The Photographic Response of a Grain Size Series of AgCl Cubic Emulsions

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The photographic sensitivity of a series of sulfur-plus-gold sensitized AgCl cubic emulsions ranging in size from 0.29 to 3.14-µm (cube edge length) was established in a model color-forming single-layer format. Each emulsion was spectrally sensitized to green light with a single sensitizing dye. The measured sensitivity gains with increasing grain size fell considerably short of those expected from simple surface area per grain considerations, thus confirming the limited potential of AgCl cubic grain technology in exposure-limited photographic applications. An additional shortcoming of using increased grain volume to obtain increased sensitivity was evident by the six-fold decrease in maximum density exhibited through the thousand-fold grain volume change. As part of this study, a high-aspect-ratio {100} tabular grain AgCl emulsion (1.94 × 0.14 µm) was included for comparative purposes. This tabular grain emulsion, when sensitized in a fashion similar to that of the cubic emulsions, yielded a photographic response consistent with increased surface area per grain and more in line with the expected dye speed versus grain surface area relationship of the cubes.

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Introduction

Interest in silver chloride (AgCl) emulsion technology has increased during the past decade owing to its use in photographic output materials, most notably color paper. Relative to other silver halides such as AgBr, AgBrI, and AgI, silver chloride possesses a variety of interesting properties that make it well suited to photographic applications.[1] Silver chloride emulsions exhibit rapid development rates while being easily bleached and fixed, thus providing an overall processing efficiency advantage. Because they have a closer match to the index of refraction of gelatin, AgCl emulsions in photographic coatings also scatter less light than comparably sized AgBr emulsions. Their low native blue sensitivity also provides more flexibility in the ordering of layers of color photographic materials.

Unfortunately, the widespread use of AgCl emulsion technology has been limited by several key factors. Fundamental limitations associated with the latent image-forming steps exist in larger grain-size emulsions, this is especially true for AgCl.[2–4] Due to the instability of the {111} AgCl face, AgCl emulsion precipitations yield cubes, or low-aspect-ratio morphologies, over most of the useful excess chloride range further limiting the spectral speeds that are possible.[1] Only recently has the {100} bounded tabular grain morphology been readily achieved.[5] It is the purpose of this report to examine the photographic response of fully sensitized AgCl cubic emulsions over a wide range of grain sizes and to compare the response to that obtained for a {100} AgCl tabular grain emulsion.

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Experimental

The series of silver chloride cubic emulsions was precipitated without ripeners using conventional double-jet techniques. The pCl was held constant at 1.36 while temperature and molar addition rate were varied to produce the size series. A {100} surface silver chloride tabular emulsion was also prepared using a 0.06-mol% iodide addition immediately after nucleation to induce anisotropic growth with a double-jet process. Emulsion grain size was determined using an electrolytic reduction technique for the cubic emulsions, while the tabular emulsion was characterized from scanning electron micrographs. Grain sizing values are listed in Table I.

The emulsions were sensitized to green light using the dye benzothiazolium, 5-chloro-2(2-((5-phenyl-3-(3-sulfobutyl)-2(3*H*)-benzoxazolylidene)methyl)-1-butenyl)-2(sulfopropyl)-, inner salt compound with *N,N*-diethylethanimine (1:1), and conventional sulfur and gold sources. Sensitizing dye levels were estimated from surface area measurements and are listed in Table I.

The emulsions were coated in a hardened single-layer format at 0.86 g/m^2 of silver with 1.0 g/m^2 of a cyan dye-forming coupler and 2.1 g/m^2 of gelatin. Exposures were made through a 0.20 log H step tablet using a tungsten source with Daylight V and Kodak Wratten 9 filtration.

TABLE I.

Emulsion	Grain Size	Sensitizing Dye Level
Cube A	0.29 µm	0.45 mmol/mol Ag
Cube B	0.53 µm	0.30 mmol/mol Ag
Cube C	0.90 µm	0.19 mmol/mol Ag
Cube D	1.28 µm	0.17 mmol/mol Ag
Cube E	1.80 µm	0.10 mmol/mol Ag
Cube F	3.14 µm	0.04 mmol/mol Ag
{100} Tabular	1.94 × 0.14 µm	0.60 mmol/mol Ag

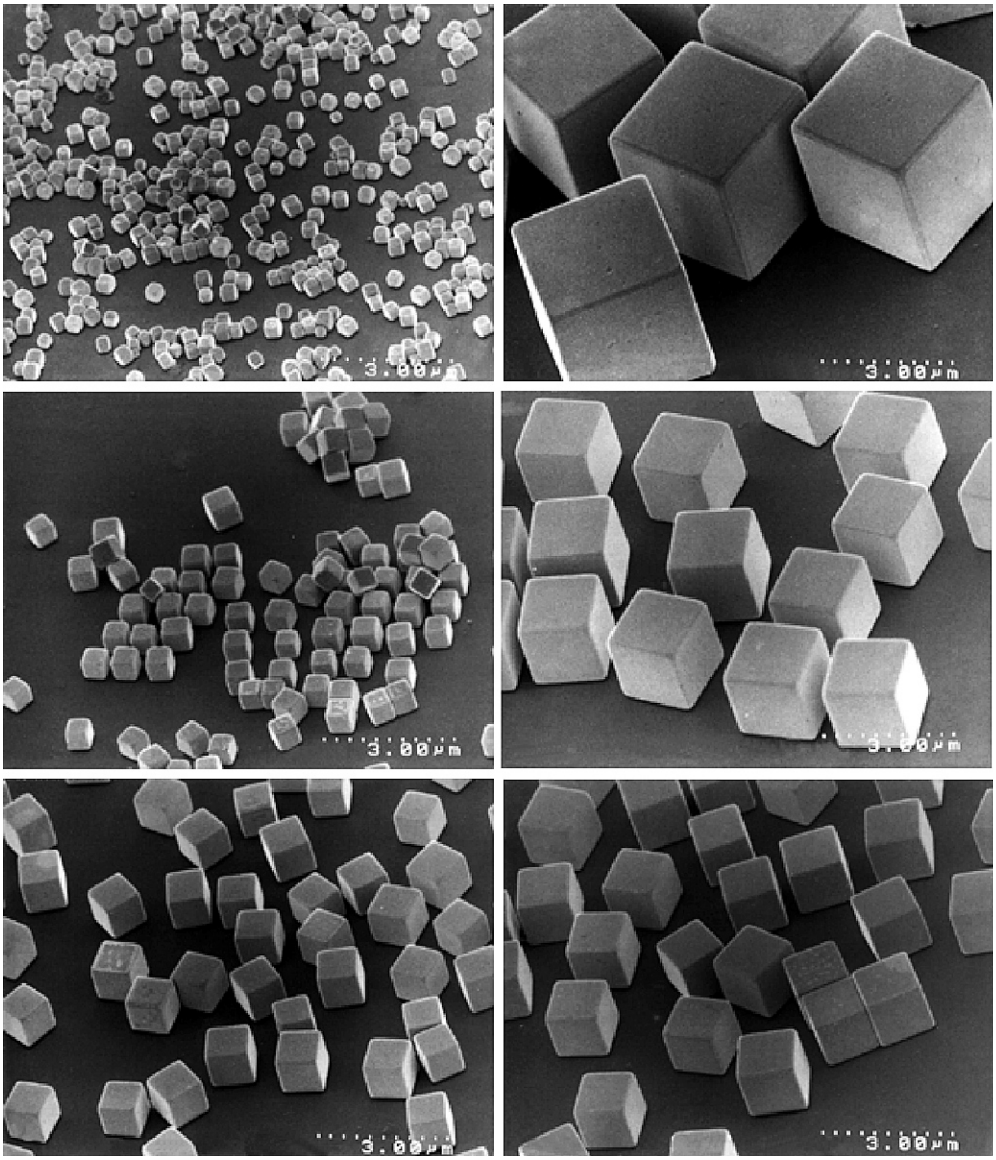

Figure 1. SEMs of the size series of cubic AgCl emulsions A through F described in Table I.

The exposed coatings were developed for 3′15" in a standard C-41 process.

The light absorption of the emulsions was determined by measuring the total reflectance and transmittance of the coatings using a Perkin-Elmer Lambda 18 UV/Vis spectrophotometer fitted with a Labsphere integrating sphere.

Results and Discussion

Cubic Grain Emulsions. Scanning electron micrographs (SEM) of the AgCl cubic grain emulsions are shown in Fig. 1. Displayed on the top of this figure are the size extremes, spanning a grain volume ratio of greater than 1000:1; these provide a useful visual perspective. The size range investigated is representative of emulsion grain sizes that can be found in various commercial color films that are based on other silver halides.

The photographic sensitivity of this series of emulsions is shown in Fig. 2 (the relative speed is referenced to the smallest grain size in the series and speed points were measured at a dye density of 0.15 above D_{min}, the minimum density or base plus fog). We see that the performance of the AgCl emulsions falls substantially below the expected curve calculated from simple geometric consideration of

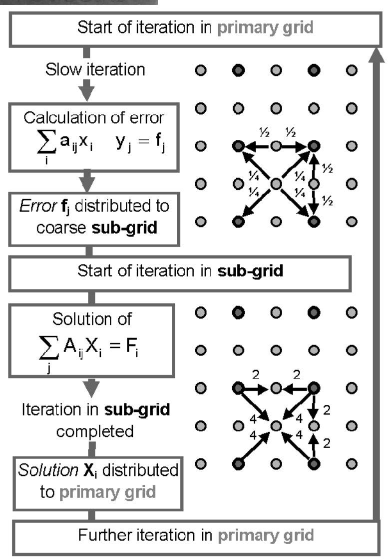

Figure 2. Predicted (based on grain geometry) and experimentally determined relative sensitivity as a function of grain volume for the size series of AgCl cubes and a {100} tabular AgCl emulsion: 0.15 spd denotes a speed point measured at a dye density of 0.15 above D_{min} or base plus fog and GN denotes a gamma-normalized toe speed.

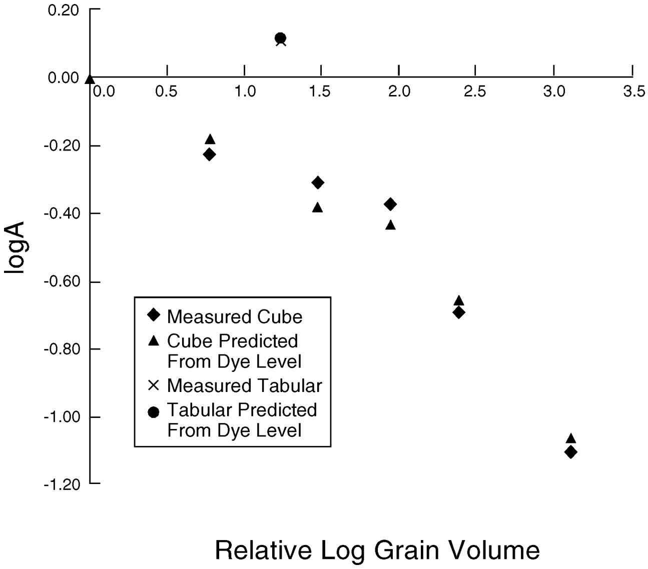

Figure 3. Relative light absorption, both measured and predicted from dye coverage, as a function of relative grain volume for the size series of AgCl cubic emulsions and the AgCl {100} tabular emulsion.

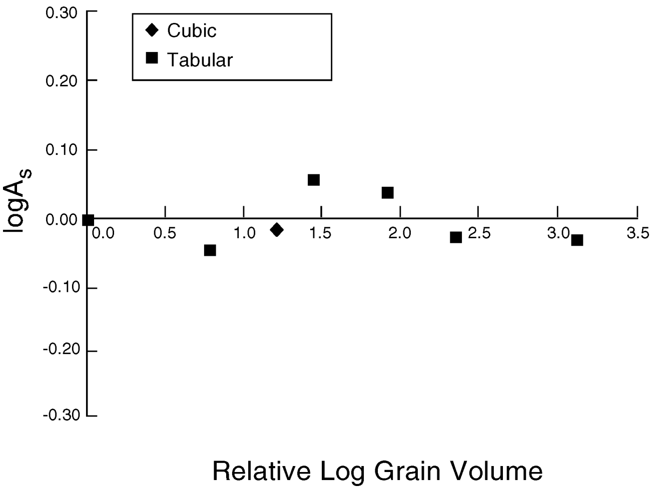

Figure 4. Relative light absorption per unit dyed grain surface or specific light absorption (A_S) as a function of relative grain volume for the size series of AgCl cubic emulsions and the AgCl {100} tabular emulsion.

dyed speed vs grain surface area. Our previous work[2] on AgBr octahedra showed that a sizable portion of this underper-formance can be traced to factors unrelated to the efficiency of latent image formation, for example, inefficiencies in light absorption (per grain) and amplification of the image.

The relative light absorption (expressed as log A) as a function of relative grain volume, both measured and predicted from sensitizing dye coverage, is shown in Fig. 3. Relative to the smallest cube, the larger cubes have less sensitizing dye per more of silver halide and show lower light absorption, as expected. The tabular emulsion, with high surface area and hence high dye coverage per mass of silver halide, shows an overall light absorption advantage. The relative light absorption per unit grain surface area or specific light absorption (expressed as log A_S) was determined by measuring the light absorption of the single-layer coatings and normalizing for the sensitizing dye lev-

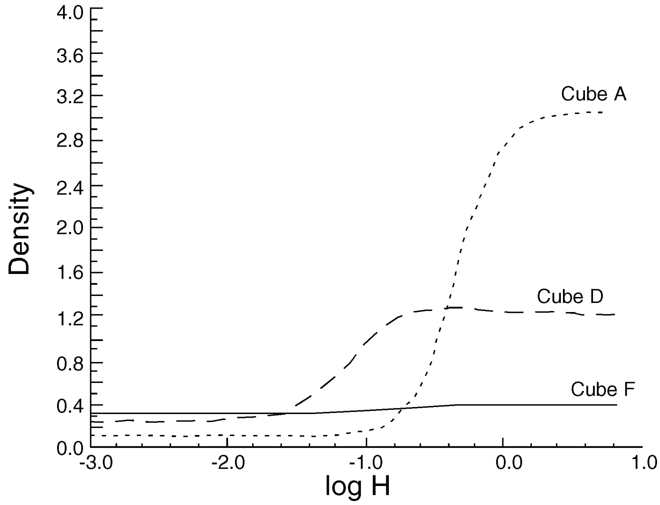

Figure 5. Characteristic (H&D) curves for AgCl cubes A, D, and F of the grain size series.

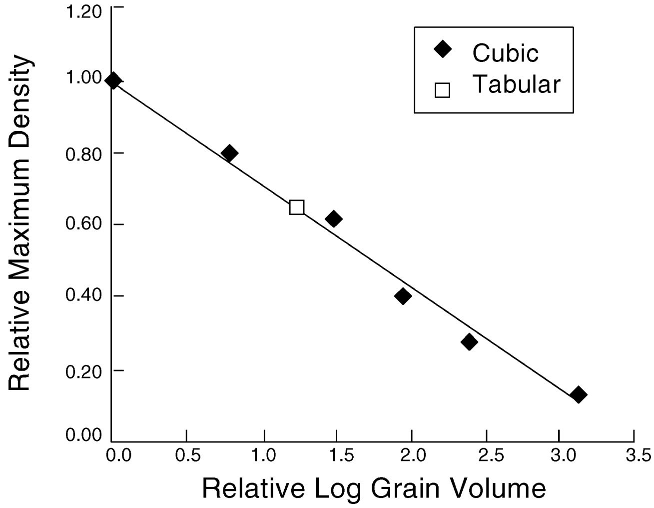

Figure 6. Relative maximum density as a function of grain volume for the grain size series of AgCl cubic emulsions and the {100} tabular emulsion.

els. Figure 4 shows the relative specific light absorption as a function of grain size. For the size range of silver chloride emulsions in this study, the differences in specific light absorption or light absorption per unit of dyed grain surface area are within experimental error, and hence not strongly dependent on grain size. Because specific light absorption (A_S) normalizes the light absorption for differences in the sensitizing dye level of the emulsion, any change would be due to differences in light scatter. In this case, it appears that changes in grain size are not resulting in significant changes in light scatter, and therefore the relative sensitivity would not be expected to deviate from the simple grain-geometry-based relationship where light scatter is considered constant (curve labeled predicted cube in Fig. 2). This indicates that the sensitivity reduction as grain size increases must be due primarily to inefficiencies in latent image and dye density formation (or amplification).

The contribution from image amplification is exemplified in Fig. 5 where the H&D curves for three of the AgCl cubic emulsions, including the size extremes, are shown. It is quite evident that the ability to form dye density is a very strong function of grain size. Figure 6 describes

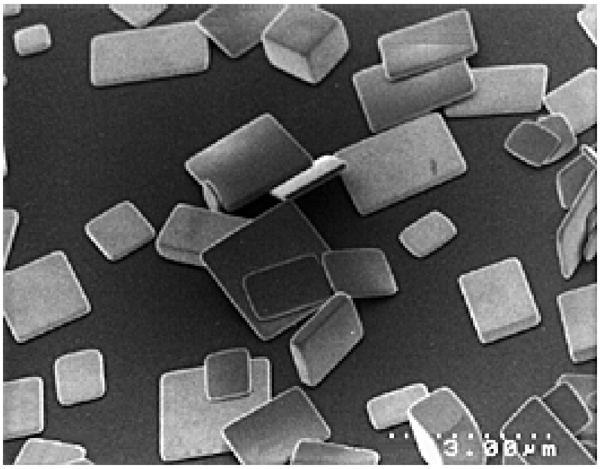

Figure 7. SEM of the {100} tabular AgCl emulsion described in Table I.

the maximum achievable dye density (D_{max}) versus grain size (as log grain volume). This relationship between dye density formation and grain size has been documented for silver bromide octahedra and is due to inefficiencies in dye formation and dye covering power.[2] Clearly, the overall photographic utility of the AgCl cubic emulsions diminishes rapidly with increasing grain size due to these effects.

In Fig. 2, we also show an attempt to recalculate the sensitivity of the series of cubic emulsions by bringing each of the H&D curves mathematically to the same gamma (GN = gamma normalized). This new curve improves the apparent sensitivity of the larger emulsions, although there still remains the significant reduction in overall sensitivity as grain size increases that can be inferred as due to inefficiencies in latent image formation. Unfortunately, the photographic utility of the larger cubes remains quite limited; alternative methods to increase dye density formation while maintaining image discrimination and improvements in latent image formation need to be discovered.

Tabular Grain Emulsion. Shown in Fig. 7 is an SEM of the {100} AgCl tabular grain emulsion that has a grain volume bracketed by cubic AgCl emulsions B and C (see Table I). The photographic response of this tabular grain emulsion is compared to that of the cubic emulsions in Fig. 2. The tabular grain emulsion has the expected advantage in spectral speed when compared to the performance of the cubes. Its speed is close to the calculated curve for the series of cubes, indicating that further efficiency gains might be possible, since we believe that most of the improvement in speed versus volume comes from the enhanced aspect ratio. The D_{max} of the tabular grain falls on the maximum density line versus grain volume line defined by the cubes in Fig. 6. This is consistent with the dye density yield being predominantly a function of grain volume rather than morphology.

Conclusions

The investigation of a grain size series of green-dyed, sulfur-plus-gold sensitized AgCl cubic emulsions confirmed that there is an appreciable decline in overall emulsion imaging capability for grain sizes that extend beyond those used for color print materials. Inefficiencies that relate to light absorption, image amplification (dye formation), and latent image formation contribute to this decline. Image amplification and latent image formation appear to be the dominant factors, especially at the largest grain sizes studied. Spectrally sensitized tabular grain AgCl emulsions have the potential of removing some of this reduction in imaging capability through enhanced light absorption and improved image amplification for a given spectral speed. It is uncertain whether the efficiency of the latent image formation step in these tabular grain crystals can be improved beyond that seen with the cubic emulsions.

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References

1. T. B. Brust and G. L. House, *J. Imaging Sci. Technol,* **41,** 413 (1997).
2. G. L. House, J. T. Kofron, and R. J. Newmiller, in *Proceedungs of the International East-West Symposium II*, IS&T, Springfield, VA, 1988.
3. T. Tani, *J. Imaging Sci. Technol.* **39,** 31 (1995).
4. T. Kaneda, T. Oikawa, N. Saeki, and T. Tani, in *Proceedings of the International East-West Symposium III*, IS&T, Springfield, VA, 1992.
5. G. L. House, T. B. Brust, D. L. Hartsell, D. L. Black, M. G. Antoniades, J. A. Budz, Y. C. Chang, R. Lok, S. A. Puckett, and A. K. Tsaur, US Patent 5,320,938 (1994).