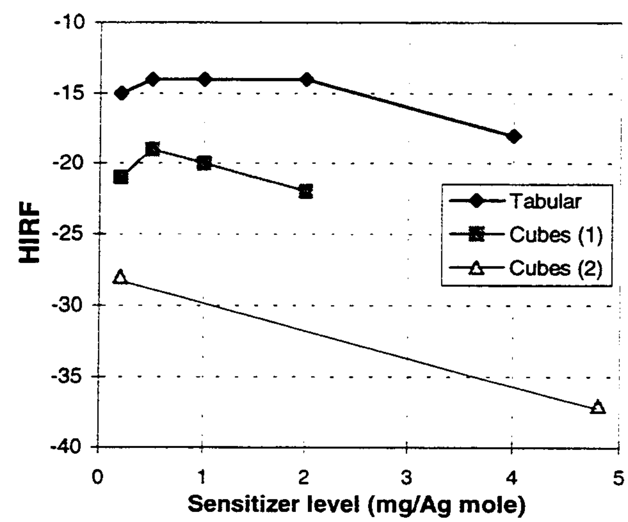

Figure 5. HIRF of tabular grain and cubic AgCl emulsions: degree of finish effect.

A tentative explanation of the above phenomena must be related to the effects of morphology on photoelectron processing efficiency. According to a classical view[21] high intensity reciprocity failure can be related to the high dispersity of latent image centers on the grain upon high irradiance, short time exposures. Such an exposure creates a burst of photoelectrons that leads to the nucleation of a large number of sub-developable latent image centers. Subsequent competition of these centers for the photoelectrons needed for their growth results in a net decrease of the number of grains with a developable latent image speck, and thus a loss of efficiency compared to those obtained at longer exposure times.

Consider the present case for the tabular and cubic emulsion with the same grain volume. Let's assume, for simplicity, that an equal number of photoelectrons is created for each grain when subjected to the same high-intensity exposure (this assumption is not exactly correct for the white light exposure of the grains, but it should not affect the logic that follows). It is also fair to assume that in the emulsions under investigation latent image detected by RA-4 (surface acting) developer is located solely at the grain surface. Furthermore, the most likely areas of the latent image formation are corners and edges of these bromide-treated grains. In case of tabular grains the high-bromide area is located along the grain perimeter (see Figure 1). From the simple geometry comparison it results that the total edge length perimeters of tabular and cubic grains under consideration are similar. The mean distance from the center of tabular grain to its edges is ca. 0.85 μm whereas for cubic grain it is ca. 0.4 μm. Thus, the local concentration of photoelectrons at the sensitivity centers immediately after the exposure event is lower for tabular grains, because a good fraction of them is much further away from the edges of the grain (as they have to travel in the lateral direction). The number of the sub-developable latent image centers created in the nucleation event is thus smaller than that for the corresponding cubic grain. As far as the growth step of these centers is concerned, photoelectrons have to travel a longer distance from the center of the tabular crystal outwards to the reaction zone; the delay that results may also counter the "dispersity" effect. The net result would be an increased efficiency at short time, high irradiance exposures vs that of cubic grain of comparable size. More direct photophysics experimentation is needed to strengthen our understanding of this fascinating phenomenon.

Summary

The sensitometric behavior of silver chloride tabular grains that do not contain parallel twin planes and are bound by <100> crystal faces is compared with that of iso-volume cubic grain emulsion. Photographic performance consistent with the high surface-to-volume ratio of tabular grains was confirmed in rapid access RA-4 chemistry. The portion of the improved HIRF behavior of tabular grain emulsion is attributed to the use of low-methionine gelatin in precipitation. An explanation for improved HIRF in tabular grain emulsion, compared to cubic emulsion precipitated in low-methionine gelatin, is proposed. This explanation is based solely on geometric considerations.

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