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

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Abstract

The photographic sensitivity of a series of sulfur-plus-gold sensitized AgCl cubic emulsions ranging in size from 0.29 μm 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/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 μm x 0.14 μm) was included for comparative purposes. This tabular grain emulsion, when sensitized in a fashion similar to that the cubic emulsions, yielded a photographic response consistent with increased surface area/grain and more in line with the expected dyed speed vs grain surface area relationship of the cubes.

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. 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. 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. Only recently has the {100} bounded tabular grain morphology been achieved. It is the purpose of the present paper 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.

Experimental

The series of silver chloride cubic emulsions was precipitated without ripeners using conventional double-jet techniques. The pH 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 mole percent 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 using scanning electron microscopy. 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 (3H) benzoxazolidene) methyl) -1-butenyl)-2 (sulfopropyl)-, inner salt compound with N,N-diethylenimine (1:1), and conventional sulfur and gold sources. Sensitizing dye levels were estimated from surface area measurements and are also listed in Table I.
Table I

<table>
<thead>
<tr>
<th>emulsion</th>
<th>grain size</th>
<th>sensitizing dye level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cube A</td>
<td>0.29 μm</td>
<td>0.45 mmol/mol Ag</td>
</tr>
<tr>
<td>Cube B</td>
<td>0.53 μm</td>
<td>0.30 mmol/mol Ag</td>
</tr>
<tr>
<td>Cube C</td>
<td>0.90 μm</td>
<td>0.19 mmol/mol Ag</td>
</tr>
<tr>
<td>Cube D</td>
<td>1.28 μm</td>
<td>0.17 mmol/mol Ag</td>
</tr>
<tr>
<td>Cube E</td>
<td>1.80 μm</td>
<td>0.10 mmol/mol Ag</td>
</tr>
<tr>
<td>Cube F</td>
<td>3.14 μm</td>
<td>0.04 mmol/mol Ag</td>
</tr>
<tr>
<td>{100} Tabular</td>
<td>1.94 μm by 0.14 μm</td>
<td>0.60 mmol/mol Ag</td>
</tr>
</tbody>
</table>

The emulsions were coated in a hardened single-layer model format at 0.86 g/m² of silver with 1.0 g/m² of a cyan dye-forming coupler and 2.1 g/m² 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. The exposed coatings were developed for 3'15" in a standard C-41 process.

Results and Discussion

Cubic Grain Emulsions

Scanning electron micrographs of the AgCl cubic grain emulsions are shown in Figure 1. Displayed on the top of this figure are the size extremes which span a grain volume ratio of greater than 1000:1 and which provide a useful visual perspective. The size range investigated is representative of emulsion grain sizes that can be found in various commercial color films which are based on other silver halides.

The photographic sensitivity of this series of emulsions is shown in Figure 2. (the relative speed is referenced to the smallest grain size in the series and speed points were estimated by using a fixed density above D-min, the minimum density). It can be seen that the performance of the AgCl emulsions falls substantially below the expected curve calculated from simple dyed speed vs grain surface area considerations. Previous work by the present author on AgBr octahedra has shown that a sizable portion of this under-performance can be traced to factors unrelated to the efficiency of latent image formation.

Inefficiencies in light absorption (per grain) and amplification of the image contribute to this fall-off. This latter point is exemplified in Figure 3 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 4 describes the maximum achievable dye density (D-max) vs grain size (as log grain volume). Clearly, the overall photographic utility of the AgCl cubic emulsions diminishes rapidly with increasing grain size.

Fig. 1. Scanning electron micrographs of the size series of cubic AgCl emulsions A through F described in Table I.

Fig. 2. Predicted and experimentally determined relative sensitivity as a function of grain volume for the size series of AgCl cubes and a {100} tabular AgCl emulsion.
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 it is believed that most of the improvement in speed vs volume comes from the enhanced aspect ratio. As anticipated, the D-max of the tabular grain falls on the maximum density line vs grain volume line defined by the cubes in Figure 4.

![Fig. 5. Scanning electron micrograph of the {100} tabular AgCl emulsion described in Table I.](image)

**Conclusions**

The investigation of a grain size series of green dyed, sulfur-plus-gold sensitized AgCl cubic emulsions has 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. These latter two factors appear to be the dominant ones, 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.

**References**