# Formation of Tabular Crystals in the Course of Ostwald Ripening of AgBr Emulsions

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## Abstract

The pBr value intervals which ensure the formation of tabular crystals with different sizes, were found out. It was determined that the ripening of tabular crystals with an equivalent diameter of 200 nm and isometric grains with edge length at most 1000 nm in the presence of an excess of bromide ions (pBr<0.5) result in the formation of large (>5000 nm) tabular crystals.

## Introduction

The pBr value in the course of the synthesis of photographic emulsions is one of major parameters governing the properties of resulting grains. In spite of a great number of revealed regularities about the influence of $Br^-$ ions on the process of the formation of grains of various habits, which are well-known, the problems concerning the crystallization of homogeneous photographic emulsions of the tabular habit are to be solved.

The synthesis of photographic emulsions containing tabular silver halide grains, is usually carried out when the reaction mixte contains a great excess of $Br^-$ ions (pBr = 1,0-1,6), irrespective of the chosen technique of the synthesis (two-jet crystallization or Ostwald ripening (OR)) [1]. The adjustment of pBr value in the course of crystallization allows us to govern the rate of the course of OR at the expense of changing the solubility of silver halide. Though it is considered that neither the way of introducing the additional KBr into the system nor the concentration of excess $Br^-$ ions essentially influence dispersion characteristics of the tabular-grains obtained in the course of OR [2].

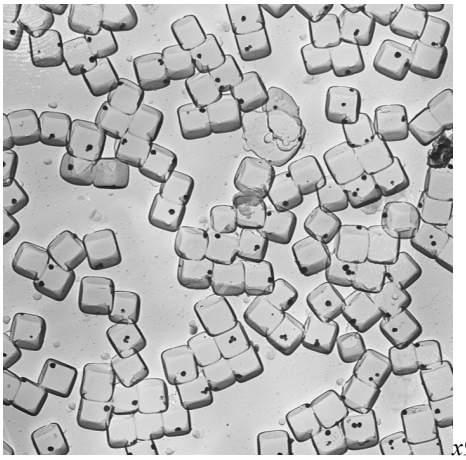
Meanwhile, it is known, that the dependence of solubility of small particles from their size according to the Gibbs-Thomson equation has a logarithmic character [3]. Besides, $Br^-$ ions are the substance modifying the habit of AgBr grains. Therefore, it is possible to expect qualitative changes in the recrystallization process resulting in increased solubility of AgBr i.e. a rather low value of pBr in the reaction mixte.

To verify this assumption a series of experiments on finding out the role of super high concentrations of excess of $Br^-$ ions during tabular-grains formation in the course of OR of photographic emulsions containing isometric AgBr crystals has been carried out.

## Experiment

The study of the influence of the concentration of excess $Br^-$ ions in the pBr = 0,0-0,5 range on OR of AgBr grains having different habits and sizes was carried out. To carry out the experiment by the method of controllable two-jet crystallization two series of monodisperse photographic emulsions of cubic and octahedron habits were synthesized. Isometric grains of each shape had an average equivalent diameter d = 0,1, 0,2, 0,3 and 0,7 μm. The resulting emulsions were subjected to OR in the excess of $Br^-$ ions at T = $60^0$C for 2 hours. In the course of ripening, emulsion samples for studying the process of ripening with an optical microscope were selected.

As was expected, gradual decrease of the pBr value from 1,6 up to 0 in the course of OR of emulsions with octahedron and cubic grains, having an average equivalent diameter d = 0,3 and 0,7 μm, does not result in appreciable changes of grain sizes. Octahedron grains do not change their habit while cubic grains become rounded without changing their average equivalent diameter (see Fig. 1). At the end of the course of ripening (maximum time of ripening 3 hours) a number of very large (d = 3-5 μm) AgBr twin crystals are observed.



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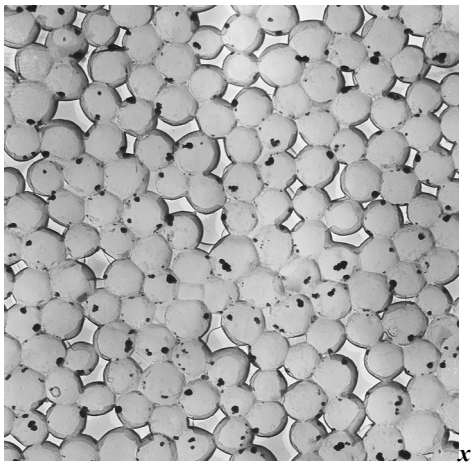

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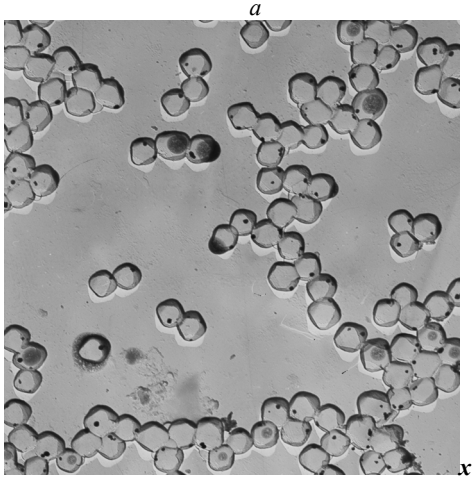
a



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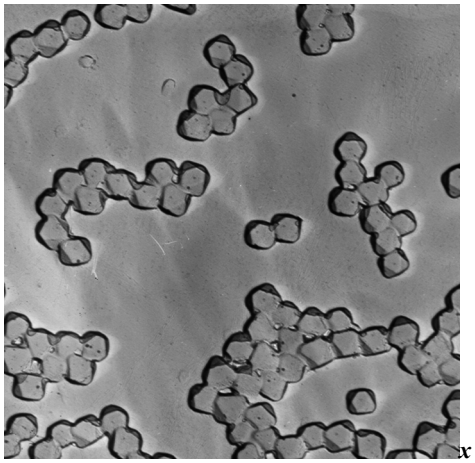


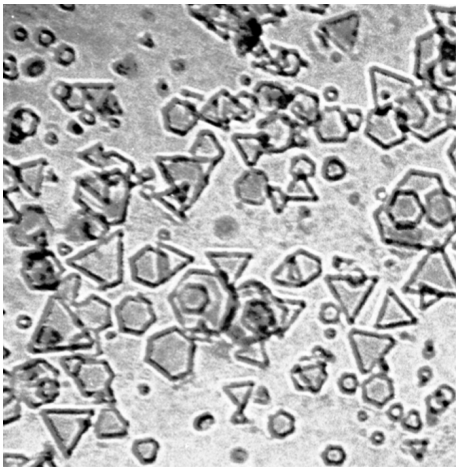
2 x 5400

b

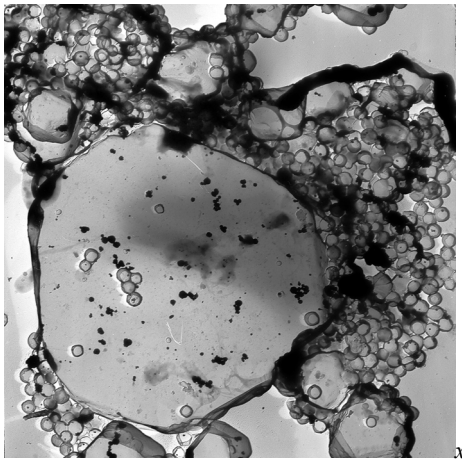
*Figure. 1. Electron micro photos of AgBr grains of the photographic emulsions: cubic (a) and octahedron (b) with an average equivalent diameter d = 0,7 μm. 1 - grains of initial emulsions; 2 - grains after ripening in a reaction mixte at pBr = 0.*

Gradual decrease of the pBr value up to 0,5 in the course of OR of emulsions with octahedron and cubic grains, having an average equivalent diameter d = 0,2 μm is not accompanied by essential changes of the morphology of initial grains either. However, after the increase in the concentration of $Br^-$ ions up to pBr ≤ 0,5, OR of emulsions with octahedron grains results in a very fast formation of (within 15 - 30 min.) large tabular crystals with d = 5-10 μm. As an impurity, large isometric twin crystals with d = 1-3 μm are used. Optical micro photos of resulting grains are presented in Fig. 2a. The difference in OR of cubic and octahedron grains (d = 0,2 μm) shows that the formation of embryos of tabular grains is mostly due to the synthesis of grains in the excess of $Br^-$ ions. Therefore, our experiments on OR of fine emulsions where carried out on grains synthesized at pBr = 1,8.

Changes of d and $S_T$ in the course of OR of photographic emulsions containing grains of octahedron habit with d = 0,2 μm when changing pBr are shown in Fig. 3 and Fig. 4 (curve 1).



a x400



b x2000

*Figure. 2. Optical (a) and electron (b) micro photos of AgBr crystals obtained due to OR of photographic emulsions containing the grains of octahedron (a) and cubic (b) habit with an average equivalent diameter d = 0,2 μm at pBr = 0.*

Ostwald ripening of emulsions with cubic grains having an average equivalent diameter d = 0,2 μm, at pBr = 0 for 2 hours is not accompanied by visual changes. At the end of the process of ripening individual tabular-grains and twin crystals with d = 1-3 μm are formed (Fig. 4, curve 2). Electron micro photos of resulting grains are shown in Fig. 2b.

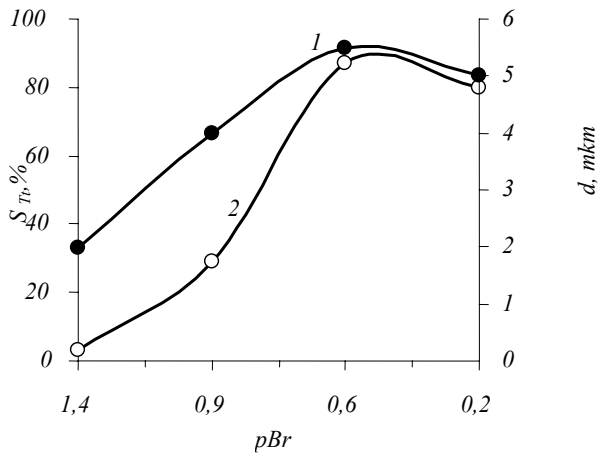



*Figure. 3. Change of an average equivalent diameter (d - 1) of tabular grains and the crystallographic uniformity factor ($S_T$ - 2) in the course of OR of photographic emulsions containing octahedron grains with d = 0,2 μm when changing pBr.*

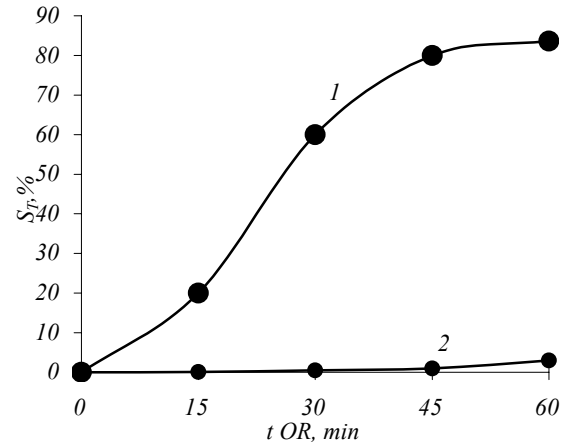
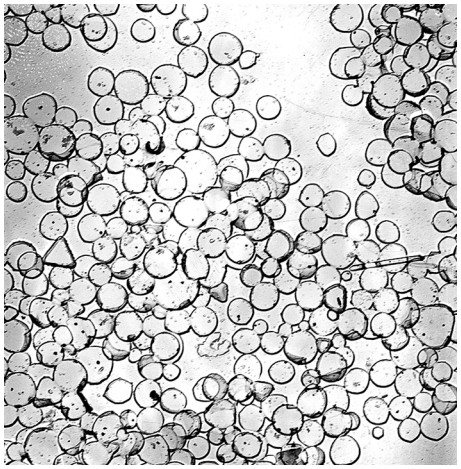



*Figure. 4. Change of crystallographic uniformity factor ($S_T$)( in the course of OR of photographic emulsions containing grains with d = 0,2 μm) when changing pBr of the synthesis. 1- pBr = 1,8; 2- pBr = 2,8.*

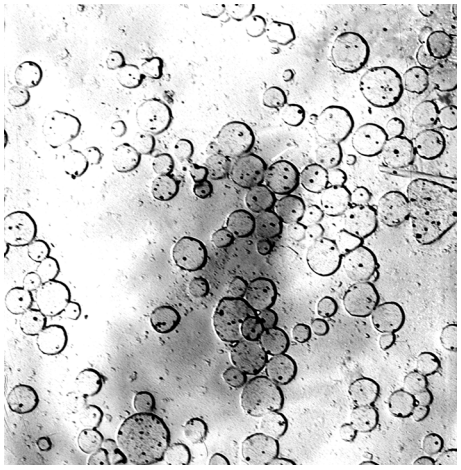
Electron micro photos of grains obtained after OR of AgBr fine-grained emulsions (d < 0,1 μm) at gradual adjusting the pBr value in the reaction mixte up to 0 are shown in Fig.5. As seen from the figure, at the first stage of OR of emulsions when adjusting the pBr value up to ≈ 1, rather homogeneous tabular, mainly disk-shaped, grains with an average equivalent diameter d = 0,8 μm are formed (Fig. 5 a). Further increase of the concentration of $Br^-$ ions up to pBr = 0,5 results in the decrease in the uniformity of tabular-grains and is accompanied by the growth of individual tabular grains (Fig. 5 b, 5 c). Finally, at pBr < 0,5 tabular grains formed at the first stage undergo deep recrystallization during which they practically completely disappear; accompanied by simultaneous formation of very large tabular crystals. Electron micro photos of these crystals are shown in Fig. 5 d. The results testify to the fact that it is very hard to get homogeneous tabular grains by the OR method. The fluctuations of the $Br^-$ ions concentration during the synthesis of a fine emulsions (in the place of addition the ÊBr solution) result in the formation of the embryos of large tabular crystals. For lower pBr values of embryos of large crystals grow quickly not only due to the dissolution of fine grains but also due to the dissolution of thinner tabular grains. As a result of these processes heterogeneous tabular grains are formed by the OR method.

These experiments allowed us to state the dependence of crystallographic characteristics of tabular grains from the technique of creating the pBr value during OR of initial grains.

Grains with high uniformity in the size and the habit are obtained while adjusting the pBr value in two stages. At the first stage the pBr value was reduced up to 0,7, then after 60 min. of OR the pBr value was reduced up to 0,2. The above technique is preferable for the preparation of tabular crystals with hexagonal habit (see Fig. 6).



a



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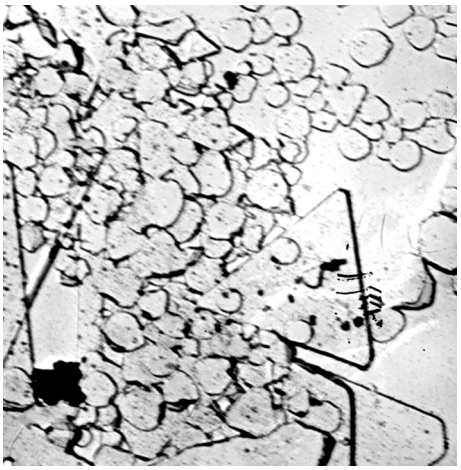
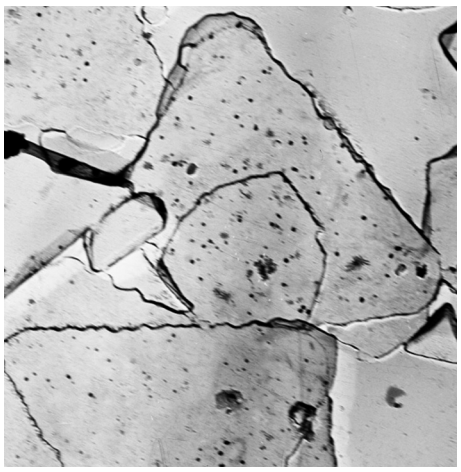


c



d

*Figure. 5. Electron micro photos of tabular grains of AgBr photographic emulsions obtained due to OR of isometric AgBr grains with an average equivalent diameter d = 0,1 μm, when gradually changing the pBr value from 1 up to 0 (x5400.). a – pBr = 1; b – pBr = 0,7; in c– pBr = 0,5; d – pBr = 0.*

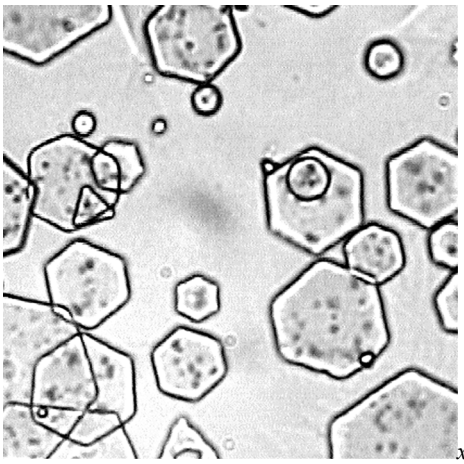


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*Figure. 6. An optical micro photo of AgBr crystals of the hexagonal shape obtained under OR.*

## Conclusion

Based on the experimental data, it can be concluded, that the dispersive characteristics of grains obtained in the course of OR of emulsions containing isometric AgBr grains with the equivalent diameter which does not exceed d = 0,2 μm, depend on the pBr value at which the process of ripening is carried out and the technique of decreasing the pBr value. The pBr for the synthesis of grains (d = 0,2 μm) determines the number of the embryos of tabular grains. Besides, the effect of the recrystallization of AgBr tabular grains with an average equivalent diameter d ≈ 1 μm when increasing the concentration of Br ions up to pBr ≤ 0,5 has been found out, tabular grains with the diameter d ≈ 5-10 μm being formed under these conditions.

## References


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## Biography

Larisa V. Sotnikova was born in Kemerovo (Russia) on October 26, 1966. In 1989 she graduated from Kemerovo State University, the Chemestry Faculty. Since 1989 she has been working at Kemerovo State University, the Department of Inorganic Chemistry as a Scientific Researcher. Doctor of Chemistry since 1998. Field of research is silver halide photographic emulsion crystallization and chemical sensitization processes, the author of more than 50 scientific publications.