

An Effect of a Desensitization by the Shell Precipitation on Chemically Sensitized AgHal Core Microcrystals

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Abstract

Photographic systems with a separate photographic change carriers capiture in depth and on a suface of emulsion microcrystals ("core-shell") have a great importance for photographic techology (direct positive, infra-red films and etc.) and also for scientific investigation. We have precipitated AgBr(I) core microcrystals (with AgI content from 0 up to 6 mol. %), which then were subjected to chemical sensitization of various types (reduction, S, S+Au, Au). A sensitometric study of the covered by shell of various thickness and halide composition initial microcrystals has been carried out. An effect of the loss of internal sensitivity is found. A nature of this effect is proposed and ways of its elimination are offered.

Introduction

It is known[1-3] that emulsion grains of the "core/shell" type have a sertain advantages over ordinary regular grains. The "core/shell" type grains with inner sensitivity centers are preferable for infra-red films. According to Berg,[4] inner latent image is more stable than surface one. A precipitation of shell AgBr on AgBr(I) core with an iodide content up to 30% molar is not a problem now[5]. However an inner fog density, discovered by the inner development, reaches an undesirably high level. Authors worked out an acceptable level of the inner fog dendity[6] but the inner image density was also decreased. The last effect was caused by a desensitization of inner sensitivity centers during the shell precipitation. Presented paper is dedicated to the explanation of the desensitization effect and to some ways of the desensitization elimination.

Experimental and Discussion

Cubic grains AgBr(I) of size 0,2 - 0,6 mcm; Cv = 15 % and iodide content 0 - 6 moll % have been prepared by means of the double jet precipitation[7] and underwent the chemical sensitization. Then the grains have been covered with 150 nm shell AgBr.[6] Layers of these grains have been exposed (Tcal = 2850 K, t=0,05 sec) and developed in the methol-hydroquinone developer with addition of 4 g/l $Na_2S_2O_3$.

It is shown that the desensitization effect expresses in the image optical density decrease and it becomes greater with the increase of the iodide content in the core. AgBr(I)/AgBr and AgBr(I)/AgCl heterojunction boundary is enriched with electron traps. The trap concentration increases with the iodide content growth. It is plausible to suppose that at the iodide concentration higher than 2% the number and depth of traps becomes so significant that photoelectrons are being trapped on the structural traps. This supposition is supported by the growth of the inner dechroic fog density at higher exposition level. "Core/shell" grains with larger cores have greater "volume/surface" relation and hence lower molar trap concentration. $AgBr_{0,94}I_{0,06}$ core of the size 0,6 mcm gave us Dmax>1,5 and sensitivity level twice higher than core of the size 0,4 mcm. Fig. 1 shows dependence of the inner image density on the core iodide content for different core size.

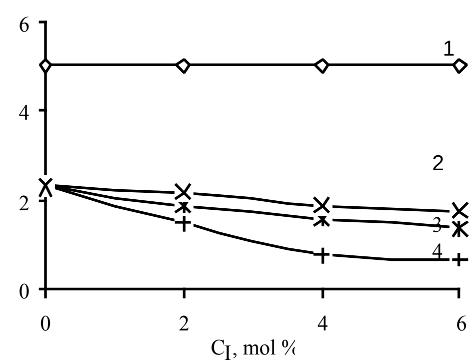

Figure 1. Inner image density versus core iodide concentration. 1.core without shell; 2 - core is 0,6 mcm; 3 - 0,4mcm; 4 - 0,2mcm.

Mentioned above results prove that iodide is not the main desensitization matter. We have studied relation between a type of the core sensitization and the inner sensitivity. According to Belous,[8] silver sulphade centers are unstable during the shell precipitation. This was a reason to except sulfur sensitization from our experiments and to concentrate our attention at sulfur plus gold and reduction sensitization. The last type has been carried out at the pAg = 4,3 and T = 60°C.

In order to increase level of sensitometric characteristics we accomplished reduction sensitization with gold sensitization. For this purpose we applied AuSCN. A drastic growth of the fog density (D>1,0) didn't allow us to get a suitable sensitometric characteristics. Reduction sensitization centers form on the grain surface randomly.[9] A high density of small silver particles leads to the grain fogging by gold. Hence the reduction sensitization may be applied in case when sensitivity is not the basic guideline of the film.

We have also studied inner development by developers of different composition. The process has been carried out at 20+/-0,5°C. The developer composition was varied with $Na_2S_2O_3$ concentration. Table 1 shows data on the inner developer sensitometric effect.

Table 1

concentration $Na_2S_2O_3$ (g/l developers)	Dmax	Do
2	-	0,04
4	1,2	0,08
6	0,8	0,12

The optimum $Na_2S_2O_3$ concentration is 0,4 g/l. It is explicit that inner Dmax level significantly differs from those of uncovered core. We guess that lost of density is caused by a growth of silver ion concentration in the developer and formation of the "compact" silver particles, which revealed a low covering power. An application of the more active developer D-19 with 0,4 g/l addition of $Na_2S_2O_3$ resulted in significant growth of the fog density. Less active developer "M" with 2 g/l menthol; 31 g/l Na_2CO_3; 1 g/l hydroquinone; 4 g/l KBr; 20 g/l Na_2SO_3; 1 l aqua.

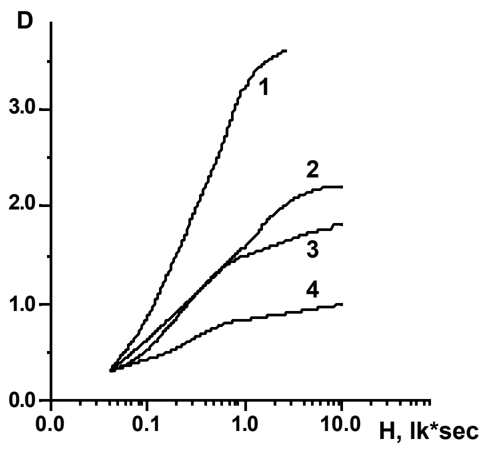

Figure 2. D-Log E curves. 1-"core " emulsion. Standard development. 2 - "core/shell". Standard inner development. 3. "core/shell". Inner D-19; 4. "core/shell". Inner "M".

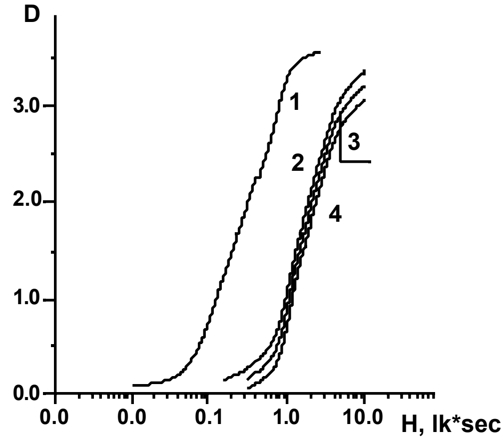

Figure 3. D-Log E curves. 1-"core" emulsion. Standard development. 2-"core/shell".Standard inner development + BTA. 3-"core/shell". Inner D-19 + BTA; 4-"core/shell". Inner "M" + BTA.

An application of this developer allowed to increase Dmax over 2 by 15-th min of the development. That is the "soft" developer is the condition of the inner image high density development. An addition of the benzotriazole (BTA) increases Dmax up to 5 by Do = 0,03 regardless the developer type. The BTA addition increases the development time up to 20 min. Fig. 2 and 3 show typical D - Log E curves of optimal developed layers. The role of the BTA is not connected with reduction of the development rate and is a subject of further study.

Conclusions

A contemplation of the found results allows to conclude that ineffective development of inner latent image along with the increase of structural electrons traps are the couse of the inner image desensitization. The elimination of the desensitization effect can be achieved by the increase of the grain size, decrease of the core iodide content and improving of development procedure.

References

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