Influence of Fine Emulsion Properties to the Sensitometric Characteristics of T-Crystals, Received in Result of a Physical Ripening of this Emulsion

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Abstract

It was established, that an opportunity to operate by sensitometric properties of T-crystals is available by change of source fine emulsion manufacturing conditions (pAg of a crystallization) or subjecting this emulsion of chemical sensitization. Experimental results specify on the fact, that during a physical ripening there is the carry of silver and silver sulfide centers from microcrystals of fine emulsion on growing T-crystals. In our opinion such carry is possible in that case, when the growth of T-crystals proceeds on the coalescent mechanism.

Introduction

The method of fine emulsions physical ripening is widely used for reception of photoemulsion silver halide T-crystals. However the mechanism of T-crystals formation remains not clear. At the moment the diffusion mechanism usually is used for the description of T-crystals growth.[1] However some authors specify an opportunity of T-crystals growth realization on the coalescent mechanism.[2] There are the experimental dates, which can allow to make a choice for the benefit of that or other mechanism.

Experimental and Experimental Results

Influence of Fine Emulsion Synthesis Conditions

The double jet crystallization traditionally is used for fine emulsion manufacturing, and the synthesis can be carried out at presence of bromide ions excess (pBr<3,0), or at presence of silver ion excess (pBr>8,0). The general laws of T-crystals formation at a ripening of fine emulsions were described earlier.[3] However it was experimentally shown, that the T-crystals, received at a physical ripening of synthesized at presence of silver ions excess fine emulsions, have lowered resistance to a fog.[4]

On a Figure 1 is shown the change of a fog optical density and photosensitivity at sulfur-plus-gold sensitization of emulsions with T-L-crystals[5] $AgBr/AgBr_{0.96}I_{0.04}$, received by a method of a fine emulsions ripening. This crystals have the similar dispersion characteristics. The distinction between T-L-crystals consists in conditions of initial fine emulsions manufacturing. In the first case the synthesis of fine emulsions is realized at presence of silver ion excess (pAg = 3.0), in the second case the crystallization of fine emulsions is carried out at presence of bromides ions excess (pBr = 3.0). An observable fast fogging specifies unfitness of fine emulsions, synthesized at presence of silver ion excess for photoemulsion T-crystals manufacturing.

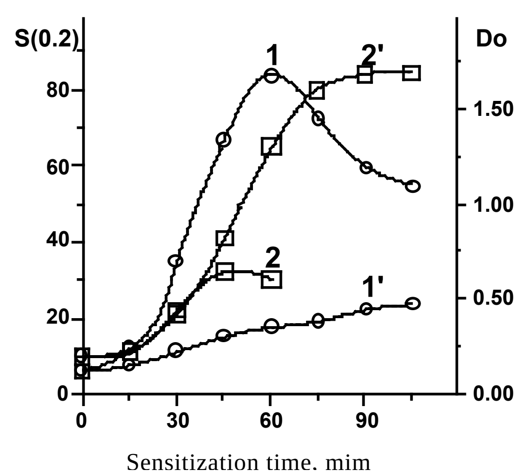

Figure 1. Changes of a photosensitivity and a fog optical density during chemical sensitization ($[Na_2S_2O_3]=1\times10^{-5}$ mol/mol AgHal; $[KSCN]=2\times10^{-2}$ g/g Ag; $[HAuCl_4]=1\times10^{-5}$ g/g Ag; temperature - 60° C). Emulsions, containing T-L-crystals $AgBr/AgBr_{0.96}I_{0.04}$, were received on the base of fine emul-sions: 1,1' - synthesized at presence of silver ions excess; 2,2' - synthesized at presence of bromide ions excess.

Influence of Chemical Sensitization of Fine Emulsions

Method of a physical ripening of fine emulsions allows to realize the untraditional approaches to creation of impurity centers (sensitivity centers) in silver halide T-crystals. In particular, chemical sensitization of initial fine emulsion (or its part) can be executed. Thus amount and the distribution of impurity centers in T-crystals can be set by conditions of physical ripening realization. We spent experimental checking of an opportunity of such variant of photographic emulsion manufacturing.

The AgBr fine emulsion, containing crystals with the average size 0.062 microns, is made by double jet technique. This emulsion have divided into four equal parts. Two parts are subjected of sulfur sensitization by sodium thiosulfate (2.5×10^{-5} mol/mol AgHal and 1×10^{-3} mol/mol AgHal accordingly) during 45 minutes (pBr = 3.0; pH = 6.8; temperature—40°C). The measured crystals sizes after sensitization are 0.064 and 0.065 microns. The third part of fine emulsion is subjected to reduction sensitization by sulfuric hydroxilamine (1.2×10^{-3} mol/mol AgHal) during 45 minutes (pBr = 3.0; pH = 6.8; temperature—40°C). The measured size of crystals after sensitization is 0.064 microns. The fourth part of fine emulsion is left without changes. The information on types of sensitization and used reactants is submitted in Table 1.

Table 1. Conditions of Fine Emulsions Chemical Sensitization

Emulsion No.	Sensitization type	Reagent	Reagent concentration mol/mol AgBr
1	sulfur	sodium thiosulfate	1×10^{-3}
2	sulfur	sodium thiosulfate	2.5×10^{-5}
3	reduction	sulfuric hydroxilamine	1.2×10^{-3}
4	-	-	-

All four parts are subjected to a physical ripening in identical conditions (temperature—70°C; pBr=1.0 duration—30 minutes), therefore are received four emulsions, containing AgBr T-crystals with the close dispersive characteristics (d=2.5 μm). Thus, the preliminary chemical sensitization of fine emulsions does not influence to the dispersive characteristics of received T-crystals.

Emulsions with T-crystals are subjected to chemical sensitization and the sensitometric researches by the standard techniques are carried out. It is established that photographic layers with T-crystals on the basis of fine emulsion 11 results in intensive fog formation (D_o>2.5) on sites, not subjected to light impact. Thus, impurity centers, formed on fine emulsions crystals, during a ripening pass (though partially) to formed T-crystals.

We investigate the chemical sensitization of a various type on the other emulsions with T-crystals. The experimental results are shown on Figures 4.2-4.4.

In our case the unselective impurity centers distribution in formed T-crystals (as on a surface, and in depth) is caused by conditions physical ripening realization. Obviously the decrease of the subsequent chemical sensitization efficiency is resulted by presence of internal electrons traps in T-crystals.

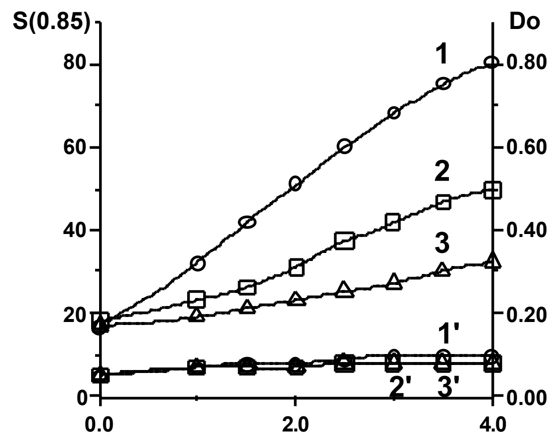

Figure 2. Change of a photosensitivity and a fog optical density during chemical sensitization (t=54°C; [KSCN] = 5×10^{-3} g/g Ag; [$HAuCl_4$]=1×10^{-5} g/g Ag) emulsions, containing the AgBr T-crystals, received on the base of fine emul-sions: 1,1'-unsensitized (No.4); 2,2'-subjected reduction sensitization (No.3); 3,3'-subjected sulfur sensitization (No.2).

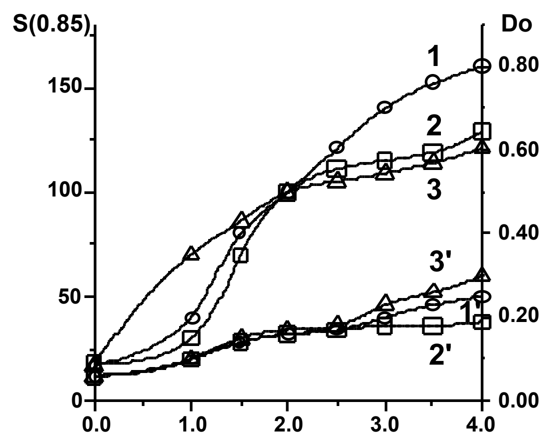

Figure 3. Change of a photosensitivity and a fog optical density during chemical sensitization (t=54°C; [$Na_2S_2O_3$]=5×10^{-6} mol/mol AgHal; [$HAuCl_4$]=1×10^{-5} g/g Ag) of emulsions containing the AgBr T-crystals, received on the base of fine emulsions: 1,1' - unsensitized (No.4); 2,2' - subjected reduction sensitization (No.3); 3,3' - subjected sulfur sensitization (No.2).

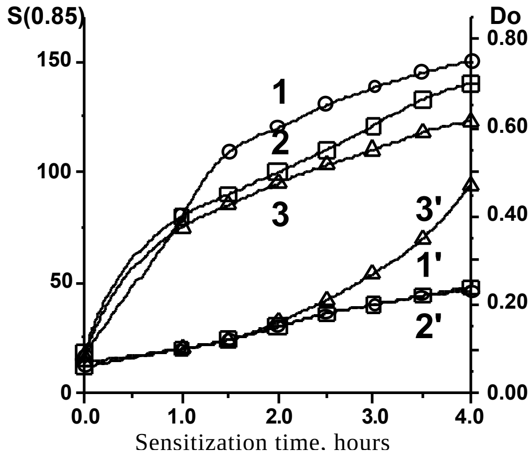

Figure 4. Change of a photosensitivity and a fog optical density during chemical sensitization (t = 54^{0}C; [$Na_2S_2O_3$] =1 × 10^{-5} mol/mol AgHal; [$HAuCl_4$] = 1 × 10^{-5} g/g Ag) of emulsions, containing the AgBr T-crystals, received on the base of fine emulsions: 1,1'-unsensitized (No.4); 2,2'-sub-jected reduction sensitization (No.3); 3,3'-subjected sulfur sensitization (No. 2).

Discussion

It is possible to reach a conclusion on the basis of the above-stated experimental results that impurity centers, formed at the stage of synthesis or chemical sensitization of fine emulsion, reveal self in AgHal T-crystals, received at a physical ripening of this fine emulsion. Thus, there is the carry of impurity centers from fine emulsion crystals on formed T-crystals during a ripening. These facts can testify that the growth of silver halide photoemulsion T-crystals proceeds on the coalescent mechanism.

It is possible try to explain the carry of Ag_2S centers on the basis of the diffusion mechanism of growth. Their dissolution and selective deposition on a T-crystal should in this case take place. However driving forces of clusters formation process are not absolutely clear. It is known, that destruction of Ag_2S centers down to a level of individual molecules at shells growth on chemically sensitized iso-metric micro-crystals (the growth on the ionic mechanism) occurs[6].

It is more difficult to explain on the base of the ionic mechanism carry of silver centers from fine crystals on a formed T-crystal. In particular, unintelligibly, whether some this process should occur through a stage of a dissolution of a silver particle. On the other hand, opportunity of inclusion silver clusters in a growing lattice of silver halide is extremely problematic.

Opposite, it is possible rather simply to explain experimental facts on the basis of the coalescent mechanism of T-crystals formation. In this case the growth comes true at the expense of direct association of fine emulsion crystals and growing T-crystal at the minimum participation of dissolution/deposition processes. In our opinion the results of experiments confirm a hypothesis about the essential contribution of coalescence processes to growth of silver halide T-crystals.

References

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